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المرحلة الرابعة

Chapter two: Microwave spectroscopy

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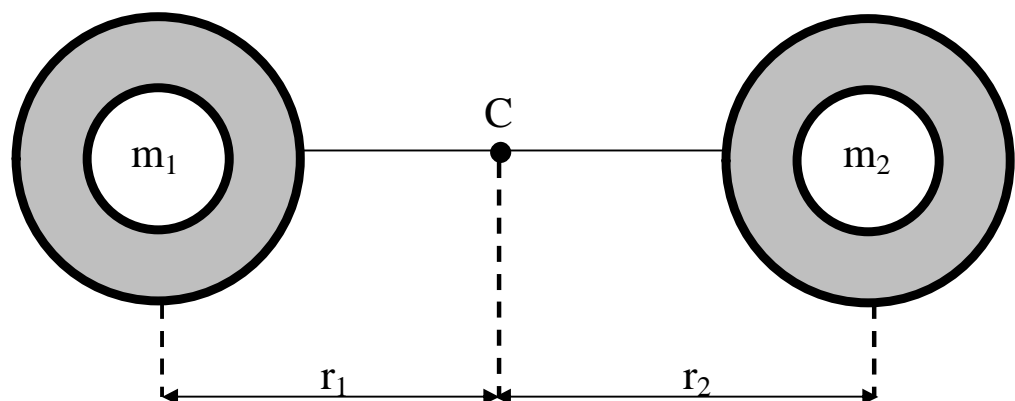
The rotation spectrum of molecules represents the transitions which take place between the rotation energy levels and the rotation transition take place between the microwave and far I.R region at wave length (1mm-30cm).

- **Rotation of linear molecules.**
- **Rotation of rigid linear diatomic molecules classically.**

Rotation of linear molecules.

The simplest explain of linear molecules that consist from two masses (m_1 and m_2) and the inter distance is(r).

by suppose the distance between them is fixed



from center of mass definition $m_1 r_1 = m_2 r_2$ -----(1)

$$\mathbf{r} = \mathbf{r}_1 + \mathbf{r}_2 \text{ -----(2)}$$

$$\text{then } \mathbf{r}_1 = \frac{m_2 r}{m_1 + m_2}, \quad \mathbf{r}_2 = \frac{m_1 r}{m_1 + m_2} \quad \text{-----(3)}$$

The moment of inertia (I)

$$I = \sum_i m_i r_i^2 \quad \text{----- (4)}$$

m_i : The mass of atom i .

r_i : The distance of i .

Then(I)for molecule contain two atoms

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

Sub eq. (3) in (5)

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

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

μ : reduced mass .

Rotation of rigid linear diatomic molecules classically.

Rotation of rigid linear diatomic molecules quantum mechanically:-

The angular momentum (p) for rigid rotator

$$P = \sum_i (m_i v_i) r_i \quad \times \quad \frac{r_i}{r_i}$$

$$P = \sum_i \frac{m_i v_i r_i^2}{r_i}$$

$$\text{angular velocity } (\omega) = \frac{v_i}{r_i}$$

$$P = \sum_i m \omega r^2 \qquad I = m r^2$$

$$P = I \omega$$

according to quantum chemistry the angular momentum
(p)

$$P = M_j \hbar = \sqrt{j(j+1)} \hbar$$

j=quantum No. for rotation energy level.

where j=0,1,2,3,4,-----

$$\hbar = \frac{h}{2\pi}$$

The kinetic energy of molecules: $E = \frac{1}{2} m v^2$

m: mass

v: velocity

$$E = \frac{1}{2} m v^2 \times \frac{r^2}{r^2}$$

$$E = \frac{1}{2} I \omega^2 \qquad I = m r^2$$

$$P = I \omega$$

$$E = \frac{1}{2} I \omega^2 \times \frac{I}{I} = \frac{I^2 \omega^2}{2I} = \frac{P^2}{2I}$$

$$E = \frac{j(j+1) \hbar^2}{2I} = \frac{j(j+1)}{8\pi^2 I} h^2$$

$$h = 6.63 \times 10^{-34} \text{ J.s}$$

J: rotation quantum no. (0, 1, 2)

$$E = h \nu \qquad \text{or} \qquad \nu = \frac{\Delta E}{h} \qquad (\text{Hz})$$

$$\nu' = \frac{\Delta E}{hc} \qquad (\text{cm}^{-1})$$

$$\epsilon_j = \frac{E_j}{hc} = \frac{h}{8\pi^2 I c} j(j+1) \quad (\text{cm}^{-1})$$

