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CSIR–NET

Chemical Science

Council of Scientific & Industrial Research (CSIR)

Volume - 5

Physical Chemistry - 2

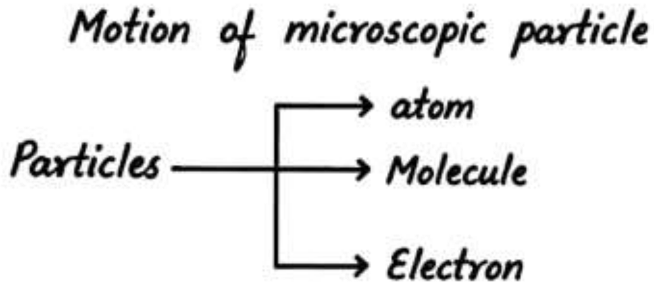
SIERRA INNOVATIONS

INDEX

1 CHAPTER Physical Spectroscopy

Spectroscopy :-

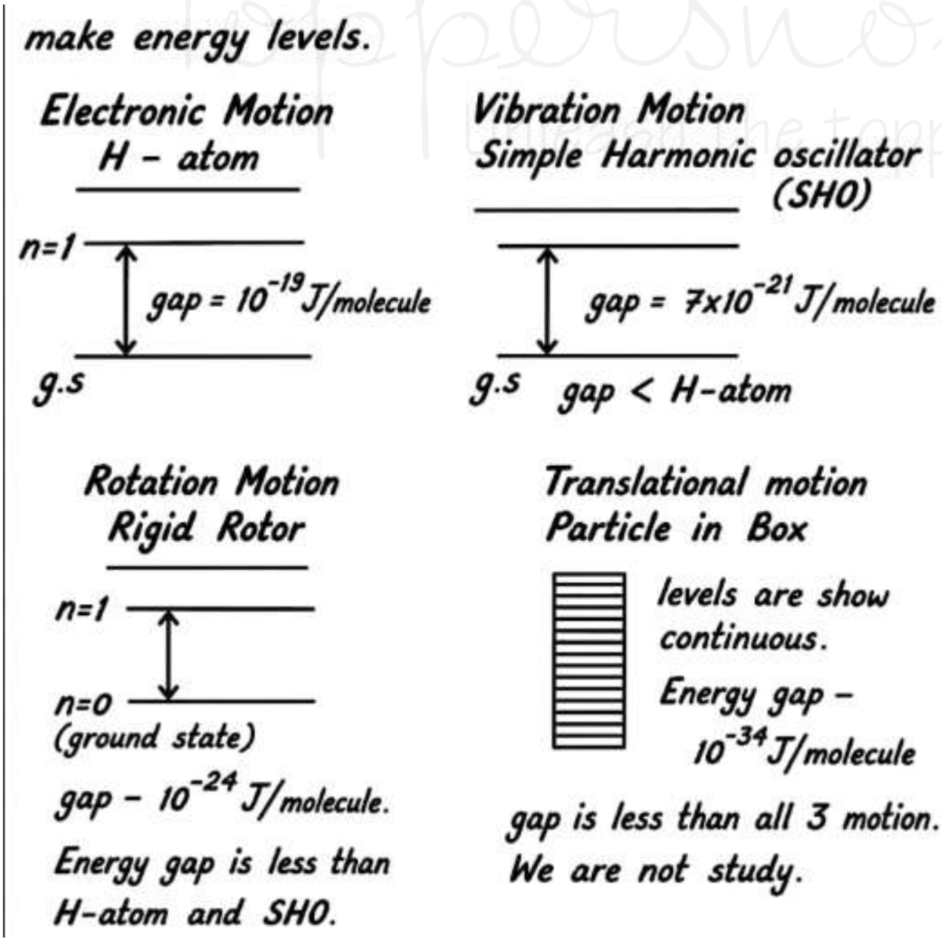
- Interaction of (EMR) radiation with matter's energy level corresponding to various motion.
- Spectroscopy is application of quantum chemistry. In quantum chemistry we find out-



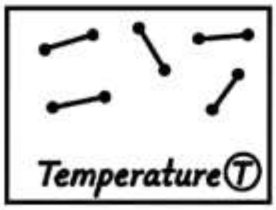
- Total four types of motion are present.

Motion	Model
Translational motion	PTB Model (Particle in box)
Rotational motion	Rigid rotor
Vibrational motion	Simple Harmonic oscillator
Electronic motion	H-atom

- All types of motion are quantised in nature



Energy gap order :- H-atom > SHO > Rigid Rotor > Particle in box



(diatomic molecule)
(gaseous sample)

$$\text{Thermal energy} = k_B T$$

k_B = Boltzman constant

$k_B = 1.38 \times 10^{-23}$ J/kmole

Thermal energy at 27°c temp $= 1.38 \times 10^{-23} \times \frac{J}{molecule} \times 300K$

$$\text{Thermal energy} = 4 \times 10^{-21}\ J/molecule$$

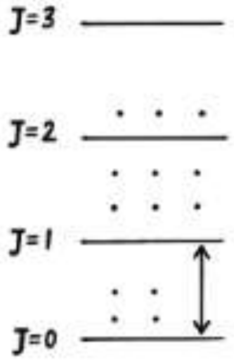
- Each molecule contains $4 \times 10^{-21} \frac{J}{molecule}$ Energy.
- Translational motion → Maximum population find in Highest energy level.
- Rotational motion → Maximum population find in Mid energy level.
- vibrational motion → Maximum population find in ground state (I max) energy level.
- Electronic motion → Maximum population in ground state.

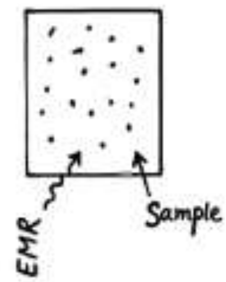
Rotational spectroscopy / Microwave spectroscopy.

- Interaction of EMR with matter's rotation energy level
- It is also called microwave spectroscopy because used in microwave radiation.

EMR Electro Magnetic radiation):

In EMR perpendicílar magnetic field, electric field and propagating xatio all three properties are present.

