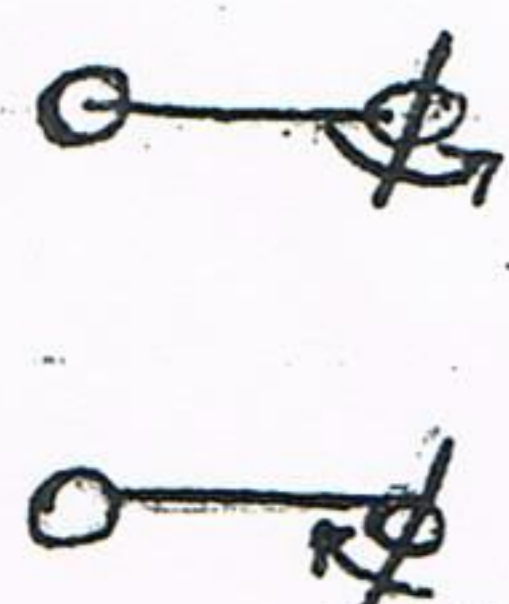
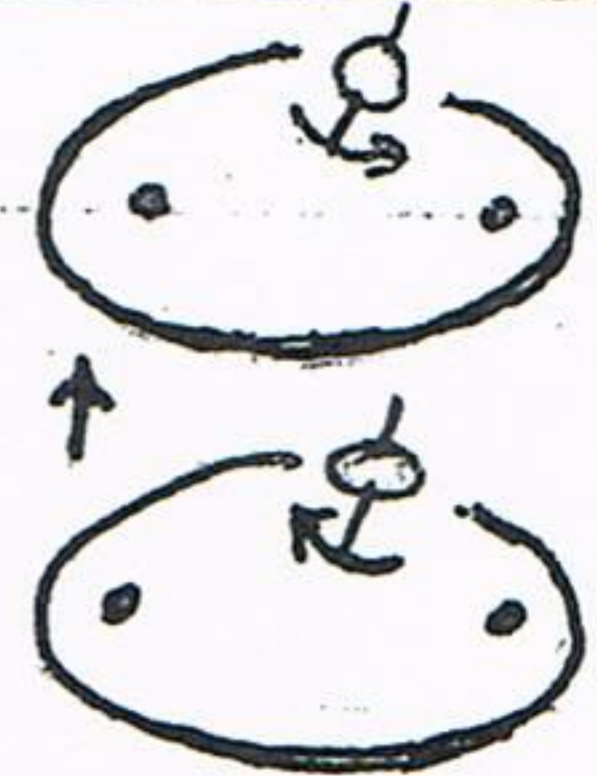
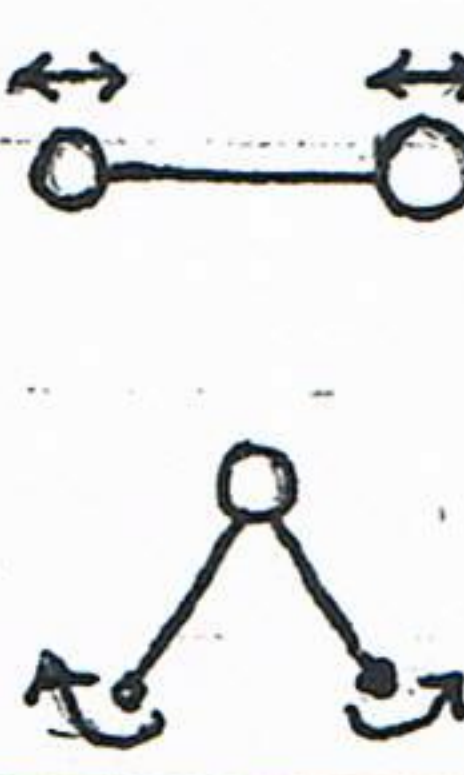
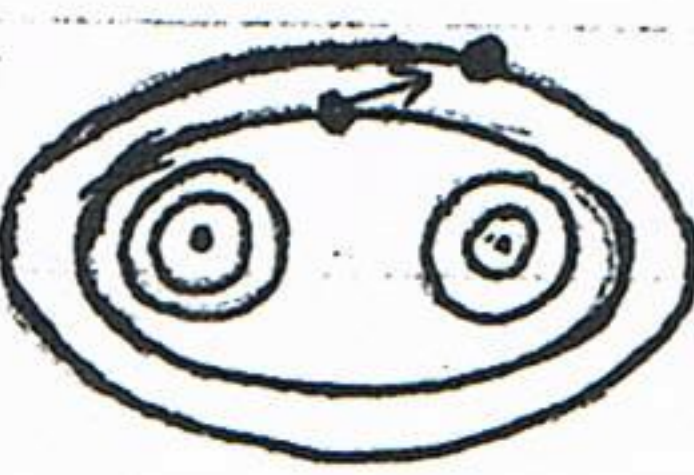


Regions of the spectrum

n.m.r	e.s.r	Microwave	InFra-red	Visible and Ultra-violet	X-ray	γ-ray
						
10^2	1	100	$\frac{4}{10}$	cm^{-1}	10^6 (wavenumber)	10^8 ($\tilde{\nu}$)
10m	100cm	1cm	100 μm	1 μm	10nm (wavelength)	100pm (λ)
3×10^6	3×10^8	3×10^{10}	3×10^{12}	3×10^{14} Hz	3×10^{16} (frequency)	3×10^{18} (v)
10^{-3}	10^{-1}	10	10^3	10^5 Joules/mole	10^7 (energy)	10^9 (E)

Fig(1) The regions of the electromagnetic spectrum.

1. Radio Frequency region, $3 \times 10^6 - 3 \times 10^{10}$ Hz ; 10m – 1cm wavelength, Nuclear magnetic resonance (n.m.r) and electron spin resonance (e.s.r).
2. Microwave region, $3 \times 10^{10} - 3 \times 10^{12}$ Hz ; 1cm – 100 μm wavelength, Rotational spectroscopy. a molecule such as HCl in which H-atom carries a permanent net positive charge and the other a net negative charge is said to have a permanent electric dipole moment. if its consider the rotation of HCl, then we see that the plus and minus charges change places periodically and the component dipole moment in a given direction fluctuates regularly Fig (2-a). This fluctuation is plotted in Fig (2-b) and its seen to be exactly similar in form to the fluctuating electric field of radiation, thus interaction can occur, energy can be absorbed or emitted and the rotation gives rise to a spectrum. (All molecules having a permanent moment are said to be "microwave active" if there is no dipole as in H_2 or Cl_2 , no interaction can take place and the molecule is "microwave inactive".

(2)

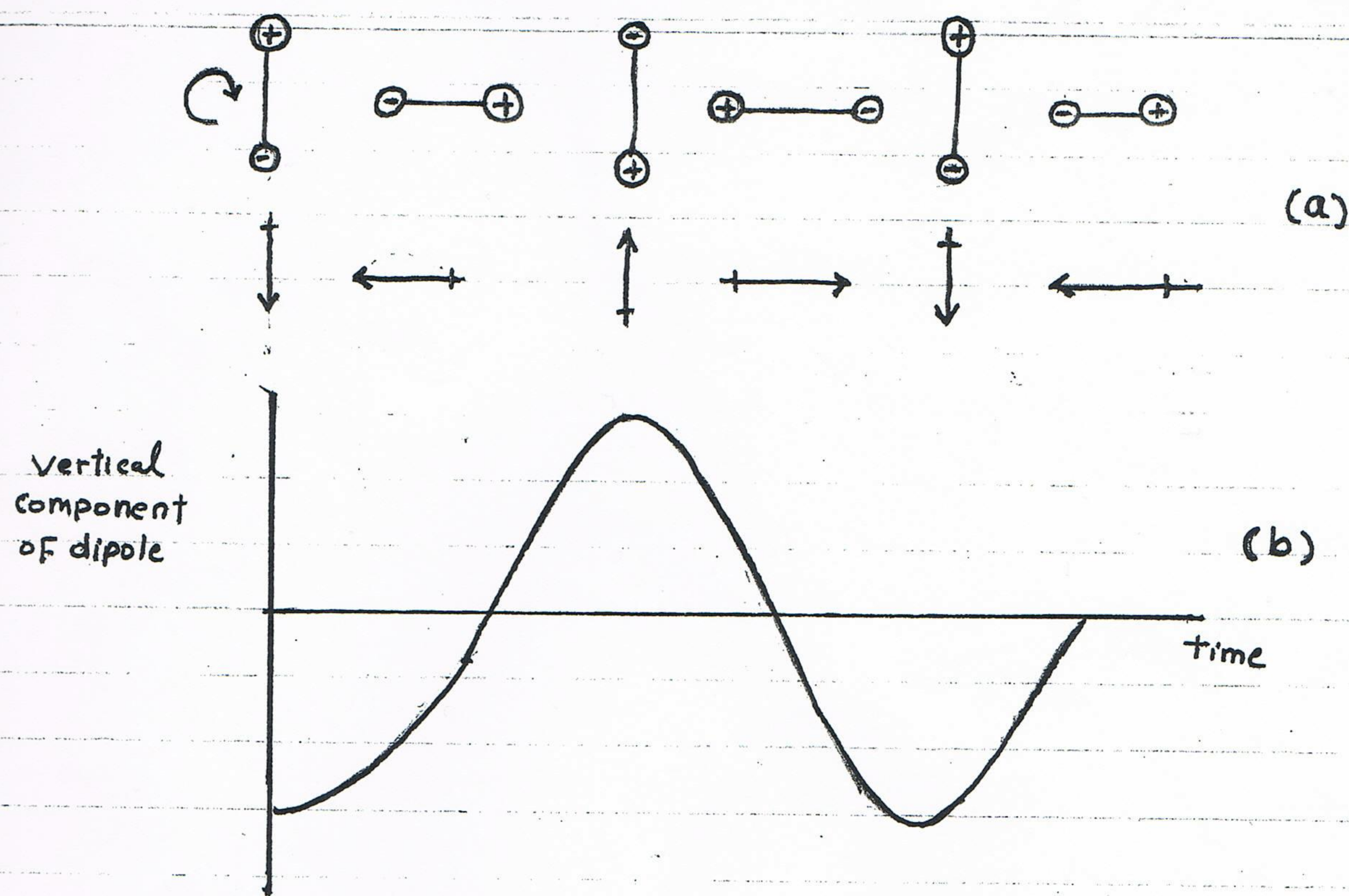
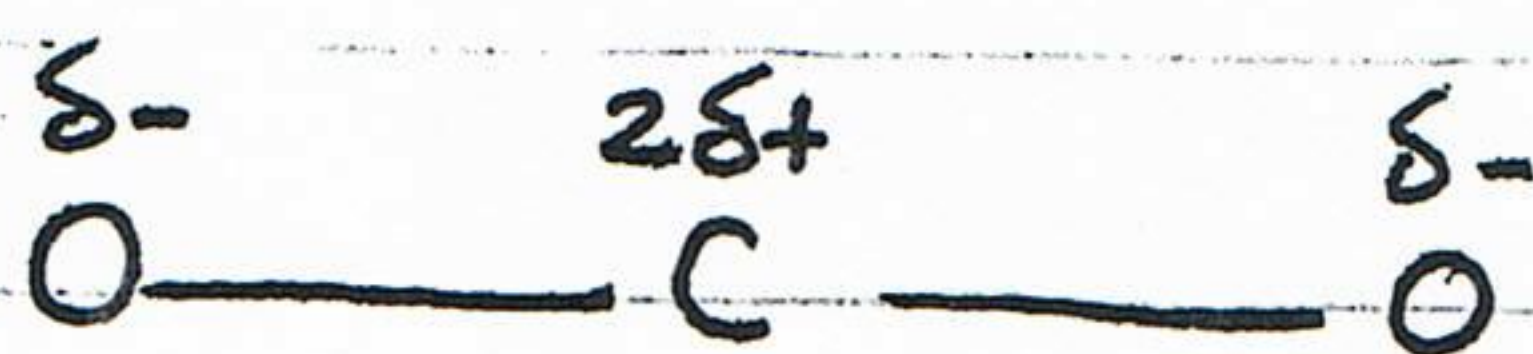


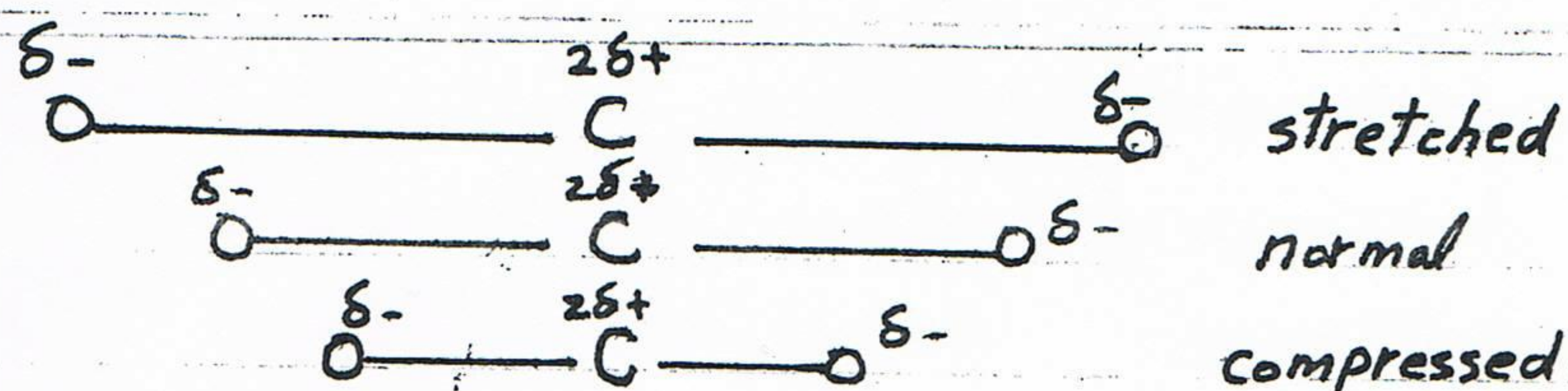
Fig (2) the rotation of a diatomic molecule, HCl, showing the fluctuation in the dipole moment measured in a particular direction.

3 - Infra-red region $3 \times 10^{12} - 3 \times 10^{14}$ Hz; $100 \mu\text{m} - 1 \mu\text{m}$ wavelength vibrational spectroscopy. here in this region it is vibration rather than rotation which must give rise to a dipole change; for example carbon dioxide molecule in which three atoms are arranged linearly with a small net positive charge on the carbon and small negative on oxygens.



this mode of vibration known as the symmetric stretch i.e. molecule is stretched and compressed alternately and both C—O bonds changing simultaneously as shown in Fig(3) and plainly the dipole moment is zero throughout the whole of this motion thus is called infra-red inactive.