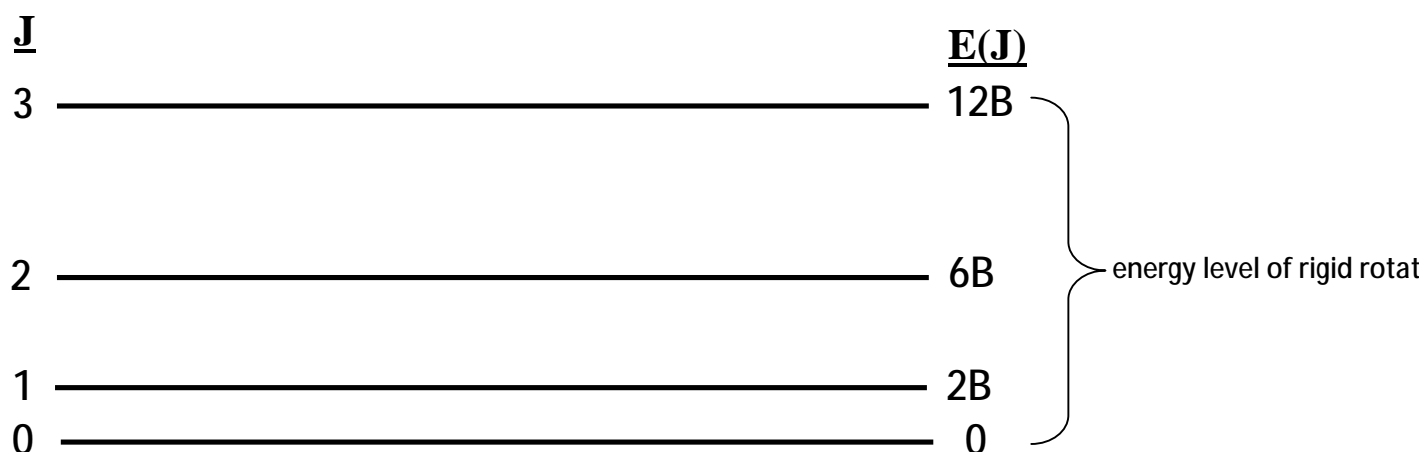
The rotation energy of rigid rotator in cm^{-1}

$$\text{Frequency or } \nu(J) = \frac{E}{h} = \frac{h}{8\pi^2 I c} J(J+1) \quad \text{in (Hz)}$$

B = rotational constant .

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

for each molecule a certain B .



Selection Rules for Rigid Rotator

R : transition probability between the states φ_i and φ_j is given by

$$R = \int \varphi_i^* \vec{\mu} \varphi_j d\tau$$

μ : the electric dipole moment of the molecule.

$$\vec{R} = \vec{i}R_x + \vec{j}R_y + \vec{k}R_z$$

$$\mu = \hat{i}\mu_x + \hat{j}\mu_y + \hat{k}\mu_z$$

$$R_x = \int \varphi_i^* \mu_x \varphi_j \, d\tau$$

R_x : probability of the transition with electromagnetic radiation of electric field directed along x – axis.