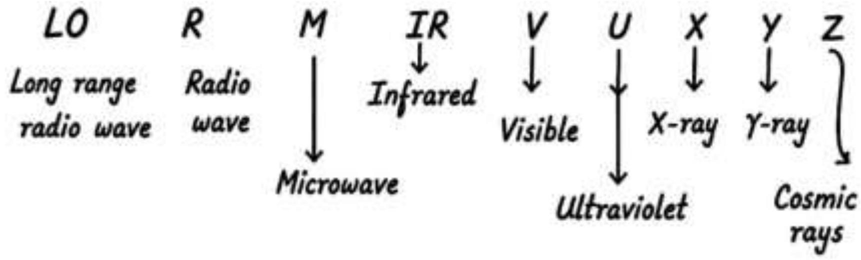




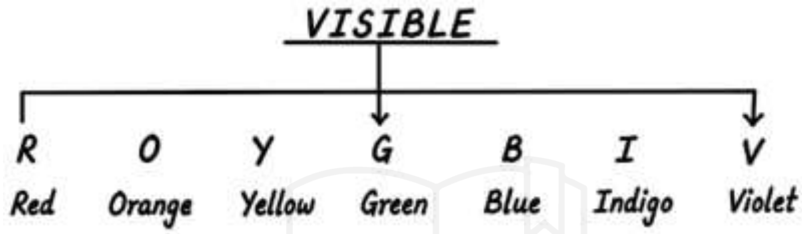
- One photon is used completely at a time.
- These traxe gaps artt all ealal and radiation is also not of a fixed wavelength, it also has a 'range'.
  $J = 1$ to $J = 3$ Not allowed in rotational spectroscopy.

$$\Delta J = \pm 1 \; Allowed$$

Electromagnetic Radiations :-



- Left to right :- Energy ↑ , wavenumber increases, ($\bar{v}$) Frequency ↑ ($v = f$)
- Right to left :- Wave length λ ↑ increases.
- visible we study separate.



Formulas are used :-

$E_{packet} = hv$

h = Planck constant ($6.626 \times 10^{-34}\ J - s$)

$hv = c$

c = speed of light ($3 \times 10^{8}\ cm/s$)

λ = wavelength

v = frequency

$\bar{v}$ = wave number

$\bar{v} = 1/\lambda \; v = c/\lambda$

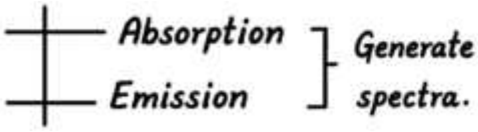
$E_{packet} = hc/\lambda$

When EMR Falls on sample shows three property:

(i) Absorption / Reflection

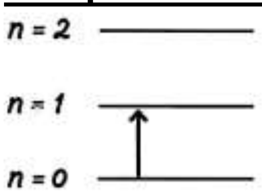
(ii) Diffraction

(iii) Interaction



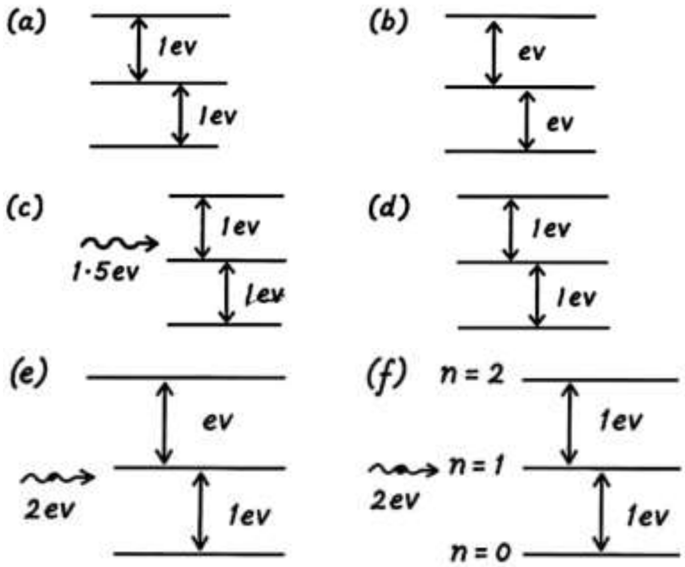
- Spectra has many properties of its own like we can find out bond length , dissociation energy from H^{+}.
- The graph generated by spectroscopy called spectra.

Interpretation of spectra :-



- When a system make a transition it absorbs or emit the energy (in the form of photon) equal to the energy difference between the energy level.

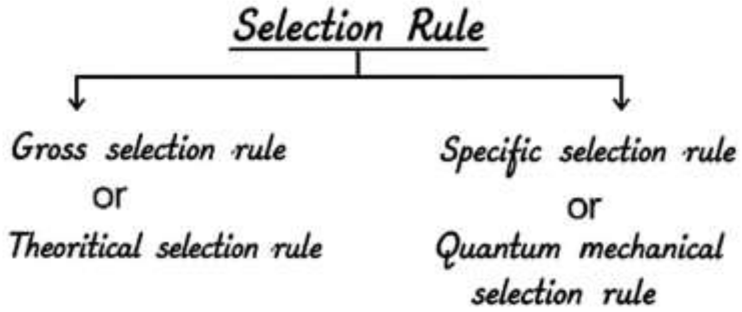
  EX. Which transition are possible ?



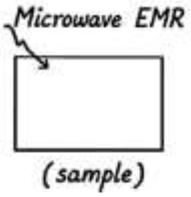
Ans. Condition $\Delta n = \pm 1$ $b, e.$

When transit will occur or not, it depends not only on energy and gap but also depend on selection rule

Radiation	Process	Information
X-rays range $\rightarrow 10^6 - 10^{19}$ Hz	Transition of inner electrons of an atom in a molecule.	Details of electronic structure.
UV - visible (range $-10^{14} - 10^{16}$ Hz)	Transition of outer e^0 (or volume e^0) of an atom in molecule.	Dissociation energy and electronic motion
IR (range $-10^{12} - 10^{14}$ Hz)	change in the vibration al state of molecule.	Dissociation energy and Force constant
Microwave or Infrared $(10^8 - 10^{12}$ $Hz)$	change in the rotational state of molecule.	Internucleardistance (Bond length)
Radio-wave	change in spin $(10^6 - 10^8$ $Hz)$ orientation of nuclei in magnetic field	Magnetic - environment of spinning nuclei from which structure may be determined.



Gross selection Rule for rotation spectroscopy :-



$\Delta J = \pm 1$

- In rotational spectroscopy molecule must have Permanent dipole moment.

Que. What dipole moment present in Co_2 molecule?

Ans: No Because it is linear molecule.

$$0 \equiv c \equiv 0 \; \mu = 0$$

Gross selection Rule for vibration spectroscopy :Molecule must have dynamic dipole moment.