(3)



Fig(3) the symmetric stretching vibration of the carbon dioxide molecule
 However there is another stretching vibration called the antisymmetrical stretch Fig(4), here one bond stretches while the other is compressed as be shown in the Fig(4) thus there is a periodic alteration in the dipole moment and the vibration is thus infrared active.

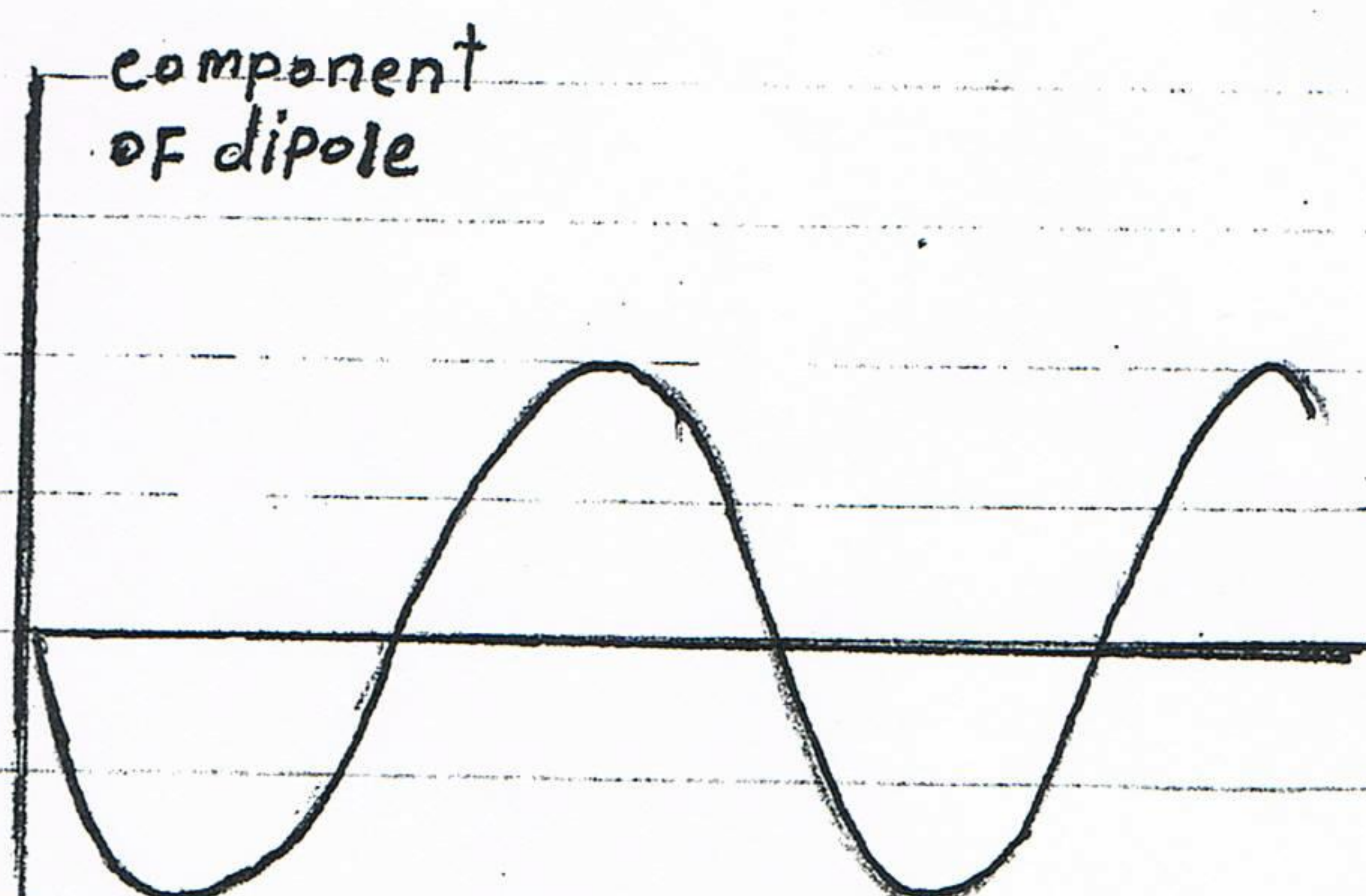
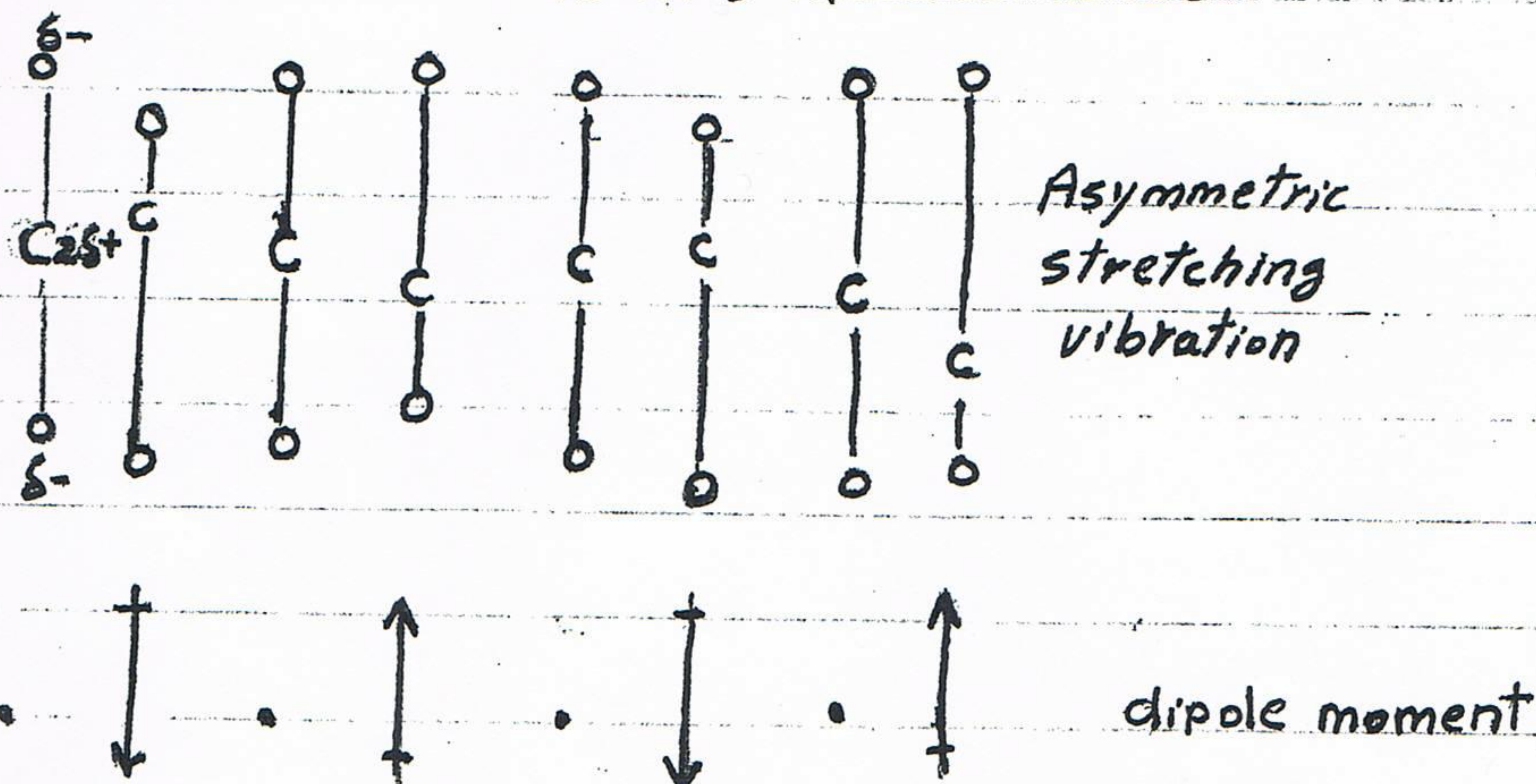


Fig (4)

4- Visible and ultra-violet regions ; $3 \times 10^{14} - 3 \times 10^{16}$ Hz ; $1 \mu\text{m} - 10 \text{nm}$ wavelength , Electronic spectroscopy

5- X-ray region ; $3 \times 10^{16} - 3 \times 10^{18}$ Hz ; $10 \text{nm} - 100 \text{pm}$, wavelength , Energy change involving the inner electrons of an atom or a molecule

6- γ -ray region ; $3 \times 10^{18} - 3 \times 10^{20}$ Hz ; $100 \text{pm} - 1 \text{pm}$, wavelength . Energy changes involve the rearrangement of nuclear particles

the Rotation of Molecules :-

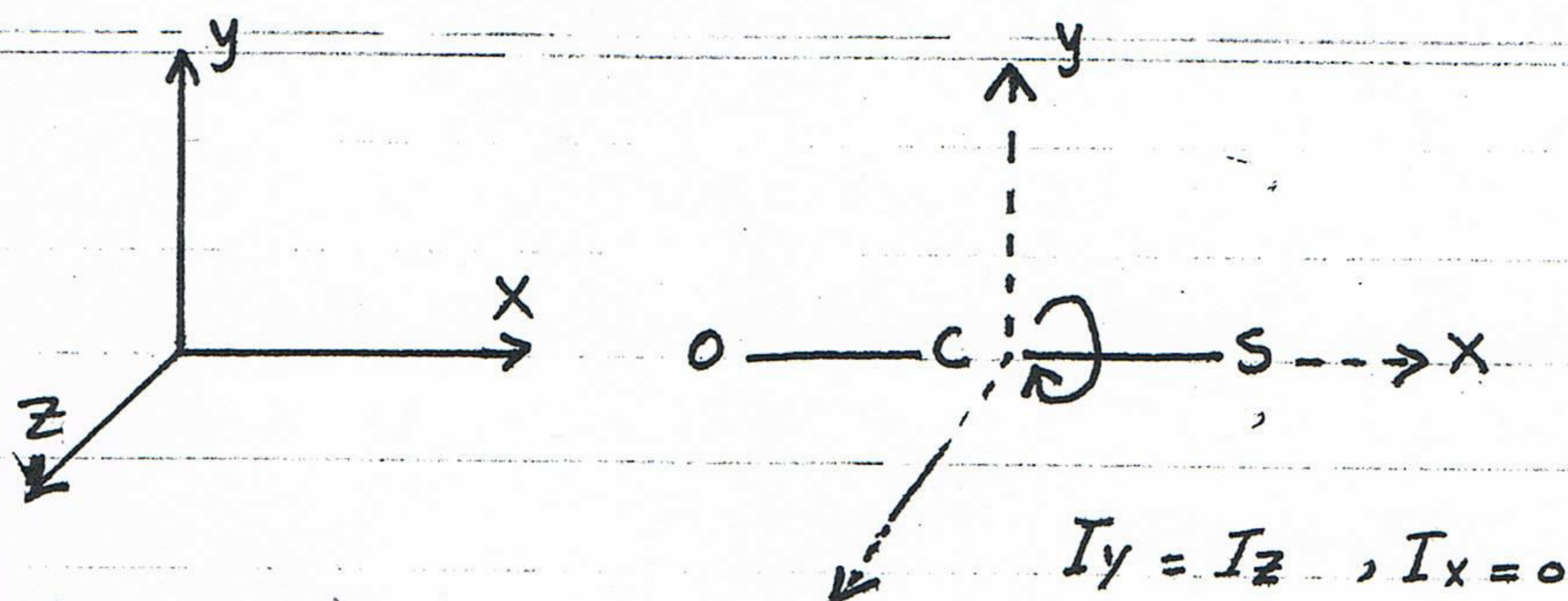
the rotation of a three dimensional body may be quite complex and it is convenient to resolve it into rotational components about three mutually perpendicular directions through the center of the gravity - the principal axes of rotation . thus a body has a three principal moments of inertia , one about each axis , which are usually designated I_A , I_B and I_C . Then the molecules may be classified into groups according to the relative values of their three principal moments of inertia .

1- Linear molecules . These are molecules in which all the atoms are arranged in a straight line , such as HCl or carbon oxysulphide OSC



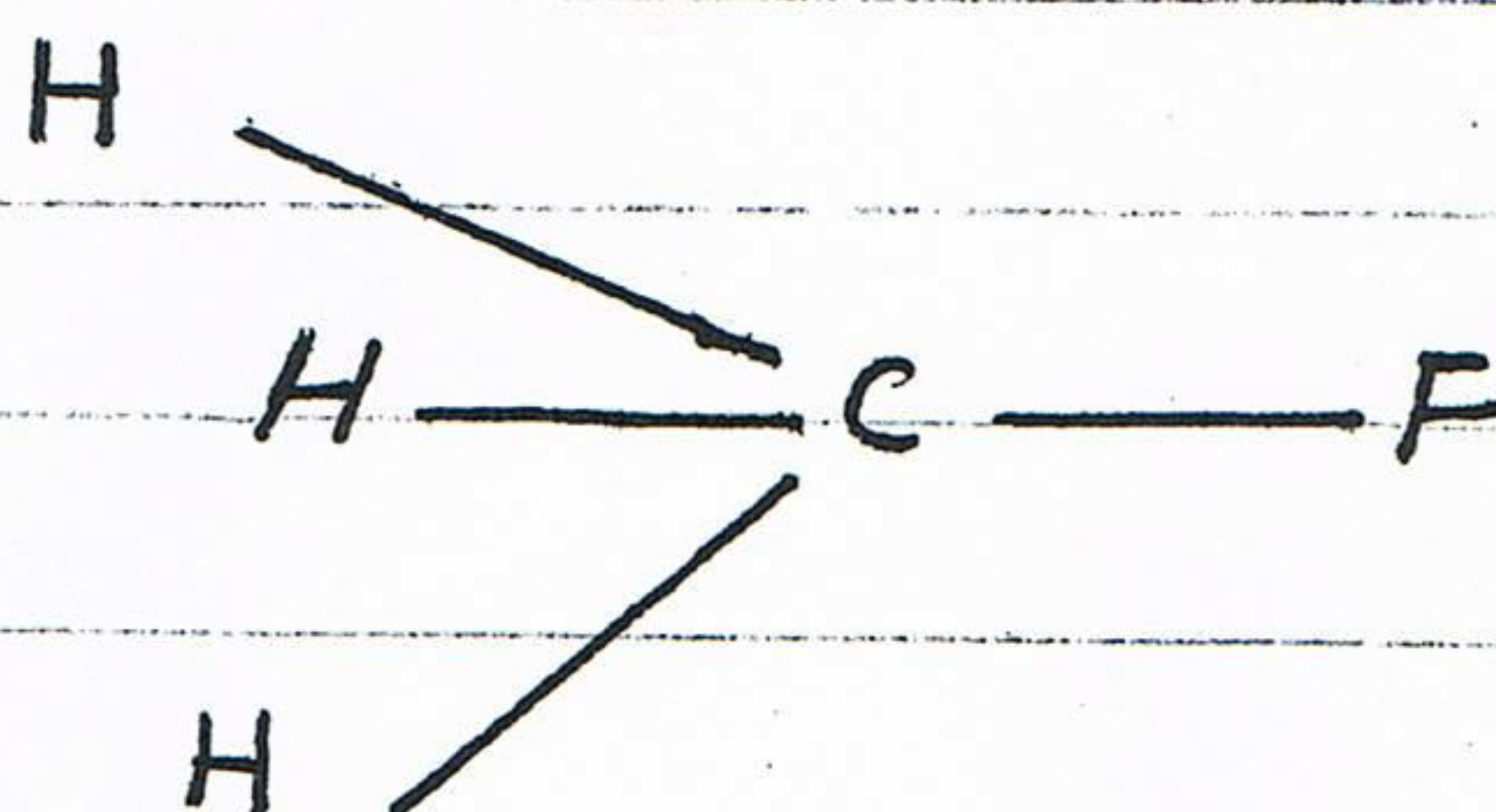
the three directions of rotation are (a) about the bond axis I_A , (b) end-over-end rotation in the plane of the paper I_B , (c) end-over-end rotation at right angles to the plane (I_C) . the moment