Intensity of transition $I \propto R^2$

for allowed transition $R^2 \neq 0$

$$\therefore R_x = \int \varphi_{JM}^* \mu \sin \theta \cos \theta \varphi_{JM} \, d\tau$$

In general $R^2 \neq 0$ when $\Delta J = \pm 1, \Delta M = 0, \pm 1$

\therefore for allowed rotation transitions

$$\Delta J = \pm 1, \Delta M = 0, \pm 1$$

$\Delta J = +1$ [means absorption]

$\Delta J = -1$ [means emission]

Intensity of rotation lines of rigid rotator

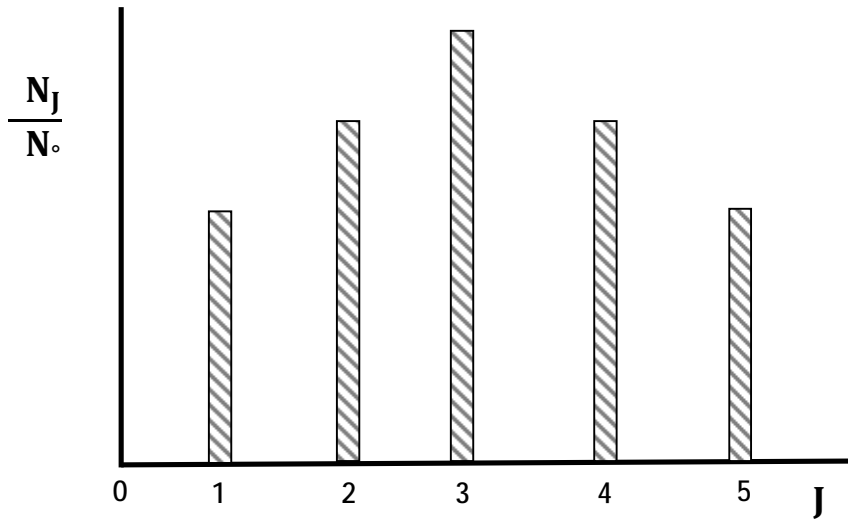
The population of rotational energy levels is given by Boltzmann thermal distribution law

$$N_J = N_0 g e^{-(E_J - E_0)/KT}$$

g : The degree of degeneracy.

N_J : No. of molecules of energy E_J .

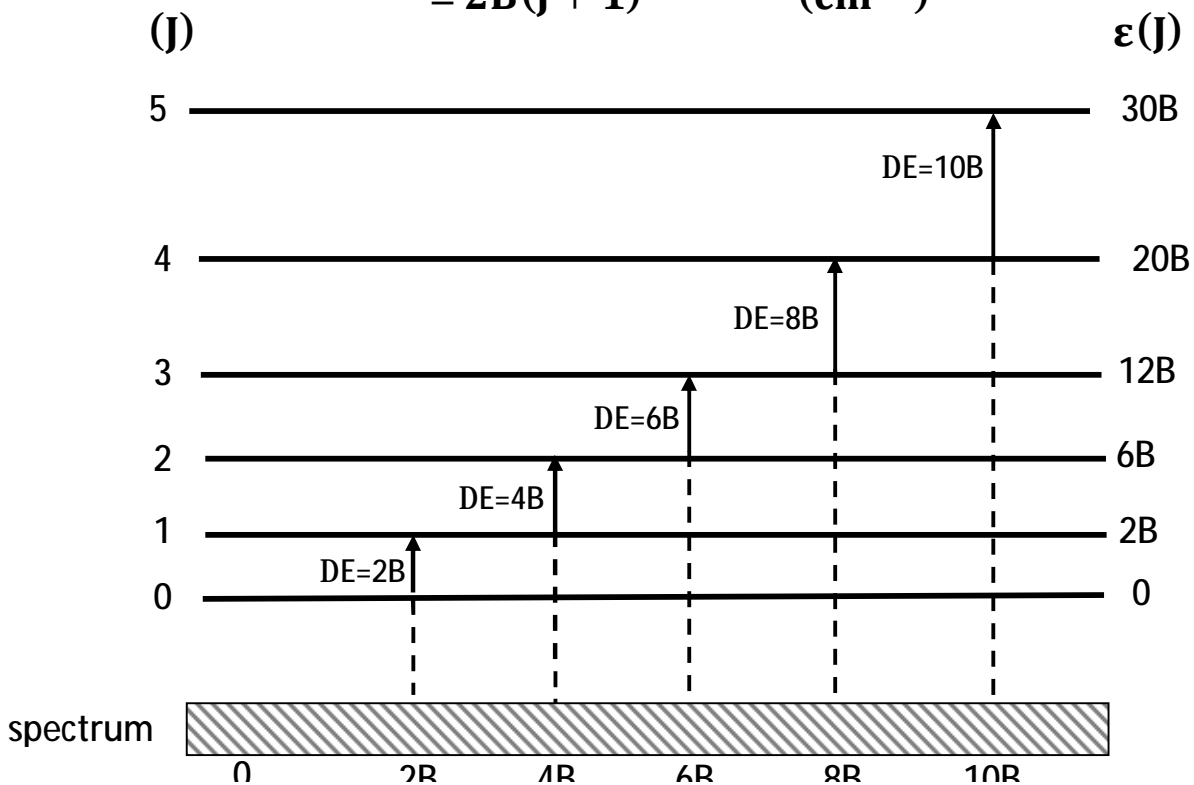
$$\frac{N_J}{N_0} = (2J + 1)e^{-BJ(J+1)/KT}$$