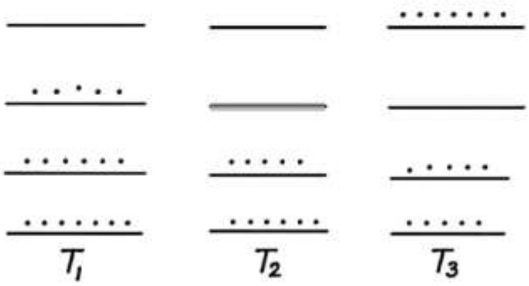
Rotational Raman spectroscopy :-

Anisotropically polarisable $\Delta J = 0, \pm 2$

Population ratio:-

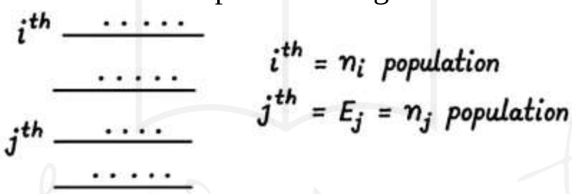
Its explained by Boltzman.

- let's a system have i^{th} and j^{th} energy level.



que. which is large in Temperature T_1, T_2, T_3

Ans. $T_2 > T_1 > T_3$ Because maximum molecule present in highest state



$$\frac{n_i}{n_j} = \frac{g_i}{g_j} e^{-\Delta E/KT}$$

$$\Delta E = E_j - E_i$$

Here T = Temperature, ΔE = difference in energy

k = Boltzman's constant

g = degeneracy (This is different for all)

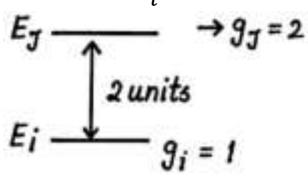
If degeneracy is not given in the questions we let's one.

que. The equilibrium population ratio $\left(\frac{n_J}{n_i}\right)$ of a doubly degenerate energy level (E_i) is lying at energy 2 units higher than a lower nondegenerate level (E_i) assuming $k_B T = 1$ units will be - NET-2013

(a) $2e^{-2}$ (b) $2e^{2}$ (c) e^{2} (d) e^{-2}

Ans. $\frac{n_J}{n_i} = \frac{g_J}{g_i} e^{-\Delta E/kT}$

$$\Delta E = 2\,unit \quad \frac{n_J}{n_i} = \frac{2}{1} e^{-2/T} = 2e^{-2}$$



que. Consider the two state system at thermal equilibrium with equal degeneracy where the excited state is higher in energy than the ground state by 0.1 ev . The ratio of population of the excited state to that of the ground state at a temperature for which [GATE -2016]

$$k_B T = 0.05 eV \ is \ -$$

Ans. $\frac{n_2}{n_1} = \frac{g_2}{g_1} e^{-\Delta E/k_B T}$

$$\Delta E = 0.1 \ k_B T = 0.05$$

$$\frac{n_2}{n_1} = \frac{1}{1} e^{-0.1/0.05}$$

$$\frac{n_2}{n_1} = e^{-2}$$

que. The relative population in two states with energy E_1 and E_2 satisfying Boltzman distribution is given by $\frac{n_1}{n_2} = \frac{3}{2} \frac{g_1}{g_2} e^{-(E_1 - E_2)/KT}$.

The relative degeneracy $\left(\frac{g_2}{g_1}\right)$ is - [NET-2012]

(a) 2 (b) 3 (c) 3/2 (d) 2/3

Ans. $\frac{n_1}{n_2} = \frac{g_1}{g_2} e^{-(E_1 - E_2)/KT}$

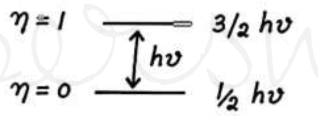
$$than \ \frac{g_2}{g_1} = \frac{n_2}{n_1} = 3/2$$

que. The frequency of Homonuclear diatomic molecule v. The temperature at which the population of the excited state will be half that of the ground state is given by .

(a) $\frac{hvm^2}{k_B}$ (b) $\frac{hv}{ln \ 2k_B}$ (c) $\frac{ln \ 2}{hvk_B}$ (d) $\frac{hvlog \ 2}{k_B}$

Ans. Degeneracy is not given let's one.

$$\eta = 2 \ 5/2hv \ \ \eta = 1 \ 3/2hv$$



$$\frac{\eta_{ES}}{\eta_{gS}} = \frac{1}{T} e^{-\Delta E/k_B T}$$

$$e^{-\Delta E/k_B T} = 1/2 \Rightarrow \frac{-\Delta E}{k_B T} = l n 2$$

$$\frac{\Delta E}{k_B T} = l n 2 \Rightarrow k_B T = \frac{\Delta E}{l n 2}$$

$$T = \frac{\Delta E}{(l n 2) k_B} \therefore \Delta E = hv$$

$$T = \frac{hv}{(ln \ 2) k_B}$$

Statement :- Intensity of spectral line in NMR may be enhanced by lowering the temperature or increasing the magnetic field.

- This statement is true.
  - ✓ First excited state
  - ✓ Ground state

$$\frac{n_{FES}}{n_{gs}} = e^{-\Delta E/kT}$$

If temperature increases than KT ↑ but $\Delta E/KT$ ↓ decreases (or) $\frac{n_{FES}}{n_{gs}}$ © means FES population > ground state population.

If temperature decreases (↓ than KT ↓ but $\Delta E/KT$ ↑ Increases (or) $\frac{n_{FES}}{n_{gs}}$ decreases means ground state population > FES population.

Rotational spectroscopy :-

- There are two things you should know before
- reading this:

  (i) Moment of inertia

  (ii) Classify the molecule as rotor.

que: what do you mean by rotor ?

Ans. Anything that can rotate is called rotor.

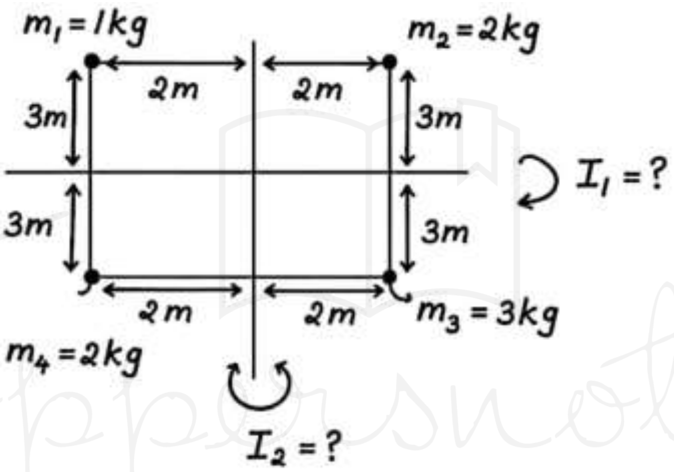
Moment of inertia (I):-

General Expression $I = mr^2$

$r =$ Perpendicular distance to object from axis of motion.