$I_B = I_C$, but I_A is very small and as an approximation, may say that $I_A = 0$. Thus $I_B = I_C$, $I_A = 0$



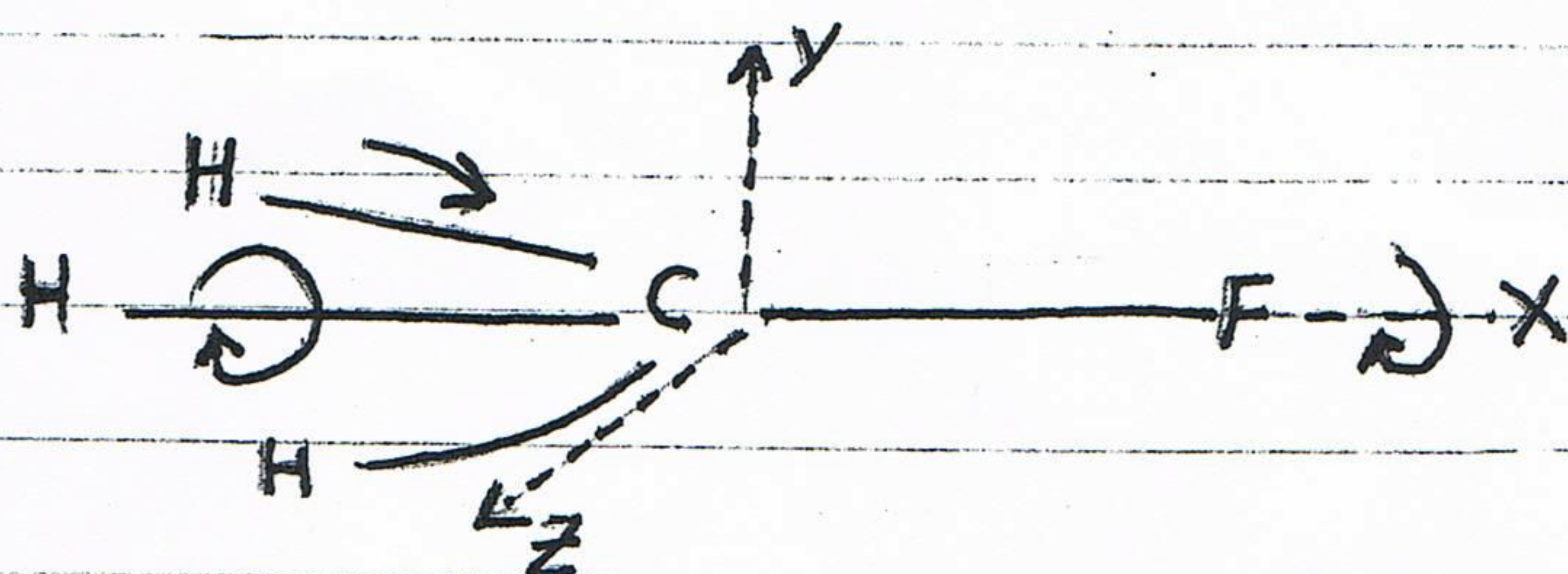
2 - Symmetric Tops!

the molecule such as methyl Fluoride CH3F

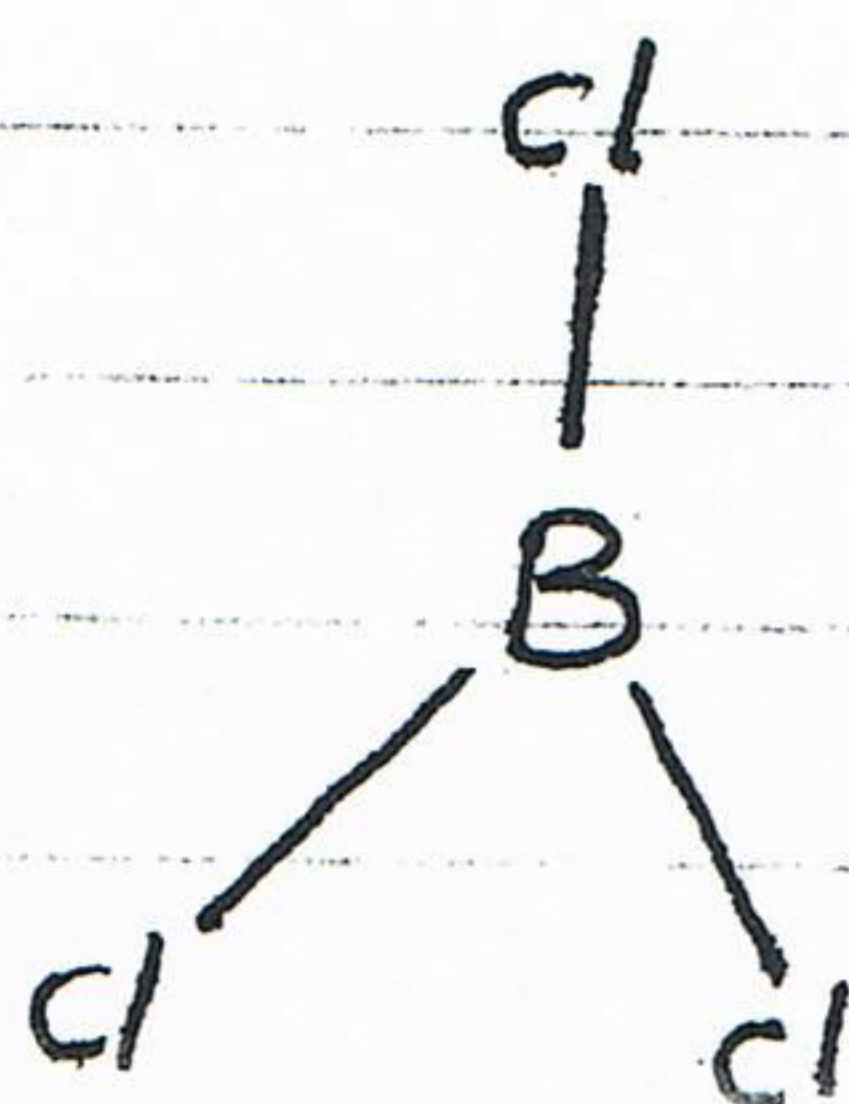


and in this case $I_B = I_C$ but the I_A about the C—F bond axis now is not negligible (the main rotational axis, since the center of gravity lies along it), then we have

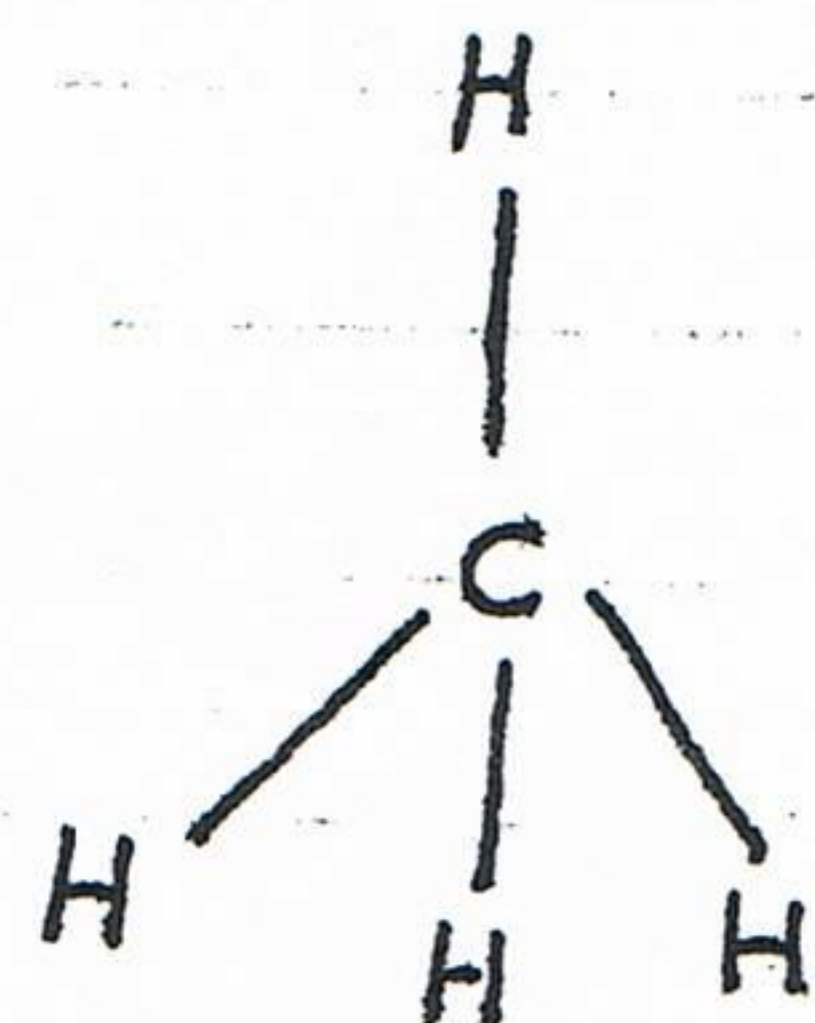
Symmetric Tops $I_B = I_C \neq I_A \quad I_A \neq 0$



There are two subdivisions of this class, one is called (Pro-late) symmetric Top as above (CH3F) $I_B = I_C > I_A$ and (oblate) such as boron trichloride where in this case $I_A = 2I_B = 2I_C$



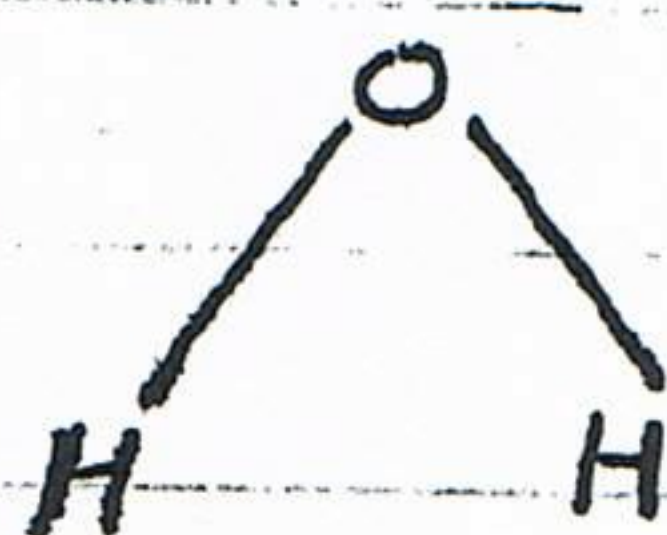
3- Spherical tops: when a molecule has all three moments of inertia identical it is called a spherical top. For example molecule of methane CH_4



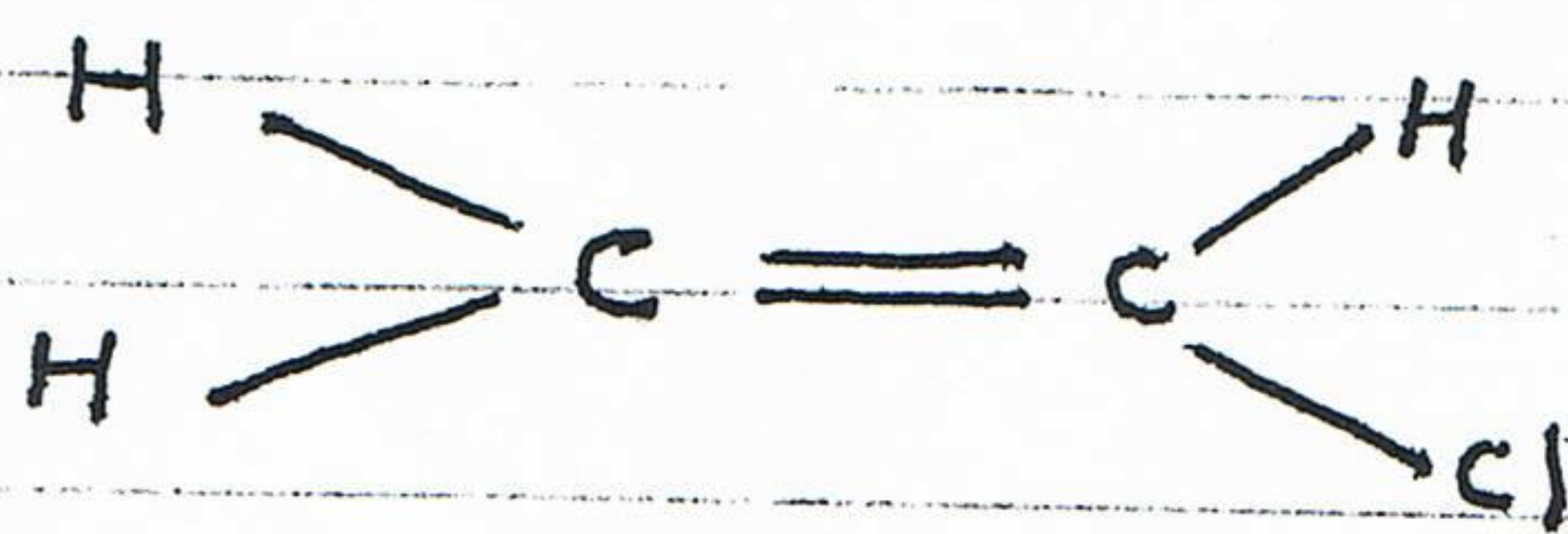
$$I_A = I_B = I_C$$

4- Asymmetric tops: these molecules, to which the majority of substances belong, have all three moments of inertia different