Note :-

To arising the molecule from J to $J+1$ we can need to energy

$$\begin{aligned} \epsilon_{J \rightarrow J+1} &= B(J+1)(J+1+1) - BJ(J+1) \\ &= B(J+1)(J+2) - BJ(J+1) \\ &= B(J^2 + 3J + 2) - (J^2 + J) \\ &= 2B(J+1) \quad (\text{cm}^{-1}) \end{aligned}$$



The allowed rotational energy level between the energy level of rigid rotator with two atoms.

Example(1):-

Calculate the reduce mass and momentum of inertia HCl by using the inter distance 1.275 \AA ? (Atomic weight for H=1.008 and Cl =34.98)

Solution:-

$$\mu = \frac{m_1 m_2}{m_1 + m_2} = \frac{(1.008)(34.98)}{((1.008) + (34.98))(6.022 \times 10^{23})}$$

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

$$I = \mu r^2 = (1.628 \times 10^{-24})(1.275 \times 10^{-8}) = 2.647 \times 10 \text{ gm.cm}^2$$

H.W(1):-

The adjacent lines in the pure rotational spectrum of $^{35}\text{Cl}^{19}\text{F}$ are separated by a frequency of $1.13 \times 10^{10} \text{ Hz}$. , what is the inter atomic distance of this molecule ?

H.W(2):-

HBr emission series of lines in IR region ,the inter atomic distance 16.94 cm^{-1} calculate the moment of inertia?

(atomic weight for H=1.008 and Br =97.92) .

Notes:

1. To convert $\text{Hz} \cdot \text{m}$ ($\cdot 3 \times 10^8$).

$\text{Hz} \cdot \text{cm}$ ($\cdot 3 \times 10^{10}$).

2. To convert atomic unit to gm ($\times 1.66 \times 10^{-24}$).

To convert atomic unit to Kg ($\times 1.66 \times 10^{-27}$).

Example(2):-

What is the change in the rotational constant B when H is replaced by deuterium in the H molecule ?

Solution:-

$$\frac{B}{B'} = \frac{I'}{I} = \frac{\mu'}{\mu}$$

$$\mu = \frac{m_H}{2}, \quad \mu' = \frac{m_D}{2} = m_H$$

$$\frac{B}{B'} = \frac{2m_H}{m_H} = 2, \quad \therefore B' = \frac{B}{2}$$

Change in rotational constant $B - B' = B/2$.

Example(3):-

The first line in the rotation spectrum of carbon monoxide has a frequency of 3.8424 cm^{-1} , calculate the

rotational constant and hence the $^{12}\text{C}-^{16}\text{O}$ bond length in carbon monoxide .

$$(A.V. NO. 6.022 \times 10^{23})$$

Solution:-

$$2B = 3.8424 \text{ cm}^{-1} \quad \therefore B = 1.9212 \text{ cm}^{-1}$$

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

$$\mu = \frac{12 \times 15.9949}{27.9949 \times 6.022 \times 10^{23}} = 1.385 \times 10^{-23} \text{ gm}$$

$$r^2 = \frac{6.626 \times 10^{-27}}{8\pi^2 \times 1.385 \times 10^{-23} \times 1.9212 \times 3 \times 10^{10}}$$

$$r = 1.131 \times 10^{-8} \text{ cm} = 1.131 \text{ \AA}$$

H.W(3):-

what is the average period of rotation of HCl molecule if it is in the $J=1$ state. The inter nuclear distance of HCl is 0.1274nm. Given the mass of H and chlorine atoms are $1.673 \times 10^{-27} \text{ Kg}$ and $58.06 \times 10^{-27} \text{ Kg}$ respectively