$$I = \Sigma m_i r_i^2$$

Ex. $m_1 = 1\ kg$



Ans. $I_1 = m_1r_1^2 + m_2r_2^2 + m_3r_3^2 + m_4r_4^2$

$$I_1 = 1 \times (3)^2 + 2(3)^2 + 3(3)^2 + 2(3)^2$$

$$I_I = 9 + 18 + 27 + 18 = 72kgm^2$$

$$I_Q = m_1r_1^2 + m_2r_2^2 + m_3r_3^2 + m_4r_4^2$$

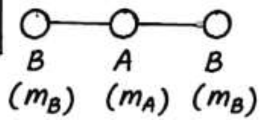
$$= 1 \times (2)^2 + 2 \times (2)^2 + 3 \times (2)^2 + 2 \times (2)^2$$

$$I_Q = 4 + 8 + 12 + 8\ kg\ m^2$$

$$I_Q = 32kgm^2$$

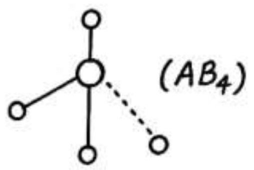
For diatomic molecule :-

$$\boxed{I = m_B r^2 + m_B r^2 = 2m_B r^2}$$



For triatomic molecule :-

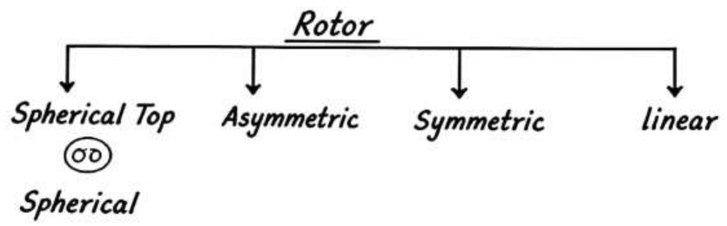
$$\boxed{I = \frac{8}{3} m_B r^2}$$



For octahedral:-

$$I = 4m_B r^2$$

Rotor:-



Spherical Rotor:-

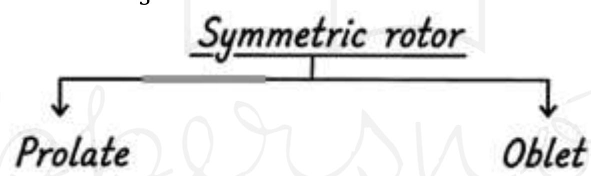
- If we try to apply three axis to a molecule like such a router then if all three are equal and also non-zero, then such a molecule is called a spherical rotor (0) spherical top rotor.
  Ex. $I_A \neq I_B \neq I_C \neq 0 \rightarrow$ Conditions
- If point group of molecule is tetrahedral, octahedral and Icosahedral.
  Ex. $CH_4, Ccl_4, SF_6, XeO_4, P_4$ etc.

Asymmetric rotor :-

- Molecules in which the higher principal axis is either C_2 or smaller than C_2 are called asymmetric rotors.
  Ex. H_2O, H_2CO etc

Symmetric rotor :-

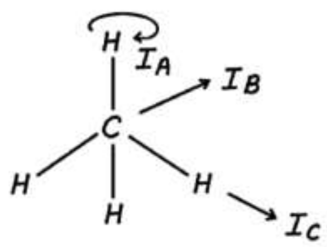
- It is classified in two types.
- Principal axis is C_3 © greater than C_3.



Linear rotor :-

- Out of three axis moment of inertia is zero along one axis. ($I_A = 0$)
- Point group - $C_{\infty v}, D_{\infty h}$, etc.

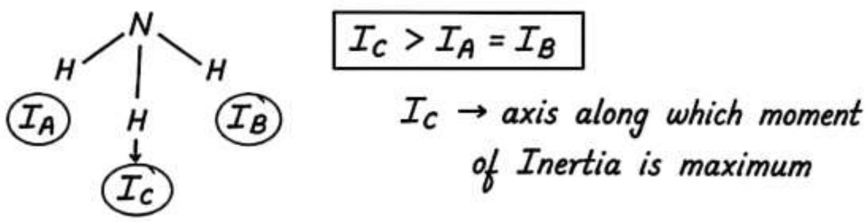
Prolate (Types of symmetric):-



$I_A \rightarrow$ along which moment of Inertia is minimum.
Here $I_c =$ maximum

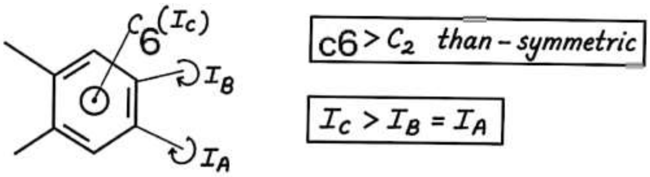
$$I_C = I_B > I_A$$

(ii) oblate (Types of symmetric):-



Que. Find out Benzene Molecule is prolate or oblate ?

Ans. oblate



Que. Identify the molecule assymmetric (prolate and oblate), Asymmetric, spherical linear rotor

(i) Chlorobenzene
Ans. Asymmetrical

(ii) CCl_4
Ans. spherical

(iii) H_2O
Ans. Asymmetrical

(iv) CH_3I
Ans. Symmetrical (prolate)

(v) NH_3
Ans. Symmetrical (oblate)

(vii) OCS
Ans. linear

(viii) $SO_4{}^{2-}$
Ans. spherical

(x) C_6H_6
Ans. Symmetrical (oblate)

(vi) BF_3
Ans. Symmetrical

(viii) BF_3
Ans. Symmetrical

(ix) UF_6
Ans. spherical

(xi) $CH_3 - C \equiv N$
Ans. Symmetrical

Rotational spectroscopy:-

- Interaction of EMR with matter's rotational energy levels.
- To understand rotation spectra required.
  (i) Bohr frequency condition (energy expression)
  (ii) Selection rule (Transition forbidden or allowed)
  (iii) Population ratio (Relative population in difference energy levels.