$I_A \neq I_B \neq I_C$ For example the molecule of water H_2O



and Vinyl chloride $\text{CH}_2 = \text{CHCl}$

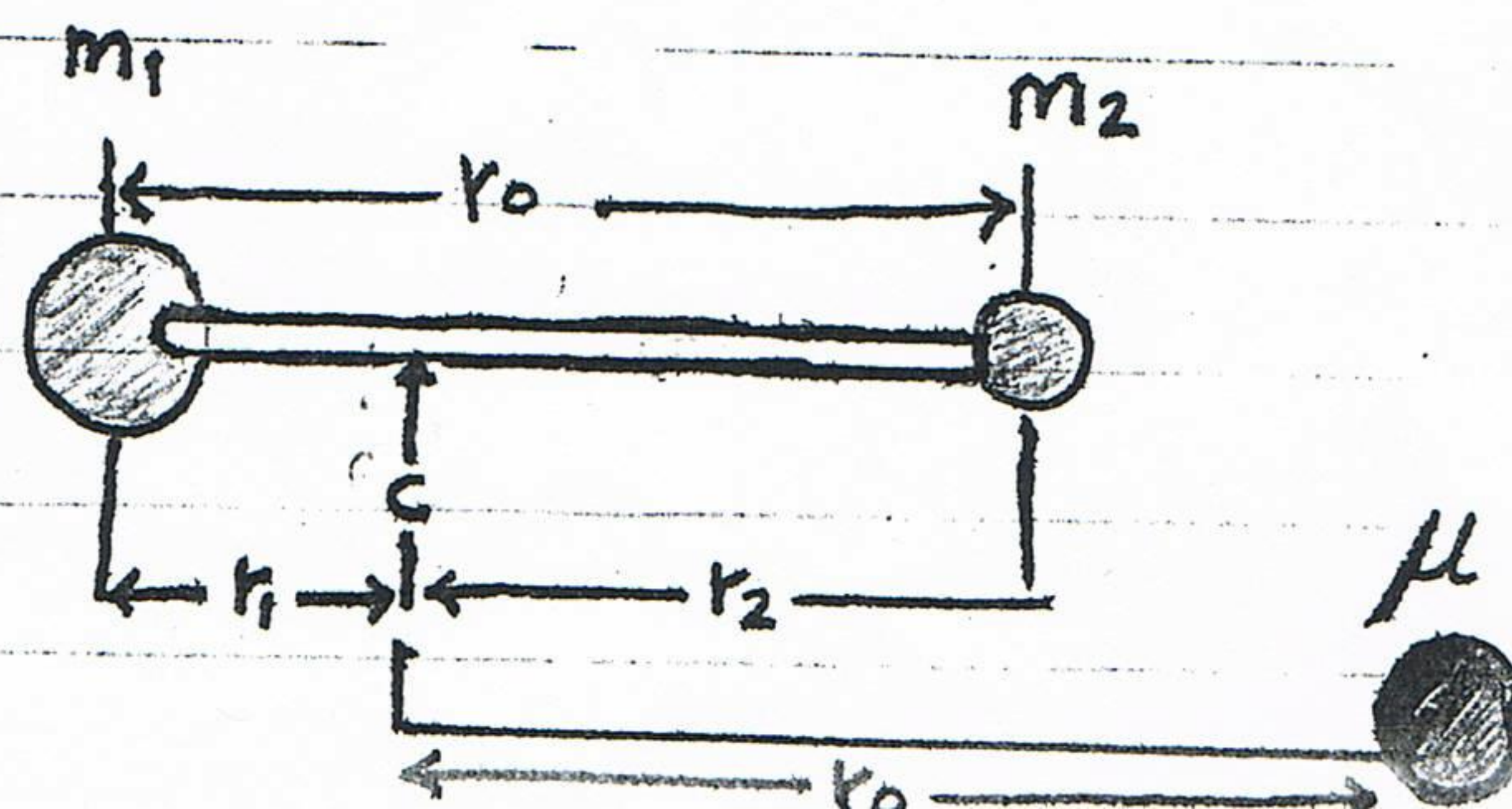


The Rigid Diatomic Molecule:

The diatomic molecule is the simplest of all linear molecules as shown in Fig (5). Masses m_1 and m_2 are joined by the rigid bond whose length is;

$$r_0 = r_1 + r_2 \quad (1)$$

Fig (5)



(7)

the molecule rotates end-over-end about a point C, the center of gravity which is defined by the balancing equation

$$m_1 r_1 = m_2 r_2 \quad \text{--- (2) then } \boxed{r_1 = \frac{m_2 r_2}{m_1} \text{ also } r_2 = \frac{m_1 r_1}{m_2}} \quad \text{--- (3)}$$

we can consider or transform the system which is consist from two particles (atoms) to a system of one particle have a mass (μ) which is defined as a reduced mass of the system where the (μ) is equal to

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \quad \text{--- (4)}$$

Since the moment of inertia about C is defined by

$$I = m_1 r_1^2 + m_2 r_2^2 \quad \text{--- (5)}$$

substitut eq(3) in eq(5) we get

$$I = m_1 r_1 \frac{m_2 r_2}{m_1} + m_2 r_2 \frac{m_1 r_1}{m_2}$$

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

$$I = r_1 r_2 (m_1 + m_2) \quad \text{--- (6)}$$

but From eqs (1) and (2)

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

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

$$\text{then } \boxed{r_1 = \frac{m_2 r_0}{m_1 + m_2} \text{ also } r_2 = \frac{m_1 r_0}{m_1 + m_2}} \quad \text{--- (7)}$$

(8)

replacing eq(7) in eq(6) we obtain that:-

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

$$I = \left(\frac{m_1 m_2}{m_1 + m_2} \right) r_0^2 = \mu r_0^2 \quad (8)$$

this is mean that the rotation of molecule around the axis through the center of gravity and perpendicular to the molecular axis is equal to the rotation of one particle have a mass(μ) and at the distance (r_0) from the rotational axis. according to the classical mechanic the kinetic energy of a rigid rotation for the diatomic molecule is equal to

$$T = \frac{1}{2} m_1 v_1^2 + \frac{1}{2} m_2 v_2^2 \quad (9)$$

and since the (r_1) and (r_2) are constant during the rotation of molecule, then we can use the relation of the angular velocity

$$\omega = \frac{v}{r} \quad \text{or} \quad v = \omega r \quad (10)$$

$$\text{therefore } T = \frac{1}{2} m_1 \omega^2 r_1^2 + \frac{1}{2} m_2 \omega^2 r_2^2 \quad (11)$$

sub eq(7) in eq(11) we get

$$T = \frac{1}{2} m_1 \omega^2 \frac{m_2^2 r_0^2}{(m_1 + m_2)^2} + \frac{1}{2} m_2 \omega^2 \frac{m_1^2 r_0^2}{(m_1 + m_2)^2}$$

$$T = \frac{1}{2} \omega^2 r_0^2 \left[\frac{m_1 m_2^2}{(m_1 + m_2)^2} + \frac{m_2 m_1^2}{(m_1 + m_2)^2} \right]$$

$$T = \frac{1}{2} \omega^2 r_0^2 \left[\frac{m_1 m_2 (m_2 + m_1)}{(m_1 + m_2)^2} \right]$$

(9)

then $T = \frac{1}{2} \omega^2 r_0^2 \left(\frac{m_1 m_2}{m_1 + m_2} \right) = \frac{1}{2} \omega^2 \mu r^2$

$$T = \frac{1}{2} I \omega^2 \quad (12)$$

multiply the eq (12) by $\frac{I}{I}$ we obtain

$$T = \frac{I^2 \omega^2}{2I}$$

but From the definition of the angular momentum (L)

$$L = mvr = m(\omega r)r = I\omega$$

therefore $T = \frac{L^2}{2I} \quad (13)$

by use of the schrodinger's equation its be shown that the rotational energy levels allowed to the rigid diatomic molecule are given by the expression

$$E_J = \frac{h^2}{8\pi^2 I} J(J+1) \text{ Joules} \quad \text{where } J = 0, 1, 2, \dots \quad (14)$$

I : is the moment of inertia either I_B or I_C , $h = 6.63 \times 10^{-34} \text{ J.s}$ or, $h = 6.63 \times 10^{-27} \text{ erg.s}$
 J : is an integer and its called, rotational quantum number Take values From zero upwards, and restrict the eq (14) by giving only discrete rotational energy levels.

Its interested in difference between energies such as Frequency, wavenumber of radiation emitted or absorbed $\nu = \frac{\Delta E}{h} \text{ Hz}$ $\tilde{\nu} = \frac{\Delta E}{hc} \text{ cm}^{-1}$

in rotational region spectra are usually expressed in cm^{-1} unit

$$F(J) = \frac{E}{hc} = \frac{h^2}{8\pi^2 I hc} J(J+1) \text{ cm}^{-1} \quad (15)$$

(10)

where $C = 3 \times 10^{10} \text{ cm}^{-1}$, since the wavenumber in cm^{-1} unit, equ (15) is usually abbreviated to :

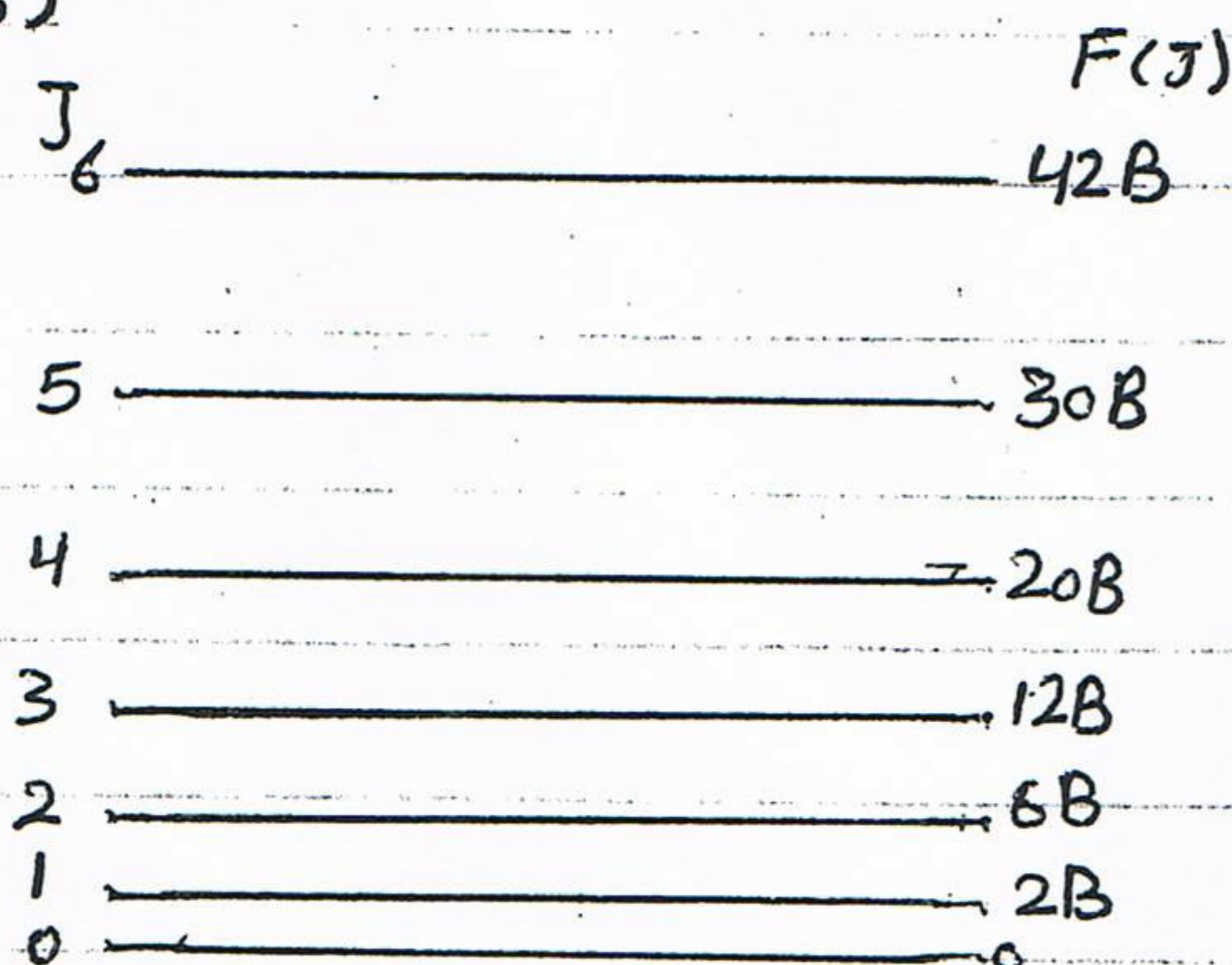
$$F_J = BJ(J+1) \text{ cm}^{-1} \quad J=0,1,2,\dots \quad \text{--- (16)}$$

where B is called the rotational constant which is given by

$$B = \frac{h}{8\pi^2 I_B C} \text{ cm}^{-1} \quad \text{--- (17)}$$

by substituting the values of J in equ (16) we obtain to values of the energy levels in cm^{-1} For ($J=0$ we have $F_J=0$), when ($J=1$ then $F_J=2B$), ($J=2$, $F_J=6B$) and from equ (16) we can show the allowed energy levels diagrammatically as in

Fig (6)



Fig(6) The allowed rotational energy Levels of a rigid diatomic molecule.