H.W(4):-

1-A:- Calculate the energy and wave – length of the photon absorbed when a $^{200}\text{Hg}^{35}\text{Cl}$ molecule ($r_0=2.23^\circ\text{A}$) makes the rotational transition $J=0 \rightarrow J=1$ and $J=1 \rightarrow J=2$.

B: - In what region of the electromagnetic spectrum are these lines found?

2- Suppose that the equilibrium separation in the $^1\text{H}^{35}\text{Cl}$ molecules is the same and equal to 1.27°A . Compute for each molecule

A:- The constant B .

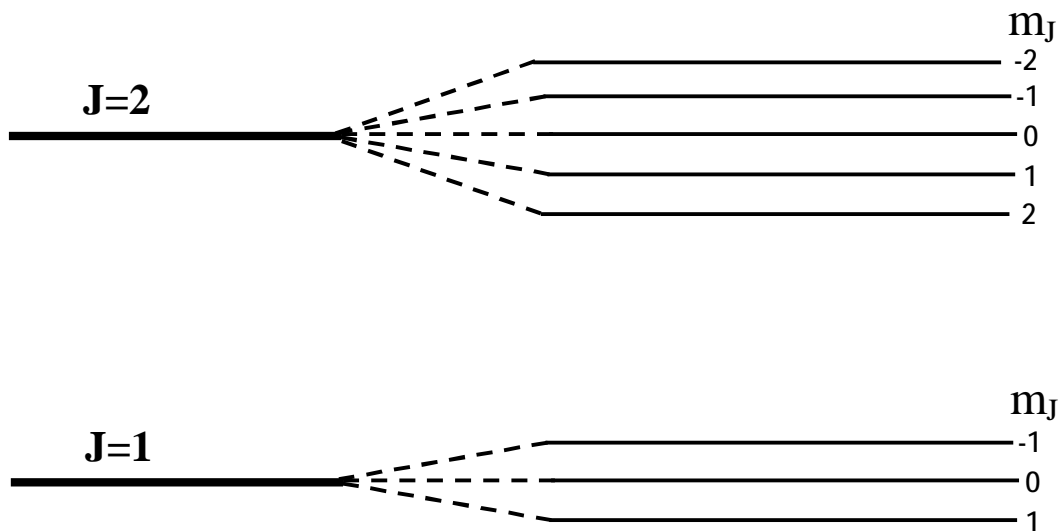
B:- The energy of the first two excited rotational levels.

C:- The frequencies and wave length corresponding to the transition $J=0 \rightarrow J=1$ and $J=1 \rightarrow J=2$.

Stark effect:-

Stark effect is the splitting of a spectral line in the presence of an electric field. It is the splitting of a rotational absorption line into various m_J components when the absorbing molecules are subjected to electric field of several hundred volts/m .

That is , the m_J degeneracy of the energy levels is lift by the electric field . Stark effect is of fundamental importance in the analysis of rotational spectra.



Stark effect is employ in micro wave technique by applied strong electric field parallel or perpendicular on spectra lines which pass through sample then the electric field united with dipole then the electric field united with dipole moment and produce the sublevels.

Microwave spectrometer:-

Different spectroscopy designed different spectrometers using various types of Microwave component. However , base on the following parts:-

1. Source:-

Most of the spectrometer have in the past used klystrons which emit monochromatic microwave radiation of very high stability the freq. can be varied mechanically over a wide range or electrically over a small range.

2. Measurement of frequency :-

Cavity wave meter , accuracy between ± 1 to ± 5 μHz . are used to get a rough estimate of the freq. of the microwave radiation . Accurate freq. measurements can be done directly by freq. counters or by the use of a beat technique.