Bohr Frequency:-

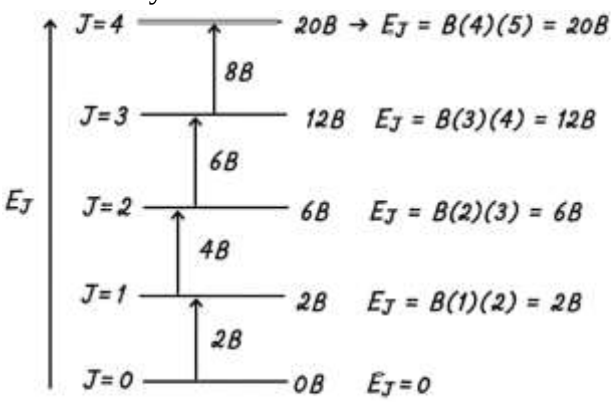
- From Schrodinger eqn.

$$E_J = BJ(J+1)(J = 0,1,2,3 \ldots)$$

$$B = rotationalconstant = \frac{h^2}{8\pi^2 I} = \frac{h^2}{8\pi^2 \mu r^2}(Joule)$$

$$degeneracy = 2J+1$$

- In SHO energy level gap increases by 2B.



Selection Rule :-

(i) Gross selection rule (or) Theoretical selection rule

(ii) Specific selection rule (or) quantum mechanical selection.

Gross selection Rule :-

According to Gross selection Rule molecule must have permanent dipole moment.

que: which molecule show interact.

Ex. (a) $H_2 = NO$ (b) $O_2 = NO$

(C) $N_2 = NO$ (d) co = Yes

$E_J = BJ(J+1)$

let's us assume a transition from J to $J+1$

Ex. $\Delta E_{17\to 18} = 2B(17+1)$

$= 36B$

Ex. $\Delta E_{32\to 33} = 2B(32+1)$

$= 66\ B$

If levels are not successive then we use old traditional method.

$$\Delta E_{J\to J+1} = E_{J+1} - E_J$$

$$\Delta E_{J+1} = B(J+1)(J+1+1) - BJ(J+1)$$

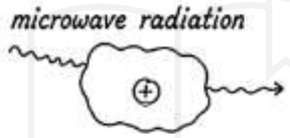
Ex. $\Delta E_{18\to 21} = E_{21} - E_{18}$

$$\Delta E_{18\to 21} = B(21)(21+1) - B(18)(18+1)$$

$$= 21B(22) - 18B(19)$$

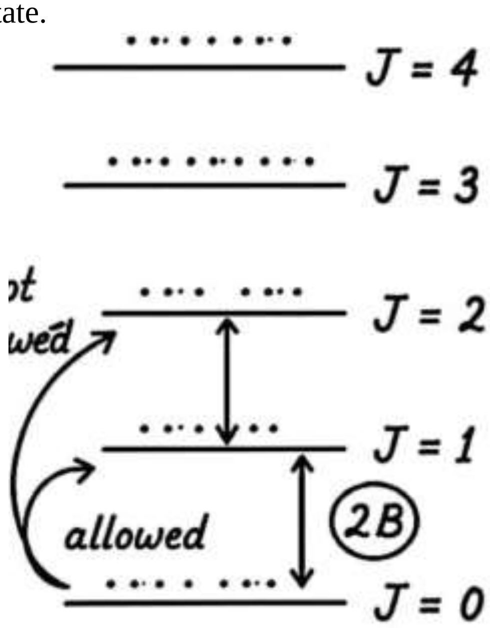
$$= 462B - 342B$$

$$= 120B$$

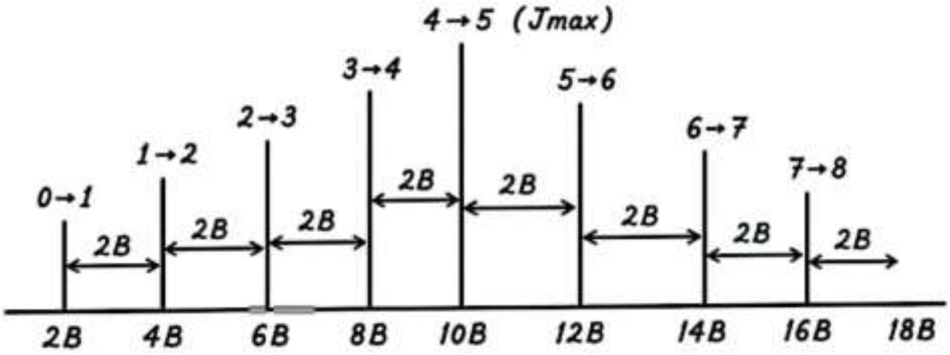


Rotationally active sample (gaseous)

- Suppose there is a rotationally active sample which is in the gaseous phase.
- Because in the gaseous phase rotation occurs propely, microwave radiation will show interaction with it, since the molecule is rotationally active. And the energy (wavelength) of this radiation will also lie in a certain range.
- The radiation is such that the molecule absorbs it in order to move from one energy level to another. That means when then radiation comes out ; the absorbed photons will be missing. The machine reads this and we see the lines in the spectra.
- Let the sample's temperature be T and if the sample's temperature is low - then maximum population in the ground state.
- Therefore in a spectroscopic machine the sample is made completely cold so that the maximum population is in the ground state.



- The more molecule goes up the more intensity will be meaning the height will appear higher in the spectra.
- Let suppose that there are many levels and in one of them there is maximum population, that is called Jmax.



most populated state = $4 \rightarrow 5(10B) \rightarrow$ $maximum\ population$

- These lines are called spectral lines.

$$Difference\ between\ successive\ \ spectral\ lines\ = 2B$$

- If suppose gap between spectral lines is 10 .

$$10 = 2B = \frac{2h^2}{8\pi^2\mu r^2}$$

$$r = \ internuclear\ distance.$$

Que. For a diatomic molecule AB energy for rotational transition from $J = 0$ to $J = 1$ state is $3.9\ cm^{-1}$ The energy for the rotational transition from $J = 3$ to $J = 4$ is -

(a) $3.9\ cm^{-1}$ (b) $7.8\ cm^{-1}$

(c) $11.7\ cm^{-1}$ (d) $15 \cdot 6\ cm^{-1}$

Ans. $\Delta E_{0\rightarrow 1}\ \ = 3.9\ cm^{-1} = 2B$

$\Delta E_{3\rightarrow 4} = 2B(J+1)$

$= 2B(3+1) = 8B \simeq 4(2B)$

$\Rightarrow 4(3.9) cm^{-1}$

$\Delta E_{3\rightarrow 4} = 15.6\ cm^{-1}$

$$B\ \ = \frac{h^2}{8\pi^2\mu r^2} \Rightarrow\ unit\ \rightarrow Joule$$

$$= \frac{(J\cdot S)^2}{kgm^2} = \frac{J^2S^2}{kgm^2} = \frac{J^2}{kgm^2}/s^2 = \frac{J^2}{J} = \ Joule$$

$$1\,Joule\ = \frac{kgm^2}{s^2}$$

- Joule is always defined in terms of kilogram (kg) meter (m) and second (s).