In order to determine the rotational spectrum, it's must be calculate the difference in energy between the rotational energy levels, and this can be done according to selection rules, which is

$$\Delta J = \pm 1 \quad \text{--- (18)}$$

if The molecule in state $J=0$, and let it is rising to $J=1$ by absorbing amount of energy for incident radiation, then the energy absorbed will be :

$$F_{J=1} - F_{J=0} = 2B - 0 = 2B \text{ cm}^{-1}$$

$$\tilde{\nu}_{J=0 \rightarrow J=1} = 2B \text{ cm}^{-1}$$

hence the absorption line will appear at $2B \text{ cm}^{-1}$. and for the transition from $J=1$ to $J=2$, we see

$$\begin{aligned} \tilde{\nu}_{J=1 \rightarrow J=2} &= F_{J=2} - F_{J=1} \\ &= 6B - 2B = 4B \text{ cm}^{-1} \end{aligned}$$

and the third line appear at $6B \text{ cm}^{-1}$. In general to raise the molecule from the state J to state $J+1$, we would have

$$\tilde{\nu}_{J \rightarrow J'} = F_{J'} - F_J \quad \text{where } J' = J+1$$

$$\begin{aligned} \tilde{\nu}_{J \rightarrow J'} &= B J' (J' + 1) - B J (J + 1) \\ &= B (J+1) (J+2) - B J (J+1) \\ &= B [J^2 + 2J + J + 2 - J^2 - J] \end{aligned}$$

$$\text{and } \boxed{\tilde{\nu}_{J \rightarrow J+1} = 2B (J+1) \text{ cm}^{-1}} \quad \text{----- (19)}$$

Thus the equ (19) gives the absorbed energy in cm^{-1} unit, or the wavenumber of the spectral line which produced for the transition of molecule from J to $J+1$ where the J changes by one unit, because all the transitions which are considered such $J=0 \rightarrow J=2 \rightarrow J=4 \dots$ are being spectroscopically forbidden, as be shown in Fig(7).

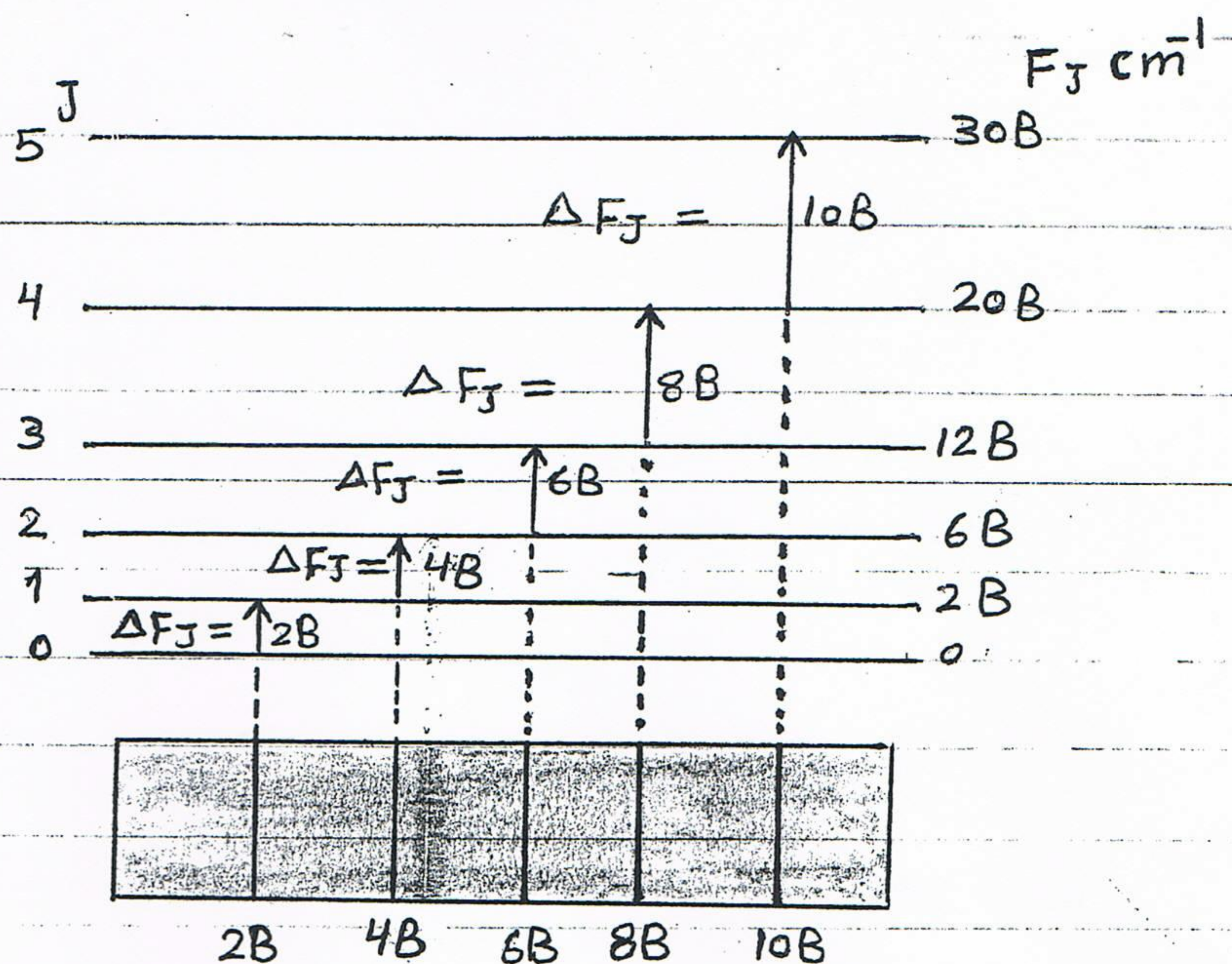


Fig (7) - Allowed transitions between the energy Levels of rigid diatomic molecule and the spectrum which arises from them.

It is clear that the difference in energy cm^{-1} between any two alternatively lines in rotational absorption spectrum is equal to constant ($2B$) For a rigid rotation of molecules, therefore From this separation we can find the value of B (rotational constant), and From (B) it can be calculate the moment of inertia I , and the bond length of the molecule.

Example:- calculate the reduced mass μ , and the moment of inertia I For HCl molecule, if the average intranuclear distance is equal to $r_{\text{ave}} = 1.275 \text{ \AA}$ atomic weights ($H = 1.008$, $Cl = 34.98$)

Solution:-
$$\mu = \frac{m_1 m_2}{(m_1 + m_2)} = \frac{(1.008 \text{ gm/mole})(34.98 \text{ gm/mole})}{(1.008 \text{ gm/mole} + 34.98 \text{ gm/mole})} \left(6.022 \times 10^{23} \frac{\text{molecules}}{\text{mole}} \right)$$

$$\mu = 1.628 \times 10^{-24} \text{ gm}$$

$$I = \mu r^2 = 1.628 \times 10^{-24} \times 1.275 \times 10^{-8}$$

$$I = 2.647 \times 10^{-32} \text{ gm} \cdot \text{cm}^2$$

example (2) / the carbon monoxide molecule absorbing energy in the microwave region of spectrum at Frequency $(1.153 \times 10^5 \text{ MHz})$, and this absorption assign to the transition From $J=0$ to $J=1$. compute the bond length (r) and the moment of inertia For CO molecule if you know the atomic weight are $m_O = 16 \text{ gm/mole}$, $C = 12 \text{ gm/mole}$.

$$\text{solution / } \tilde{\nu} = \frac{\nu}{c} = \frac{1.153 \times 10^5 \times 10^6}{3 \times 10^{10}} = 3.84 \text{ cm}^{-1}$$

For the transition $J=0 \rightarrow J=1$

$$\Delta F_J = \tilde{\nu}_{J=0 \rightarrow J=1} = 2B(J+1)$$

$$\tilde{\nu} = 2B(0+1) = 2B$$

$$\text{then } 3.84 = 2B \Rightarrow B = 1.92 \text{ cm}^{-1}$$

$$I = \frac{h}{8\pi^2 Bc} = \frac{6.63 \times 10^{-34}}{8\pi^2 \times 1.92 \times 3 \times 10^{10}} = 1.46 \times 10^{-46} \text{ kg.m}^2$$

$$\mu = \frac{m_1 m_2}{m_1 + m_2} = \frac{(12)(16)}{(12+16) \times 6.022 \times 10^{23}} = 1.138 \times 10^{-23} \text{ gm}$$

$$\mu = 1.138 \times 10^{-26} \text{ kg} \simeq 1.14 \times 10^{-26} \text{ kg}$$

$$\text{hence } r^2 = \frac{I}{\mu} = \frac{1.46 \times 10^{-46}}{1.14 \times 10^{-26}} = 1.28 \times 10^{-20} \text{ m}^2$$

$$r = 1.13 \times 10^{-10} \text{ m} \simeq 1.13 \text{ \AA}$$

Example (3) / The (HBr) Hydrogen bromide molecules are emitting a series of lines in the Far infrared region, and separation between lines was found equal to 16.94 cm^{-1} . compute the moment of inertia for molecule.

the separation distance $\tilde{\nu} = 2B$

why $\tilde{\nu}$, because of the separation between lines ($\tilde{\nu}$) and $\tilde{\nu} - \tilde{\nu} = \tilde{\nu}$
(ex) $J=0 \rightarrow 1$ $J=1 \rightarrow 2$

$$\text{then } \tilde{\nu} = 2B = 16.94 \text{ cm}^{-1} \Rightarrow B = 8.47 \text{ cm}^{-1}$$

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

$$I = \frac{6.63 \times 10^{-27} \text{ erg} \cdot \text{sec}}{8(3.14)^2 \times 8.47 \times 3 \times 10^{10}} = (3.31 \times 10^{-40} \text{ gm} \cdot \text{cm}^2)$$

$$\text{or } I = \frac{6.63 \times 10^{-34} \text{ J} \cdot \text{sec}}{8(3.14)^2 \times 8.47 \text{ cm}^{-1} \times 3 \times 10^{10} \text{ cm s}^{-1}} = (3.31 \times 10^{-47} \text{ Kg m}^2)$$

The Intensity of spectral lines:-

the calculation shows that the transition probability of all changes with $\Delta J = \pm 1$ is almost the same i.e the single molecule in the $J=0$ will move to $J=1$ is the same as that of a single molecule moving from $J=1$ to $J=2$, and, Although the probability is the same, but this does not mean, that all spectral lines will be equally intense. In Fact the line intensities will be directly proportional to the initial numbers of molecules in each level.

the second Factor (ii) is the possibility of degeneracy in the energy states. (Degeneracy is the existence of two or more energy states which have exactly the same energy). and we can approach the problem (degeneracy) in terms of its angular momentum.

From eq (12) we have $E = T = \frac{1}{2} I \omega^2$ and $L = I \omega$

I , is the moment of inertia, ω , the angular Frequency (in radians per second), L is the angular momentum, hence we get

$$E = \frac{1}{2} I \omega^2 \left(\frac{L}{I} \right) = \frac{L^2}{2I}$$

$$L = \sqrt{2IE} \quad (22)$$

therefore the energy level expression of equation (14) can be rewritten

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

$$2IE = J(J+1) \frac{h^2}{4\pi^2} \quad \text{and hence } L = \sqrt{2IE} = \sqrt{J(J+1)} \frac{h}{2\pi}$$

$$L = \sqrt{J(J+1)} \hbar = \sqrt{J(J+1)} \text{ unit} \quad (23)$$

where $\left(\frac{h}{2\pi} = \hbar \right)$ as the Fundamental unit of angular momentum. thus we see L like E is quantized.

The direction of the (L) vector i.e ($\vec{L}$) is conventionally taken to be along the axis about which rotation occurs and the number of different direction of $\vec{L}$ is limited by a quantum mechanical law which be stated (For integral values (J) the vector of angular momentum take only the directions such that its component along a given reference direction is zero, or an integral multiple of $\left(\frac{h}{2\pi} \right)$

The First Factor(i) governing the population of the levels is the Boltzman distribution

$$N_J = \exp(-E_J/KT) \quad \text{--- (20)}$$

N_J = number of molecules in the state J with energy E_J , K = Boltzman constant $= 1.381 \times 10^{-23} \text{ J.K}^{-1}$, T = temperature.

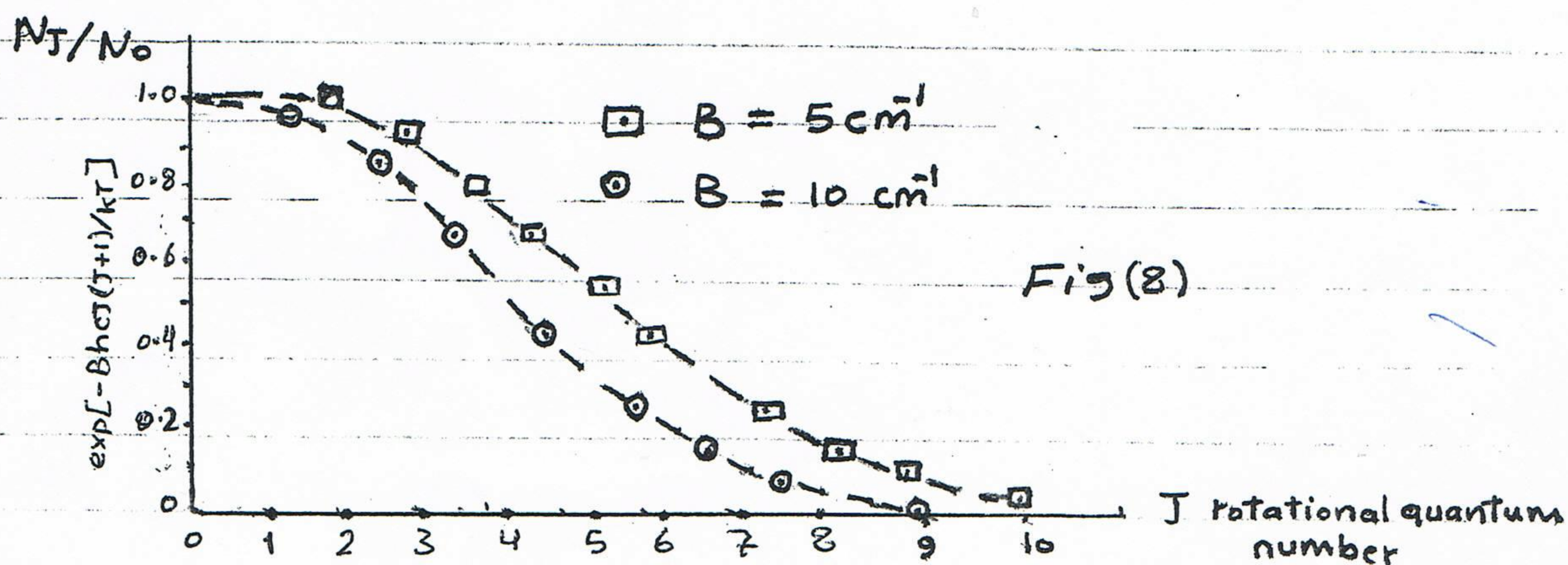
if N_0 is the number of molecules in the state $J=0$ where $E_{J=0} = 0$, then the relative number of molecules in any higher state to ground state is.