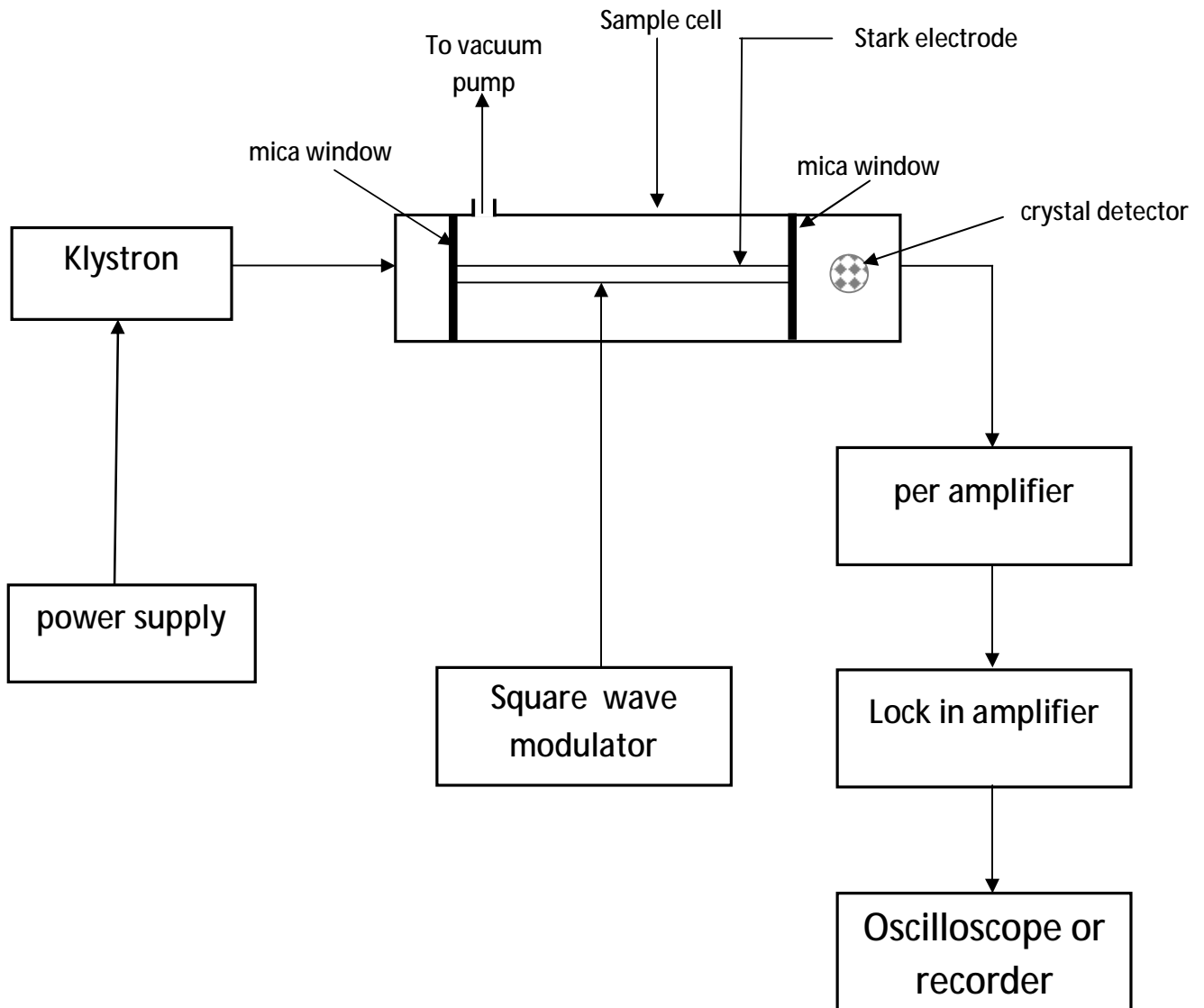
3. Guidance:-

Guidance of the radiation of microwave spectrometer to the absorbing substance. Microwave radiation from the source can be transmitted to be sample cell through hollow metallic tube (copper) called wave guides.