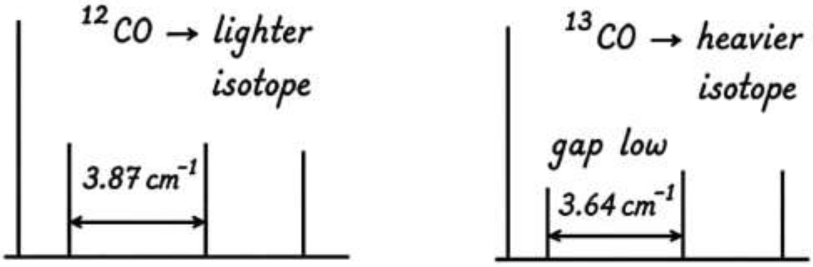
<u>Some important formula</u>

1. $B = \frac{h^2}{8\pi^2\mu r^2}$ (Joule)	2. $K\nu = c$
3. $\nu = \frac{c}{\lambda}$	4. $\nu^{-} = \frac{1}{\lambda}$
5. $E_p = h\nu = \frac{hc}{\lambda} = hc\nu^{-}$	6. $B = \frac{h}{8\pi^2\mu r^2}$ (cm^{-1})
7. $B = \frac{h}{8\pi^2\mu r^2}$ (s^{-1})	Here $c = 3\times 10^{10}\ cm\ s^{-1} h = 6.626\times\ 10^{-34}\ J.s$

$$B = \frac{h^2}{8\pi^2\mu r^2}\ (Joule)\ divide\ (hc)\ (\,Joule\ to\ cm\ ^{-1}\ convert\ \ divide\ hc\,)$$

$$B = \frac{h^2}{8\pi^2\mu r^2}\ (Joule)\ divide\ (h)\ \ (Joule\ to\ s^{-1}\ convert\ \ divide\ h\,)$$

Isotopic substitution effect on rotational spectra :-



Que: What difference is substituting these (molecules ^{12}CO and ^{13}CO) going to make to the spectra?

Ans. There was a scientist, Uilman who first thought that when generating spectra, it was found that heavier isotopes.

- ✓ The line seen in the spectra was a closer line as compared to lighter isotopes.
- ✓ In heavier a 3.64 cm gap was observed and in lighter a 3.87 cm gap was observed.
- ✓ As we know $B = \frac{h^2}{8\pi^2 \mu r^2}$
- ✓ On Isotopic substitution there is no significant impact on bond length (r) because in isotopic substitution bond formed by electron sharing.

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

  $B_1\mu_1 = B_2\mu_2$ (or) $B\mu = B'\mu'$
- ✓ If $B \downarrow\downarrow$ μ and 2B decline spacing in spectra ↓

Que: The spacing between the rotational lines of HF is $40\ cm^{-1}$. The corresponding spacing between the rotational lines in DF is approximately. [GATE-2002]

(a) 20 cm^{-1} (b) 30 cm^{-1}

(c) 60 cm^{-1} (d) 75 cm^{-1}

Ans. $B_1\mu_1 = B_2\mu_2$

$$B_{HF}\mu_{HF} = B_{DF}\mu_{DF}$$
$$\frac{20 \times 1 + 19}{20} = B_{DF} \times \frac{2 \times 19}{21}$$
$$\frac{20 \times 19}{20} = B_{DF} \times \frac{2 \times 19}{21}$$
$$B_{DF} = \frac{20 \times 21}{2 \times 20} = 21\ cm^{-1}$$
$$20 = 2B_{DF}$$
$$B_{DF} = 10\ cm^{-1}$$

- ✓ **Spacing between spectral lines $2B_{DF} = 2(10)cm^{-1}$**

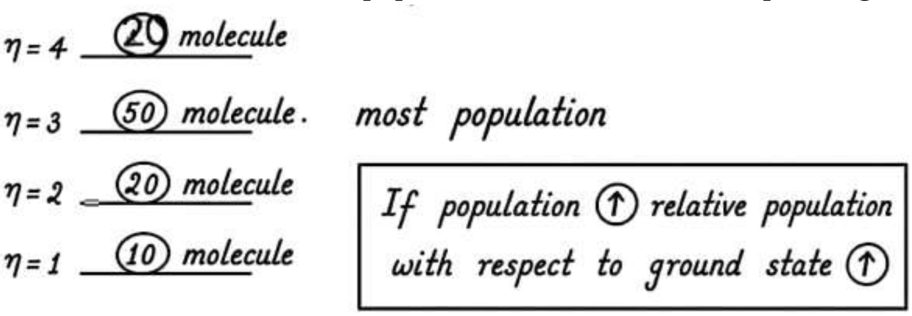
  $= 20\ cm^{-1}$.

Population Ratio :-

As per Boltzman $\frac{\eta_2}{\eta_1} = \frac{g_2}{g_1} e^{-\Delta E/kT}$

$$\Delta E = E_2 - E_1$$

let us determine the relative population of J^{th} state with respect to ground state.



Ex. $\frac{\eta_2}{\eta_1} = \frac{20}{10} = 2$ and $\frac{\eta_3}{\eta_1} = \frac{50}{10} = (5) \Rightarrow \Rightarrow$ *as more as compare* to (2)

In rotation motion ground state degeneracy is one-

$$g_J = 2J + 1$$

$$\frac{n_J}{n_0} = \frac{g_J}{g_0} e^{-\Delta E/k_B T}$$

$$\frac{n_J}{n_0} = (2J+1) e^{-\Delta E/k_B T}$$

$$As\ \Delta E = E_J - E_0$$

$$\Rightarrow BT(J+1) - 0 = BT(J+1)$$

$$thus\ \frac{n_J}{n_0} = (2J+1)e^{-BJ(J+1)/kT}$$

To determine maxima and minima we put

$$\frac{d(n_J/n_0)}{dJ} = 0$$

$$\frac{d}{dJ}(2J+1)e^{-BJ(J+1)/kT} = 0$$

than differentiate

$$J_{max} = \left[\sqrt{\frac{kT}{2B}} - \frac{1}{2}\right] - Joule \quad (maxima)$$

If B is given in Joule use above formula.

$$K = 1.38 \times 10^{-23}\, J/k$$

unit of $J_{max} = \frac{\frac{J}{k} \times K}{2B} =$ Joule

If B is given cm^{-1} then divide hc

$$J_{max} = \sqrt{\frac{KT}{2Bhc}} - \frac{1}{2}\ (B = cm^{-1})$$

If B is given in s^{-1} then divide h

$$J_{max} = \sqrt{\frac{KT}{2Bh}} - \frac{1}{2}$$

Que: Will the ground state having highest population while studying rotational spectra ?