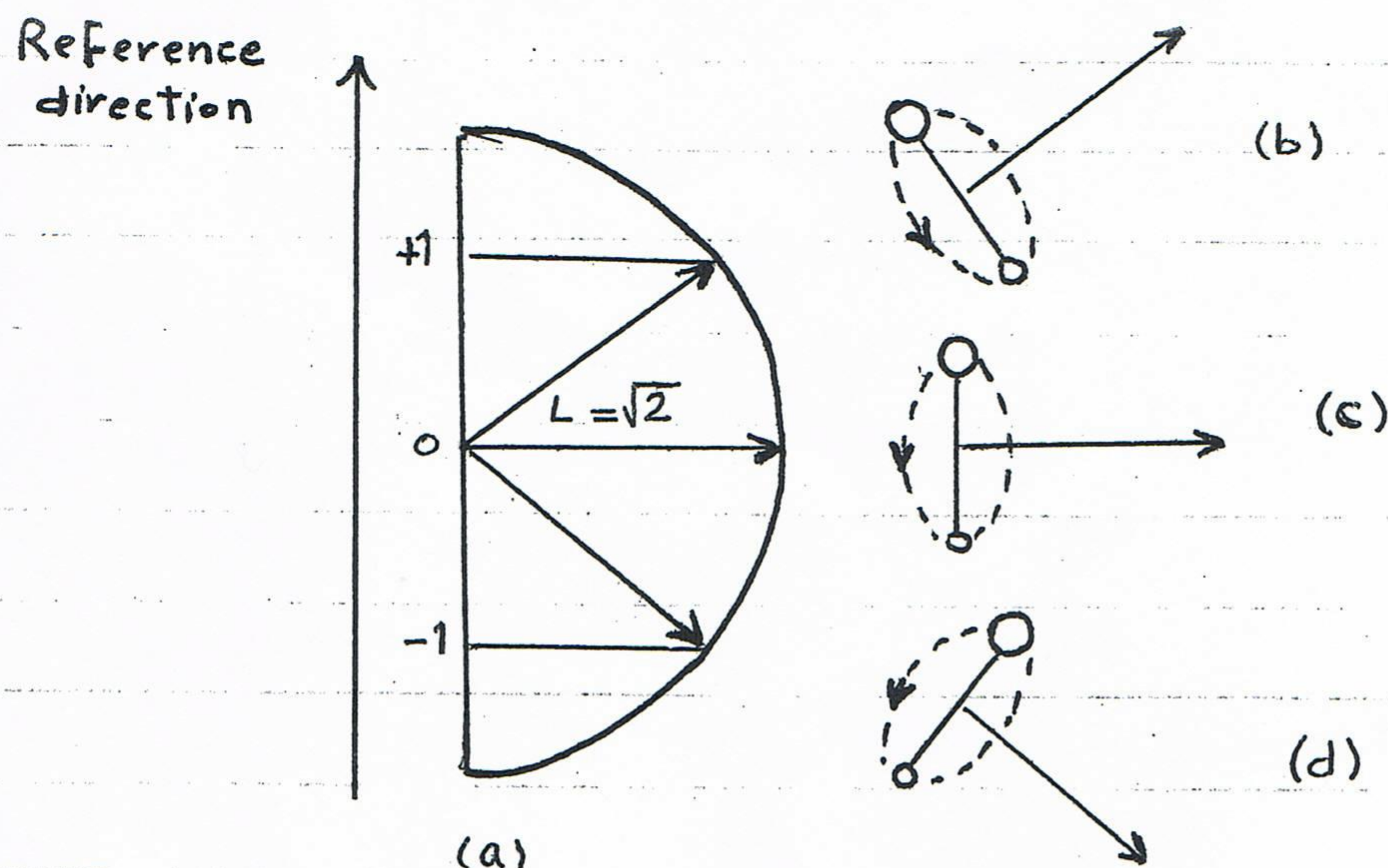
$$\frac{N_J}{N_0} = \exp(-E_J/KT) = \exp\{-Bhc J(J+1)/KT\} \quad \text{--- (21)}$$

c = is velocity of light in (cm s^{-1}) and B is in (cm^{-1}) , For example taking a typical value of $\{B = 2 \text{ cm}^{-1}\}$ and room temperature lets $\{T = 300 \text{ K}\}$ since the relative population in the $J = 1$ state is

$$\begin{aligned} \frac{N_1}{N_0} &= \exp\left[-\frac{2 \times 6.63 \times 10^{-34} \times 3 \times 10^{10}}{1.38 \times 10^{-23} \times 300}\right] \\ &= \exp(-0.019) \approx 0.98 \end{aligned}$$

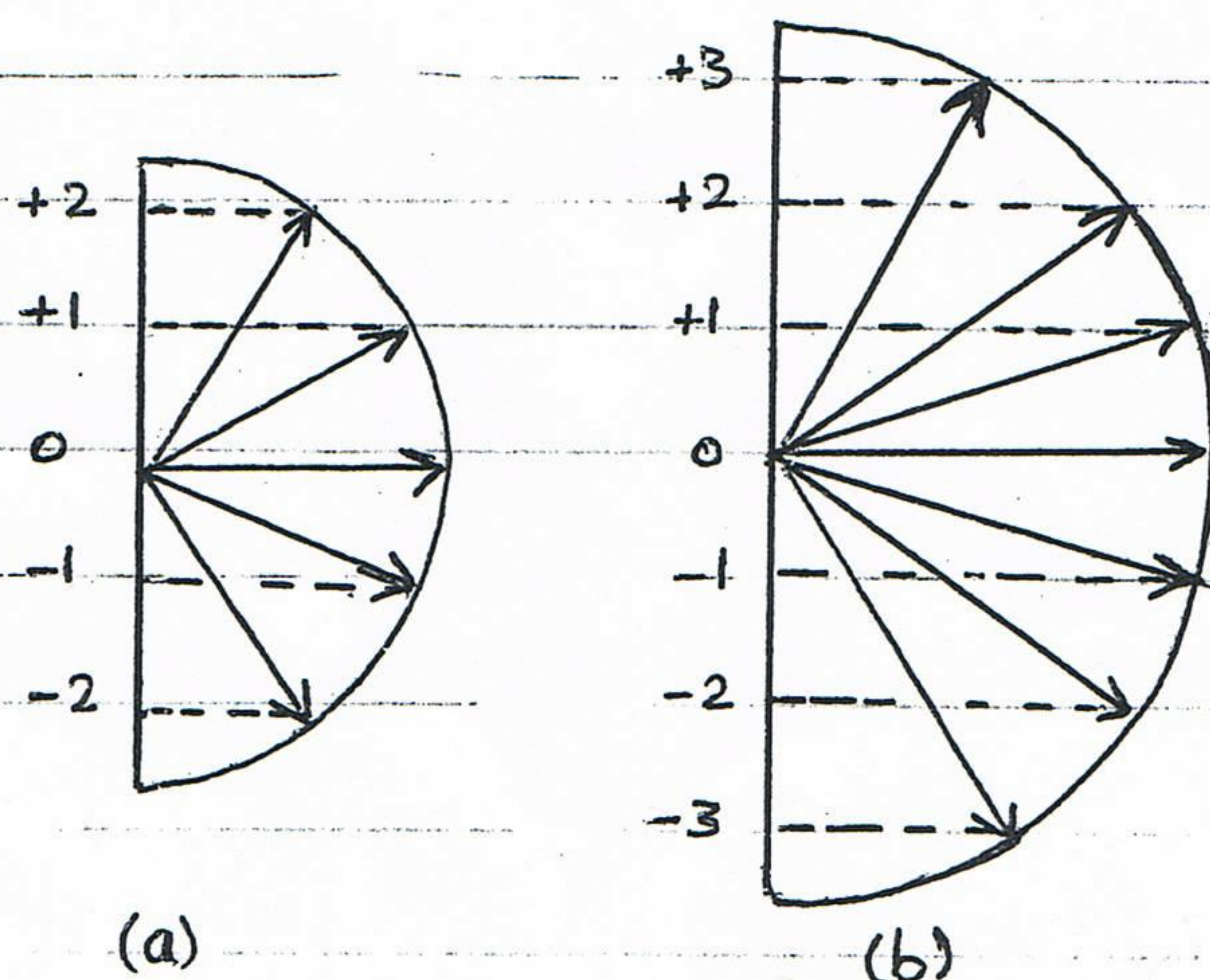
its mean that the number of molecules in state $J=1$ at equilibrium as or equal to molecules in state $J=0$. In a similar way the two graphs of Fig (8) have been calculated, showing the more rapid decrease of $\frac{N_J}{N_0}$ with increasing J and with larger B .





Fig(9) - The three degenerate orientations of the rotational angular momentum Vector For a molecule with $J = 1$.

its clear that From the Fig(9), we have a three rotational directions For $J=1$ and These are associated with the same angular momentum, hence the same rotational energy, thus we have a threefold degenerate, and Fivefold, sevenfold degeneracy respectively as in Fig(10). In general it may readily be seen that each energy level is $(2J+1)$ - Fold degenerate.

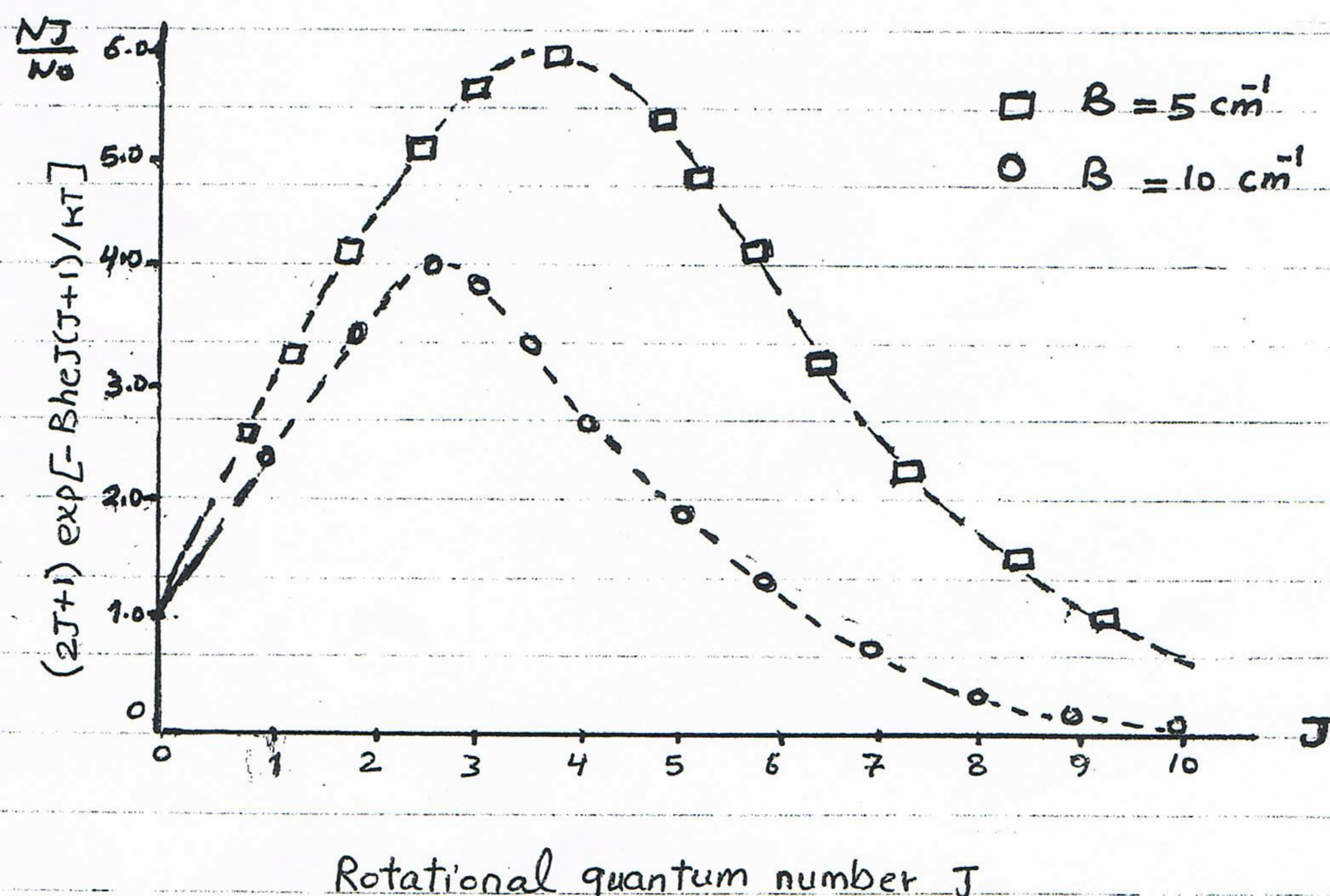


Fig(10) - the Five and seven degenerate rotational orientations For a molecule with $J=2$ and $J=3$ respectively.

thus the number of degenerate levels available increase rapidly with J , since the total relative population at an energy E_J will be

$$\frac{N_J}{N_0} = (2J+1) \exp \left\{ -BhcJ(J+1)/KT \right\} \quad \text{--- (24)}$$

Therefore the population rises to a maximum and then diminishes as be shown in Fig (11).



(Fig(11) the total relative populations, including degeneracy, of the rotational energy levels of diatomic molecule.)

By Differentiation of eq(24), will be shows that the population is a maximum at the nearest integral(J) value to

Maximum population :-

$$J = \sqrt{\frac{KT}{2Bhc}} - \frac{1}{2} \quad \text{--- (25)}$$

The effect of Isotopic substitution

when a particular atom in a molecule is replaced by its isotope - an element identical in every way except for its atomic mass. In particular there is no appreciable change in internuclear distance on isotopic substitution but the change in the total mass lead to change in the moment of inertia and hence in B value for the molecule.