4. Sample cell:-

Different types of cells have been developed depend on the nature of the experiments. Each has its own advantages and disadvantages . one of the

commonly used cells is the stark cell employing stark modulation technique. The sample cell consists of along (3-4m) rectangular wave guides.



The microwave spectrometer

Non – Rigid Rotator:-

Experimentally, it is found that the separation between adjacent lines decreases steadily with increasing J . The reason for the decrease is obviously due to the decrease in the B value. All bonds are elastic to a certain extent and the bond is not rigid as we assumed. Therefore, for a correct treatment one has to use the complete

Hamiltonian of anon-rigid rotator.

The Solution for the corresponding schodiner equation gives the following energy expression for the energy levels of the non-rigid rotator

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

Where the centrifugal distortion constant D is small positive quantity.

For a diatomic molecule, D is related to B and the fundamental vibration frequency ν (cm^{-1}) of the molecule by the relation

$$D = \frac{4B^3}{\nu^2} \quad \text{cm}^{-1} \quad \text{Called centrifugal constant}$$

The fundamental freq. of vibration

$$\nu = \frac{v}{c} = \frac{1}{2\pi c} \sqrt{\frac{K}{\mu}}$$

$$k = 4\pi^2 c^2 \mu \nu^2$$

Where the K is the force constant.

μ is the reduced mass of the molecule.

Substitution of the values of B and ν gives.

$$D = 4 \left(\frac{h}{8\pi^2 I C} \right)^3 \frac{4\pi^2 c^2 \mu}{k} = \frac{h^3}{32\pi^4 r^6 c k \mu^2}$$

From the above equation, it is evident that centrifugal distortion effects are greatest for molecules with small moments of inertia and small force constants. In a given molecule, the effect of the centrifugal distortion is to decrease the rotational energy which increases rapidly for higher rotational states.

Selection rule for non-rigid rotator

$$\Delta J = \pm 1$$

And the frequency of the transition

$$J \rightarrow J + 1$$

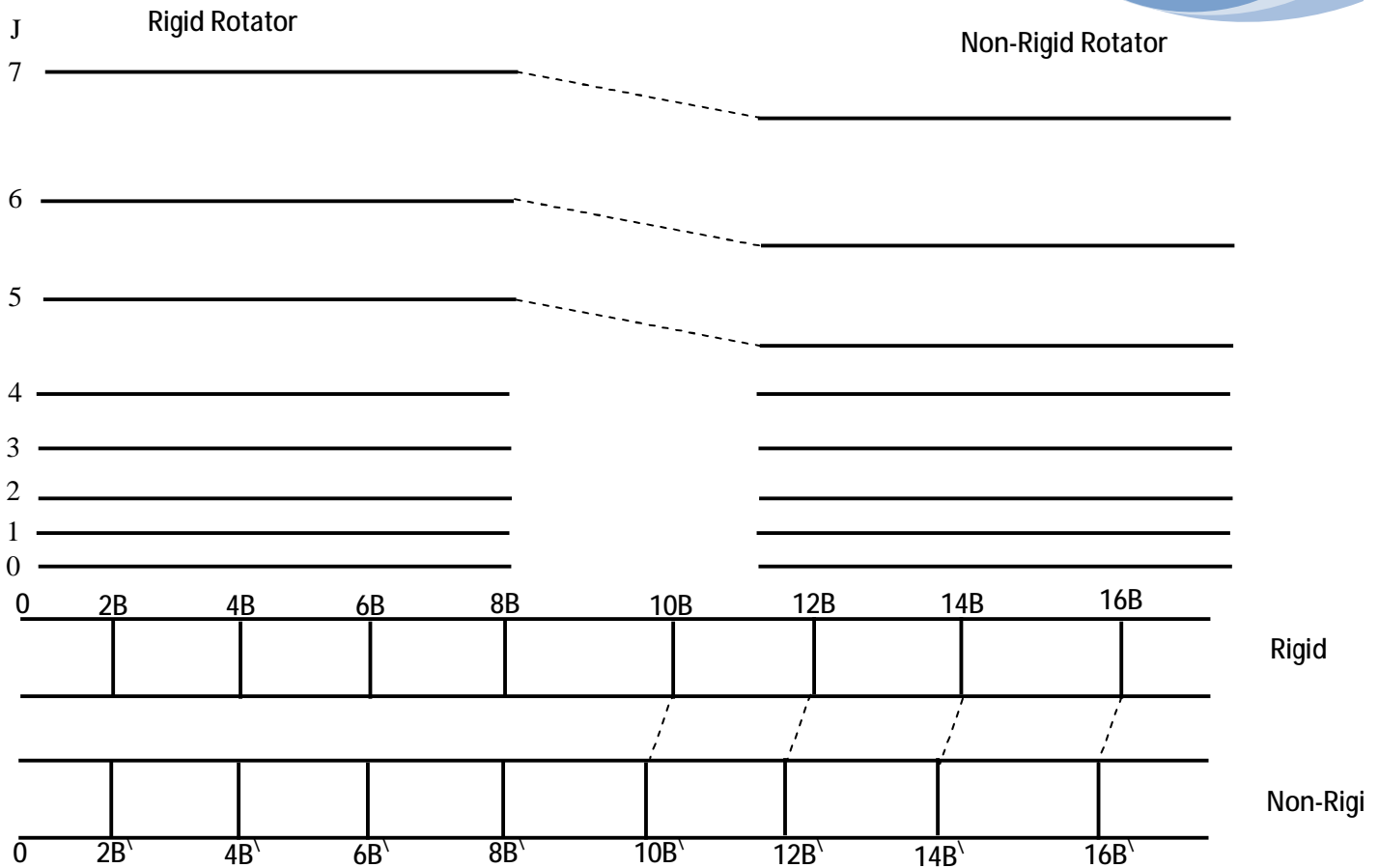
$$\nu_J = \epsilon_{J+1} - \epsilon_J = 2B(J+1) - 4D(J+2)^3 \text{ cm}^{-1}$$