(a) Yes

(b) No

(c) Need more information

Ans. No.

Que: The population of J^{th} rotational level

$$N_J = N_0(2J+1)e^{-BJ(J+1)/KT}$$

The value of J_{max} is -

(a) $\frac{KT}{2B}$

(b) $\frac{\sqrt{\frac{2KT}{B}} - 1}{2}$

(c) $\frac{\sqrt{\frac{2KT}{B}} - 1}{2}$

(d) $\frac{KT}{2Bhc}$

Ans. root is complete optim not extend

$$J_{max} = \sqrt{\frac{KT}{B}} - \frac{1}{2}$$

expand 2^{nd} case $\frac{\sqrt{\frac{2KT}{B}}-\frac{1}{2}}{2}$

$$= \frac{1}{2}\sqrt{\frac{2KT}{B}} - \frac{1}{2}$$

$$= \sqrt{\frac{2KT}{4B}} - \frac{1}{2}$$

$$\Rightarrow \sqrt{\frac{KT}{2B}} - \frac{1}{2}$$

Que: The most populated rotation state for HCl ($B = 8.5\ cm^{-1}$) at 300 K is - [GATE - 2010]

(a) 2 (b) 3

(c) 5 (d) 7

Ans. Given $B = 8.5\ cm^{-1}\ T = 300\ K$

$$K = 1.38 \times 10^{-23}\ J/K$$

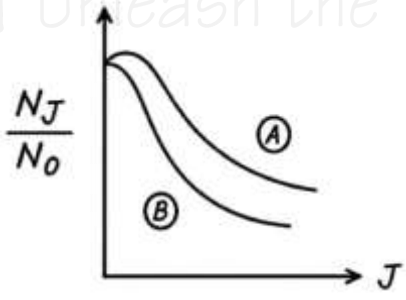
$$J_{max} = \sqrt{\frac{KT}{2Bhc}} - \frac{1}{2}$$

$$= \sqrt{\frac{1.38 \times 10^{-23} \times 300}{2 \times 8.5 \times 3 \times 10^{10} \times 6.626 \times 10^{-34}}} - \frac{1}{2}$$

$$= \sqrt{\frac{1.38 \times 50}{8.5 \times 6.626 \times 10^{-1}}} - \frac{1}{2}$$

$$= 3.5 - \frac{1}{2} = 3$$

Que: The graph between $\frac{N_J}{N_0}$ and J (rotational quantum number) is drawn below -

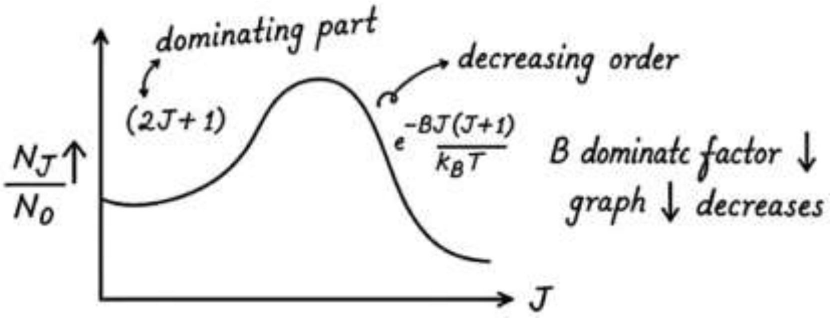


(a) $B_A = B_B$ (b) $B_A > B_B$

(c) $B_A < B_B$ (d) Can't say

Which of the following is true?

Ans. $\frac{N_J}{N_0} = (2J+1)e^{-BJ(J+1)/k_BT}$



In Graph B is highly decrease

than $B_A > B_B$

Rotor

→ **Rigid**

$E_J = BJ(J+1)$

All we have read about rigid rotor.

→ *** **Non-Rigid Rotor**

In practical life, all rotors are non-rigid.

→ In this also 3 condition apply.

- Selection Rule and population ratio is same as rigid rotor

Application of LVP

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

D = Centrifugal distortion constant

Bond has spring nature

↓

If rotation speed increases

↓

'J' increases

↓

Bond length (r) ↑ then B ↓ − 2B ↓ spacing between spectral lines

- Atoms are connected by a bond which has a spring nature.

- Assume one end of the spring is held and a block of mass (m) is attached to the other and we are rotating it.
- As the speed of rotation increases the rotational quantum number (J) increases. As speed increases the spring stretches which means the bond length increases and we are calling the bond length r (gamma).
- If r increases then B will decreases, due to which the spacing between spectral lines (2B) will also decreases.

Rigid Rotor (ideals) :-

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

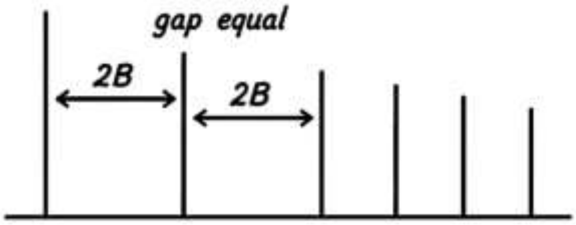
$$B = \frac{h^2}{8\pi^2 I} \ or\ \frac{h^2}{8\pi^2 \mu r^2}\ (Joule)$$

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

$$Selection\ Rule\ \Delta J = \pm 1$$

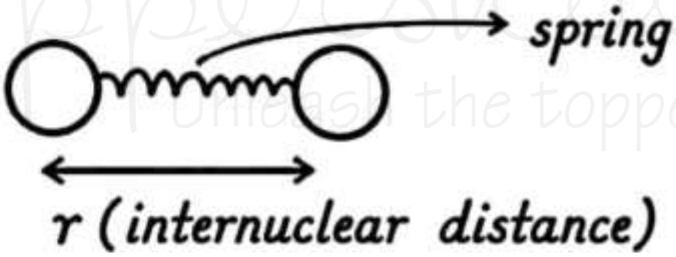
$$Population\ ratio\ \frac{n_J}{n_o} = (2J+1)e^{-BJ(J+1)/kT}$$

- Line spacing between spectral lines $= 2B$
- Gap between spectral lines decreases linearly.



- If intensity of all spectral lines is equal, then gap is also equal $= 2B$
- If it is a rigid rotor, then we assume B is constant.
- It is a molecule (diatomic molecule).
- If the bond length has a fixed value, then it will not stretch because in a rigid bond we neglect the spring nature. Therefore, increasing J will have no effect.
- If speed of rotation increases, then there is no impact on r (internuclear distance).
- Neglecting spring nature means neglecting centrifugal distortion.
- (↑) speed of rotation (↑) then No impact on r (internuclear distance).