For example carbon monoxide going from $^{12}_{16}\text{CO}$ to $^{13}_{16}\text{CO}$ there is a mass increase and hence a decrease in the B value. if B' designated for $^{13}_{16}\text{CO}$ then $B > B'$ and this change will be reflected in the rotational energy levels of the molecule as be shown in Fig (12). Furthermore by the diagram at the foot of Fig (12), the spectrum of the heavier species will show a smaller separation between the lines ($2B'$)

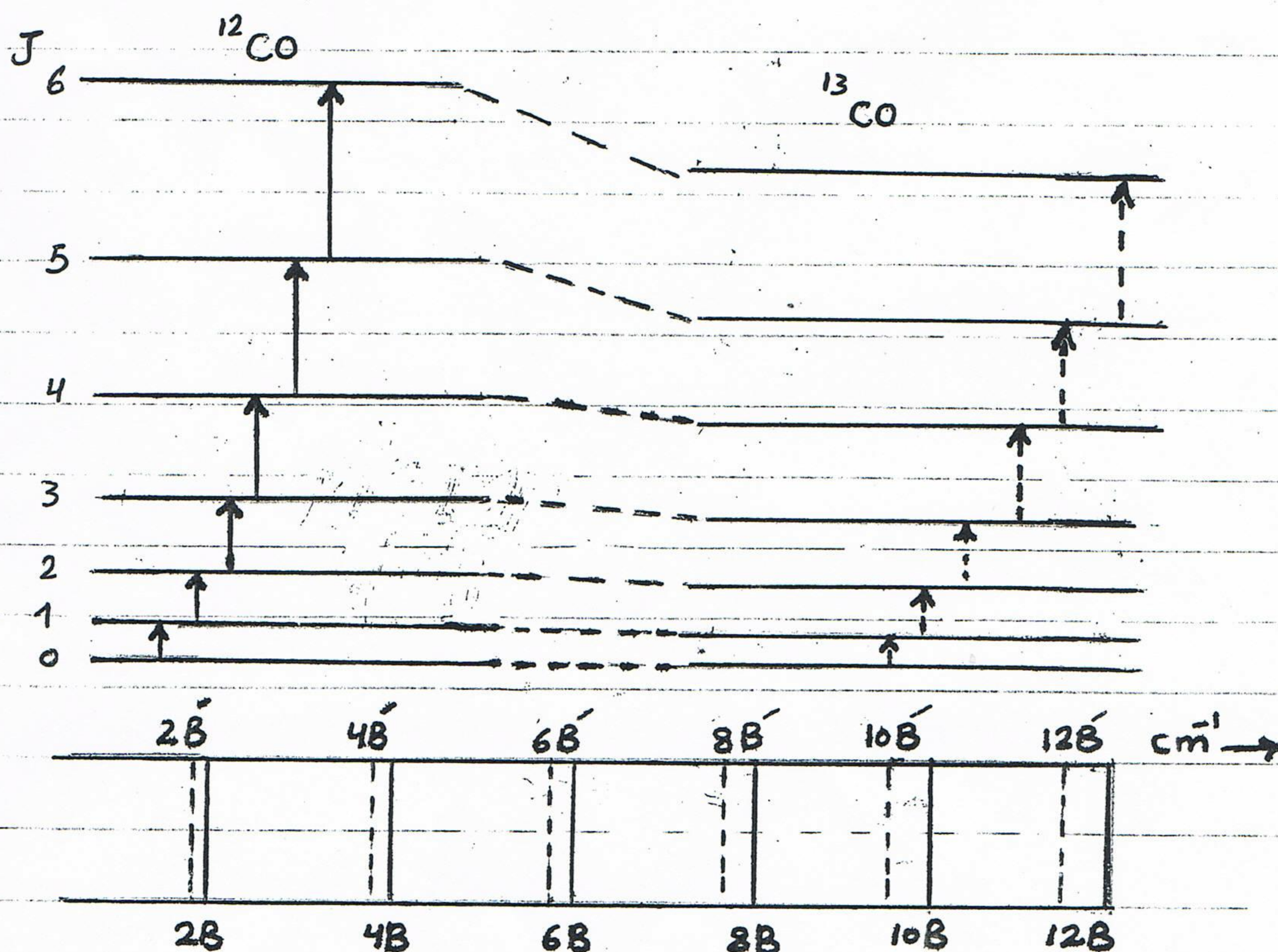


Fig (12) - The effect of isotopic substitution on the energy levels and hence rotational spectrum of diatomic molecule such as carbon monoxide.

(20)

the observation of this decreased separation has led to the evaluation of precise atomic weights. Cilliam Found the First rotational absorption of $^{12}_{16}\text{CO}$ to be at 3.84235 cm^{-1} , while that of $^{13}_{16}\text{CO}$ was at 3.67337 cm^{-1} the values of B and B' determined from these figures are

$$3.84235 = 2B(J+1) \quad J=0 \quad (\text{First transition})$$

$$B = 1.92118 \text{ cm}^{-1} \quad \text{and} \quad B' = 1.83669 \text{ cm}^{-1} \quad \text{For } ^{13}_{16}\text{CO}$$

we have immediately

$$\frac{B}{B'} = \frac{h}{8\pi^2 Ic} \cdot \frac{8\pi^2 I'c}{h} = \frac{I'}{I} = \frac{\mu}{\mu'} = 1.046$$

where μ is the reduced mass, and the internuclear distance is considered unchanged by isotopic substitution. Taking the mass of oxygen to be $15.9994 \frac{\text{gm}}{\text{mole}}$ and that of carbon-12 to be 12.00 gm/mole we have

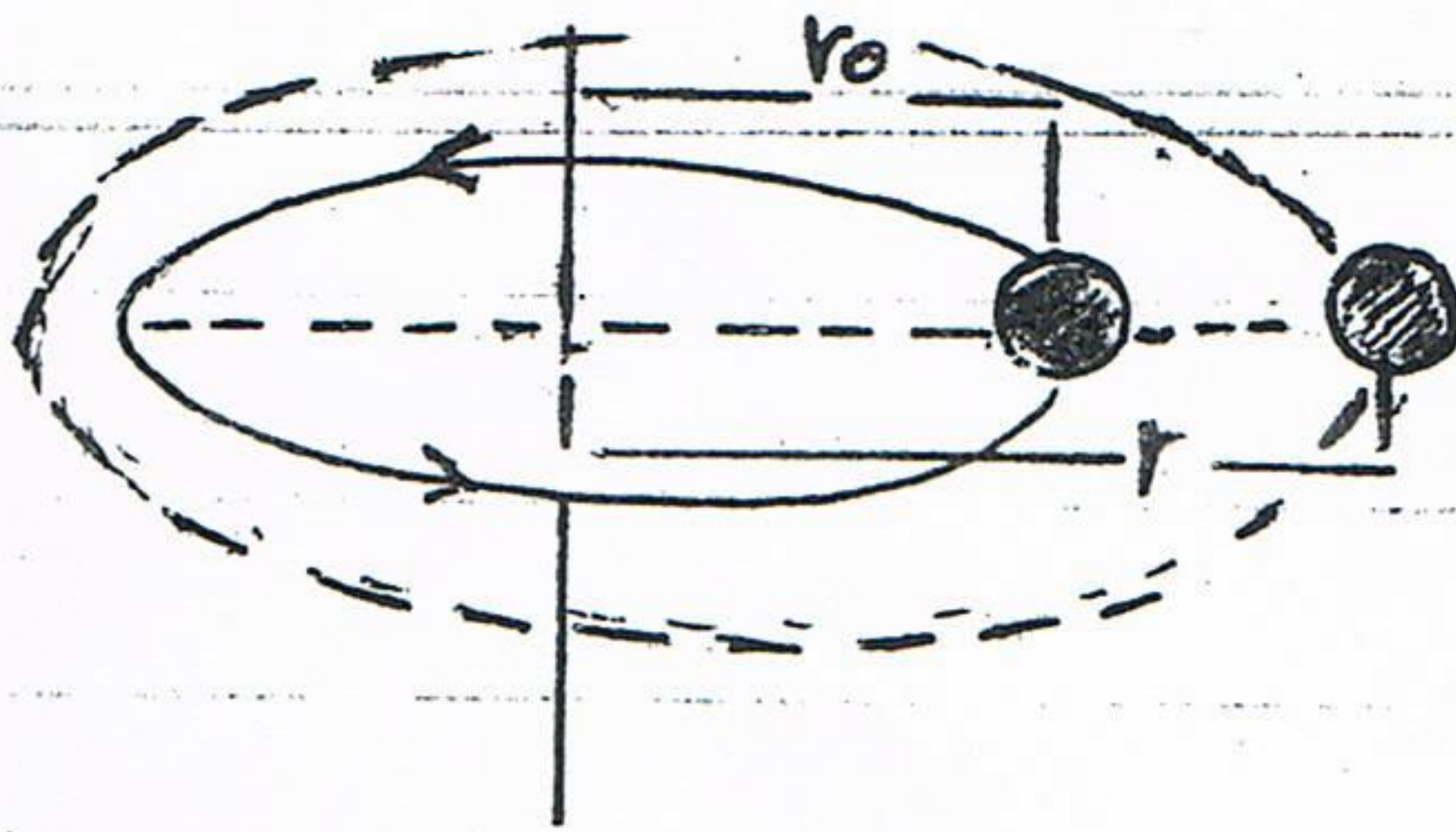
$$\frac{\mu}{\mu'} = 1.046 = \frac{15.9994 \text{ m}}{15.9994 + \text{m}} \left(\frac{1}{6.022 \times 10^{23}} \right) \times \frac{12 + 15.9994 (6.022 \times 10^{23})}{12 \times 15.9994}$$

From which m , the atomic weight of carbon-13 is found to be $(13.0007) \frac{\text{gm}}{\text{mole}}$.

The Non-Rigid Rotator :-

the stretching effect of the centrifugal forces on the bond lengths, and therefore on the momentum of inertia of a rotating system, can first be calculated on the basis of classical behavior. consider, for simplicity a single particle of mass (m) rotating about a fixed point with an angular velocity of (ω). Assume that at the rest, the particle is a distance (r_0) from the fixed point and that this length increases to a value of (r) when the particle rotates as in Fig (13).

(21)



Fig(13)

the centrifugal Force of $mr\omega^2$ is balanced by a restoring Force of $K(r-r_0)$ that accompanies bond stretching, where K is Force constant

$$K(r-r_0) = mr\omega^2 \quad \text{--- (26)}$$

$$Kr - mr\omega^2 = Kr_0$$

$$r = \frac{Kr_0}{(K - m\omega^2)} \quad \text{--- (27)}$$

Since the energy of the rotating system is made up of kinetic and potential energy contributions, the total energy can be written as

$$E = \frac{1}{2} I\omega^2 + \frac{1}{2} K(r-r_0)^2 \quad \text{--- (28)}$$

and with eq(26) becomes

$$E = \frac{1}{2} I\omega^2 + \frac{1}{2} \frac{Km^2r^2\omega^4}{K^2}$$

$$E = \frac{1}{2} I\omega^2 + \frac{1}{2} \frac{Km^2r^2\omega^4}{K^2} \left(\frac{r^2}{r^2} \right)$$

$$E = \frac{1}{2} I\omega^2 + \frac{1}{2} \frac{(I\omega^2)^2}{Kr^2} \quad \text{--- (29)}$$

(22)

the quantum restriction that the angular momentum ($I\omega$) be quantized according to $L = \sqrt{J(J+1)} \frac{h}{2\pi}$ will convert this classical result to a quantum mechanical result. the correct allowed energies are therefore, deduced to be :-

$$E = \frac{1}{2} I \omega^2 \times \left(\frac{I}{I}\right) + \frac{1}{2} \frac{(I\omega^2)^2}{Kr^2} \times \left(\frac{I^2}{I^2}\right) \left\{ \text{remember } (L = I\omega) \text{ in classical mechanic} \right\}$$

then

$$E = \frac{h^2}{8\pi^2 I} J(J+1) + \frac{h^4}{32\pi^4 I^2 Kr^2} J^2(J+1)^2$$

$$E_J = \frac{h^2}{8\pi^2 mr^2} J(J+1) + \frac{h^4}{32\pi^4 m^2 r^6 K} J^2(J+1)^2 \quad \text{--- (30)}$$

by substituting the equation (27) of (r) in equation (30) we get

$$E_J = \frac{h^2}{8\pi^2 m_0 r^2} J(J+1) - \frac{h^4}{16\pi^4 m^2 r_0^6 K} J^2(J+1)^2 + \frac{h^4}{32\pi^4 m^2 r_0^6 K} J^2(J+1)^2$$

$$E_J = \frac{h^2}{8\pi^2 m r_0^2} J(J+1) - \frac{h^4}{16\pi^4 m^2 r_0^6 K} J^2(J+1)^2$$

in terms of wave-number i.e the energy in cm^{-1} unit

$$F_J = \frac{h}{8\pi^2 I_c} J(J+1) - \frac{h^3}{16\pi^4 I^3 K c} J^2(J+1)^2 \quad \text{--- (31)}$$

$$F_{(J)} = B J(J+1) - \frac{4B^3}{\bar{\omega}^2} J^2(J+1)^2 \quad \text{--- (32)}$$

where the $\bar{\omega}$ is the vibrational Frequency in cm^{-1} unit

$$\bar{\omega} = \frac{1}{2\pi c} \sqrt{\frac{K}{m}} \quad \text{in } \text{cm}^{-1} \text{ when } (c) \text{ in } \text{cm} \cdot \text{s}^{-1} \quad \text{--- (33)}$$

(23)

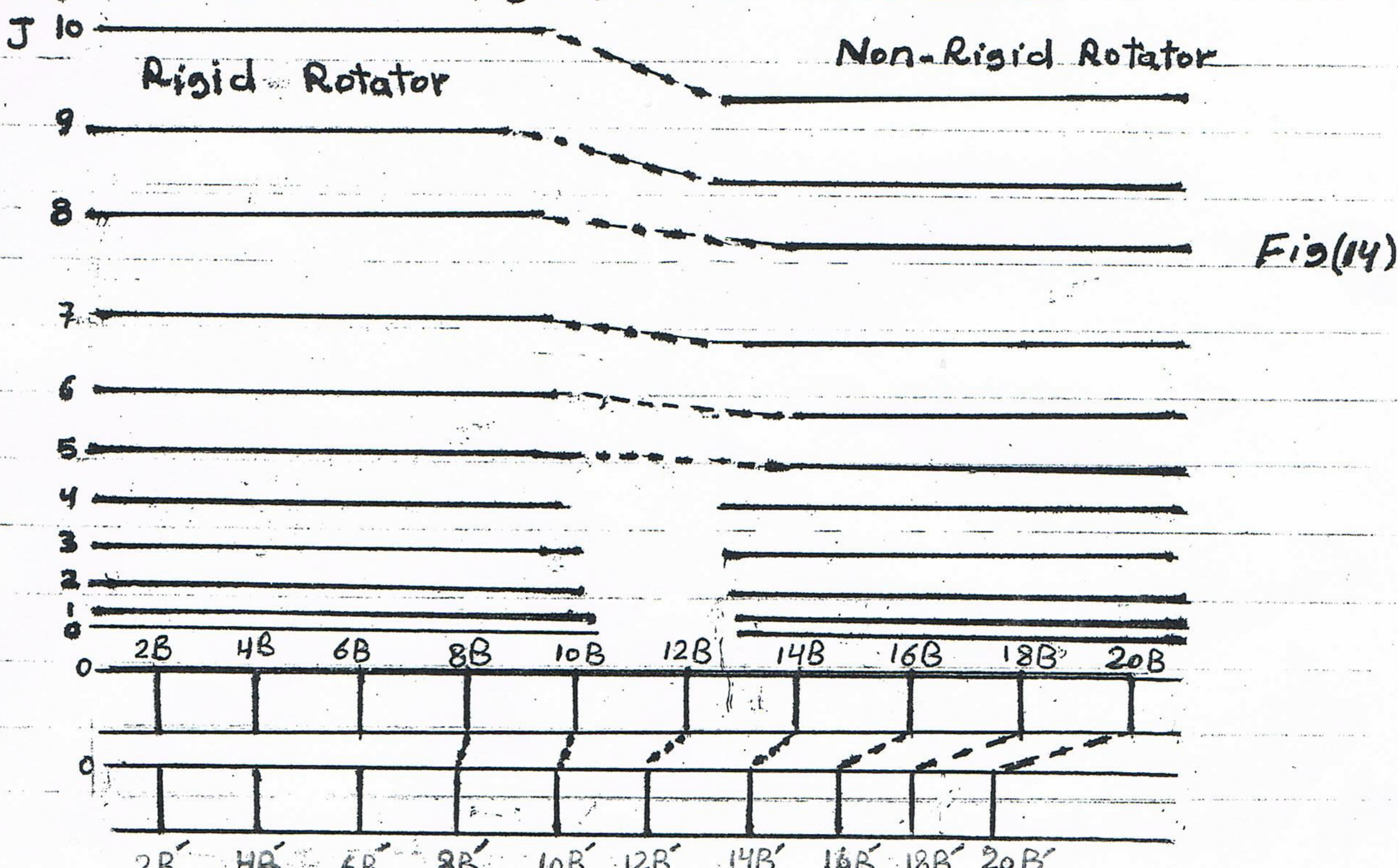
It is customary to write this expression, eq (32) For the rotational energy levels as :-

$$F(J) = BJ(J+1) - DJ^2(J+1)^2 \quad \text{--- (34)}$$

where D , known as the centrifugal distortion constant is a quantity that can be evaluated from spectral results and, according to the above derivation, can be related to other spectroscopic molecular parameters by the relation

$$D = \frac{4B^3}{\bar{\omega}^2} \quad \text{--- (35)}$$

the value of $\bar{\omega}$ is approximately $\bar{\omega} = 10^3 \text{ cm}^{-1}$ and $B = 10 \text{ cm}^{-1}$, thus the value of D will be $D = 10^{-3} \text{ cm}^{-1}$, and it's much less than the value of B , therefore the term $DJ^2(J+1)^2$ is ignorant for a small values of J . but this term will become very important in equation (34) when the values of (J) are high, as be shown in Fig (14).



(24)

the expression For the energies of the rotational transitions $\Delta J = \pm 1$ For nonrigid rotator are according to equation (34) is :-

$$\tilde{\nu} = F_{J+1}(\tilde{\nu}) - F_J(\tilde{\nu}) = B[(J+1)(J+2) - J(J+1)] - D[(J+1)^2(J+2)^2 - J^2(J+1)^2]$$

$$\tilde{\nu} = 2B(J+1) - 4D(J+1)^3 \text{ cm}^{-1} \quad \text{--- (36)}$$

Polyatomic Linear Molecules (PLM) :-

the carbon oxysulphide OCS , or chloroacetylene $\text{HC} \equiv \text{CCl}$ are considered polyatomic linear molecules (PLM) where all the atoms lie on a straight line and this type gives simple spectra in the microwave region and as for diatomic molecules the $I_B = I_C$, $I_A \neq 0$, and the energy levels are given by formula identical with equation (34). In fact the whole of the discussion on diatomic molecules applies equally to all linear molecules, three points should be underlined.

① since the moment of inertia for the end-over-end rotation of (PLM) is greater than that of diatomic molecule, the B value will be much smaller and the spectral lines more closely spaced.

② the molecule must possess a dipole moment if its to exhibit a rotational spectrum. thus OCS will be microwave active, while OCO will not. it should be noted that isotopic substitution dose not lead to a dipole moment since the bond lengths and atomic charges are unaltered by the substitution.

- ③ A non-cyclic polyatomic molecule containing N atoms has altogether $(N-1)$ individual bond lengths to be determined. Thus in the triatomic molecules OCS there is the CO distance r_{co} , and CS distance r_{cs} , on the other hand there is only one moment of inertia for rotation of OCS, and only this one value can be determined from the spectrum.

Let us consider the rotation of OCS in some detail. Fig (15) shows the molecule, where r_o , r_c and r_s represent the distances of the atoms from the center of gravity, and this is defined by the moments

$$m_o r_o + m_c r_c = m_s r_s \quad (37)$$

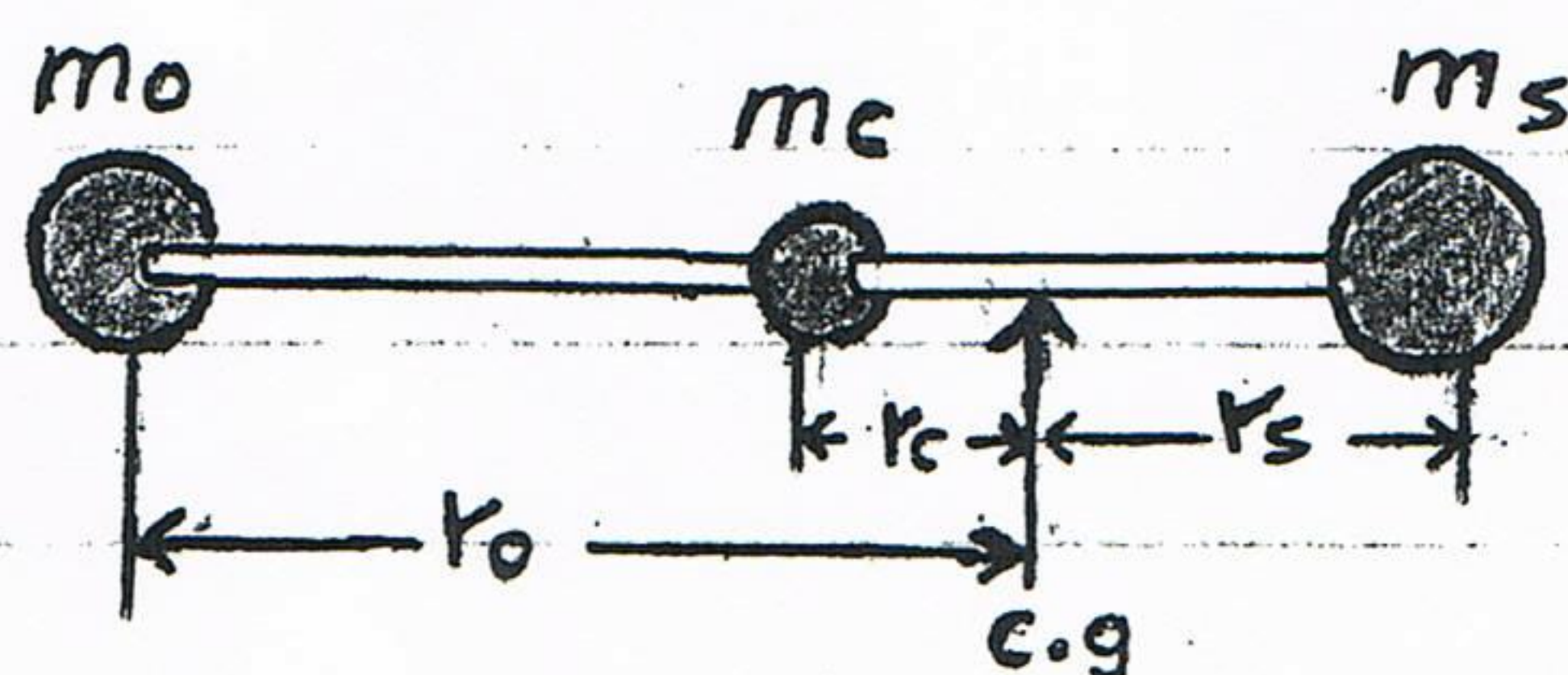


Fig (15) - the molecule of carbon oxysulphide OCS.

the moment of inertia for OCS is

$$I = m_o r_o^2 + m_c r_c^2 + m_s r_s^2 \quad (38)$$

also we have the further equations

$$r_{co} = r_o - r_c \quad (39)$$

$$r_{cs} = r_c + r_s \quad (40)$$

(26)

by substituting the eqs(39)(40) in eq(37) we obtain

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

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

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

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

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

$$Mr_c = m_s r_{cs} - m_o r_{co} \quad \text{--- (41)}$$

where $M = m_o + m_c + m_s$ --- (42)

by subs eqs (39)(40) again in eq (38) we obtain

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

$$I = Mr_c^2 + 2r_c(m_o r_{co} - m_s r_{cs}) + m_o r_{co}^2 + m_s r_{cs}^2 \quad \text{--- (43)}$$

and finally by substituting For (r_c) From (41) in equation (43) we get

$$I = m_o r_{co}^2 + m_s r_{cs}^2 - \frac{(m_o r_{co} - m_s r_{cs})^2}{M} \quad \text{--- (44)}$$

(27)

Q.1/ the rotational spectrum of BrF shows a series of equidistant lines spaced 0.71433 cm^{-1} apart. calculate the rotational constant B , and hence the moment of inertia and bond length of the molecule. Determine the wavenumber of the $J=9 \rightarrow J=10$ transition, and Find which transition gives rise to the most intense spectral line at room temperature (let 300K)

$$2B = 0.71433 \text{ then } B = 0.35717 \text{ cm}^{-1}$$

$$B = \frac{h}{8\pi^2 I c} \text{ thus } I = \frac{h}{8\pi^2 B c} = \frac{6.63 \times 10^{-34}}{78.956 \times 0.35717 \times 3 \times 10^{10}}$$

$$I = 7.837 \times 10^{-46} \text{ kg} \cdot \text{m}^2$$

$$(8\pi^2 = 78.956)$$

$$\mu = \frac{(m_F)(m_{Br})}{(m_F + m_{Br})} = \frac{(19)(79)}{(19+79)} \times 1.66 \times 10^{-27} \text{ kg}, \mu = 2.543 \times 10^{-26} \text{ kg}$$

$$\text{or } \mu = \frac{(19)(79)}{(19+79)} \frac{1}{6.022 \times 10^{23}} = 2.543 \times 10^{-23} \text{ gm}$$

$$\mu = 2.543 \times 10^{-26} \text{ kg}$$

$$I = \mu r^2 \text{ hence } r = \sqrt{\frac{I}{\mu}} = \sqrt{\frac{7.837 \times 10^{-46} \text{ kg} \cdot \text{m}^2}{2.543 \times 10^{-26} \text{ kg}}}$$

$$r = 1.756 \times 10^{-10} \text{ m}, r = 1.756 \text{ \AA}$$

$$\tilde{\nu}_{J=9 \rightarrow J=10} = 2B(J+1) = 2B(9+1) = 20B$$

$$\tilde{\nu}_{J=9 \rightarrow J=10} = 20 \times 0.35717 \Rightarrow \tilde{\nu}_{J=9 \rightarrow J=10} = 7.1434 \text{ cm}^{-1}$$

$$J_{\text{max}} = \sqrt{\frac{kT}{2Bhc}} - \frac{1}{2} = \sqrt{\frac{1.381 \times 10^{-23} \times 300}{2(0.35717 \text{ cm}^{-1}) 3 \times 10^{10} \text{ cm s}^{-1} \times 6.63 \times 10^{-34}}} - \frac{1}{2}$$

$$J_{\text{max}} = 16.57 \approx 17$$

(28)

Q.2/ the bond length of (CN^+) molecule is $(1.29 \text{ \AA})$. assign the location for the first three lines in rotational spectrum, the atomic weights are:
 $(m_C = 12 \text{ gm/mole})$ $(m_N = 14 \text{ gm/mole})$

طول الأصرة لـ CN^+ هو $1.29 \text{ \AA}$. عيّن مواقع الخطوط الثلاثة الأولى في طيف الدوران

$$\mu = \frac{(12)(14)}{(12+14)} \frac{1}{6.022 \times 10^{23}} = 1.036 \times 10^{-23} \text{ gm}$$

$$\mu = 1.036 \times 10^{-23} \text{ gm} \quad \text{or} \quad 1.036 \times 10^{-26} \text{ kg}$$

$$I = \mu r^2 = 1.036 \times 10^{-23} \times (1.29 \times 10^{-8})^2 \Rightarrow I = 1.724 \times 10^{-39} \text{ gm.cm}^2$$

$$\text{or } I = \mu r^2 = 1.036 \times 10^{-26} \times (1.29 \times 10^{-10})^2 \Rightarrow I = 1.724 \times 10^{-46} \text{ kg.m}^2$$

$$B = \frac{h}{8\pi^2 I c} = \frac{6.63 \times 10^{-27} \text{ erg.sec}}{78.956 \times 1.724 \times 10^{-39} \text{ gm.cm}^2 \times 3 \times 10^{10} \text{ cm sec}^{-1}}$$

$$B = 1.6235 \approx 1.624 \text{ cm}^{-1}$$

$$B = 1.624 \text{ cm}^{-1}$$

$$\text{or } B = \frac{h}{8\pi^2 I c} = \frac{6.63 \times 10^{-34} \text{ J.sec}}{78.956 \times 1.724 \times 10^{-46} \text{ kg.m}^2 \times 3 \times 10^8 \text{ m.sec}^{-1}}$$

$$B = 162.35 \text{ m}^{-1} \approx 162.4 \text{ m}^{-1}$$

$$\text{and } B = 162.4 \times 10^2 \text{ cm}^{-1} = 1.624 \text{ cm}^{-1}$$

$$\tilde{\nu}_{J=0 \rightarrow 1} = 2B(J+1) = 2B(0+1) = 2B = 2(1.624) = 3.248 \text{ cm}^{-1}$$

$$\tilde{\nu}_{J=1 \rightarrow 2} = 2B(J+1) = 2B(1+1) = 4B = 4(1.624) = 6.496 \text{ cm}^{-1}$$

$$\tilde{\nu}_{J=2 \rightarrow 3} = 2B(J+1) = 2B(2+1) = 6B = 6(1.624) = 9.744 \text{ cm}^{-1}$$