<u>Non - Rigid (Real System):-</u>



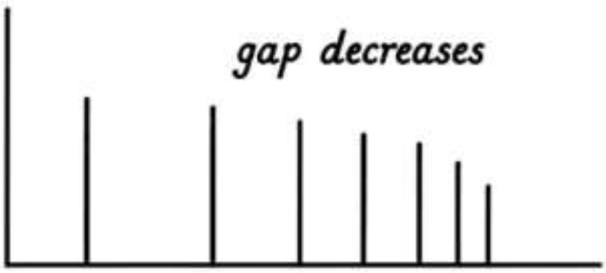
Rotation speed increases (J)

⇓

Internuclear distance (↑)

$$B \propto \frac{1}{r^2}\ r \pitchfork\ B(\downarrow)$$

Rotational constant decreases (B) then line spacing $(2B)$ decreases in spectra.



- If intensity of spectral lines is equal. Gap is decreases non - linearly. use linear variational principle

$$E_J = BJ(J+1) - DJ^2(J+1)^2$$

D = Centrifugal distortion constant

- Selection rule or population ratio are same but. Both frequency condition is change so energy expression is change.
- But in actual expression of E_J for non-rigid

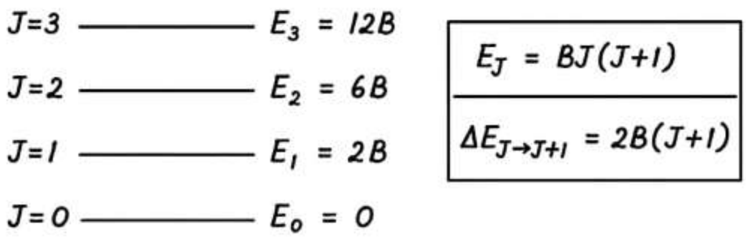
$$E_J = BJ(J+1) - DJ^2(J+1)^2 + HJ^3(J+1)^3 - kJ^4(J+1)^4 + \cdots$$

But

$$B \ggg> D \ggg> H \gg K$$

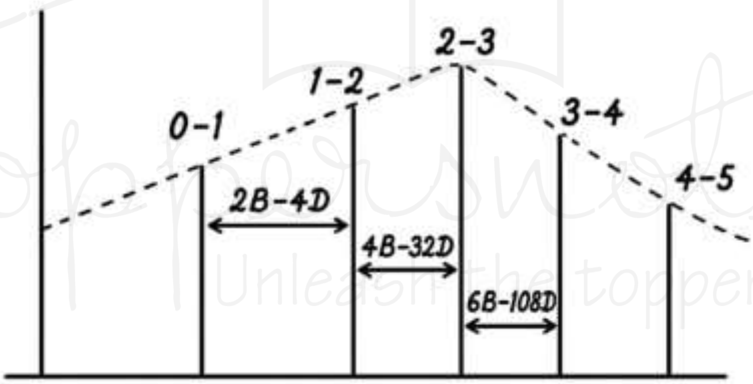
very small (may be neglected)
then reduced expression is -

$$E_J = BJ(J+1) - DJ^2(J+1)^2$$
$$E_1 = B(1)(2) - D(1)(4) = 2B - 4D$$
$$E_2 = B(2)(3) - D(2)^2(3)^2 = 6B - 36D$$
$$E_3 = B(3)(4) - D(3)^2(4)^2 = 12B - 108D$$



For Rigid

For Non-Rigid :-



graph decreases non-linearly.

Vibration spectroscopy / IR spectroscopy :-

- **EMR -** IR radiation
- Matter's energy level - vibration
- Interaction of IR radiation with matter vibration energy level called vibration / IR spectroscopy.

Gross-selection rule :-

Molecule must have dynamic dipole moment.

Que: Does CO_2 molecule have dipole moment ?

Ans: $0 = c = 0$

Carbon dioxide (CO_2) is a linear molecule.

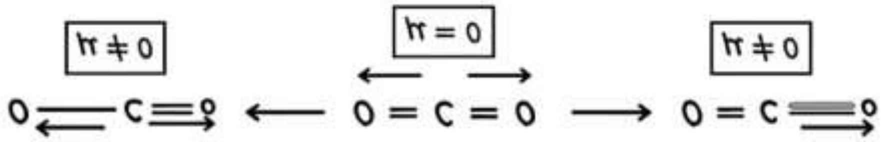
- Each $c = 0$ bond has a dipole moment but the overall molecule is non-polar because the bond dipoles cancel each other.
- So the net dipole moment $(\mu) = 0$
- Since the molecule has no permanent dipole moment it is rotationally inactive.
- During vibration because of the spring nature of the bond a dynamic dipole moment may be generated.

- For symmetric stretching.

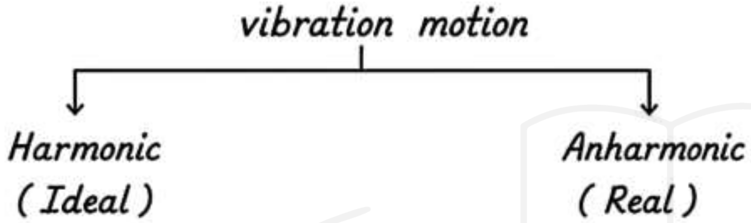
$$0 = c = 0$$
$$\mu = 0$$

- Even when the bonds stretch equally on both sides (symmetric stretching) the dipole moments cancel out due to symmetry so no dipole moment is generated.
- This modes is IR inactive.

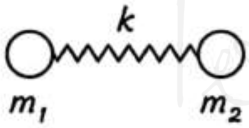
For Asymmetric stretching :-



- In asymmetric stretching one $C = 0$ bond compresses while the other stretches.
- Because of this the dipole moment do not cancel.
  So $\mu \neq 0$
- Therefore a dynamic dipole moment is generated.
- Hence, in CO_2 asymmetric stretching is (IR) vibrationally active.



<u>Harmonic (Ideal)</u> :-



vibrational Frequency $\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$

- Graph make with help of Hook's law For simple harmonic oscillator Model.

$$V = \frac{1}{2}kx^2$$

  Here. $V =$ potential energy
- Stored energy in the spring called potential energy.
- Graph is parabolic.

$$E_n = \left(n + \frac{1}{2}\right)h\nu \rightarrow Joule$$

∴ $E_J = BJ(J+1)$