Called Vibration frequency

$$J = 0, 1, 2, 3 \text{ --- -- -- -- --}$$

The first term is the same as the one due to a rigid molecule and the additional term gives the shift of the lines from that of the rigid molecule which increases with J as $(J+1)^3$.

The following figure gives the energy levels and the spectrum of non-rigid rotator. For comparison the rigid case is also included. If the J value of transitions are fixed, from the frequencies of two lines one can determine the constants B and D from which an estimate of the fundamental vibration frequency of the diatomic molecule may be estimated.



Example(4): - Rotational and centrifugal distortion constants of HCl molecule are 10.593 cm^{-1} and $5.3 \times 10^{-4} \text{ cm}^{-1}$ respectively. Estimate the vibration frequency and force constant of the molecule. (The atomic weight for $\text{H} = 1.673 \times 10^{-27}$, $\text{Cl} = 58.06 \times 10^{-27}$)

Solution:-

$$\text{Centrifugal distortion} \quad D = \frac{4B^3}{v^{\prime 2}}$$

$$\text{Vibration freq} \quad v^{\prime} = \sqrt{\frac{4B^3}{D}}$$

$$\therefore v^{\prime} = \sqrt{\frac{(4 \times 10.593)^3}{5.3 \times 10^{-4}}} = 2995.2 \text{ cm}^{-1} \quad \left. \vphantom{\frac{(4 \times 10.593)^3}{5.3 \times 10^{-4}}}\right\} \text{ atomic weight}$$

$$\mu = \frac{m_1 m_2}{m_1 + m_2} = \frac{m_H m_{Cl}}{m_H + m_{Cl}} = \frac{1.673 \times 10^{-27} \times 58.06 \times 10^{-27}}{1.673 \times 10^{-27} + 58.06 \times 10^{-27}}$$

m_1 for H
 m_2 for Cl

$$\text{Force constant } k = 4\pi^2 c^2 \mu \nu^2$$

$$k = 4\pi^2 \times (3 \times 10^8)^2 \times 1.6261 \times 10^{-27} \times (2995.2 \times 10^2)^2$$

$$= 518.3 \text{ N/M}$$

H.W(5):- Three consecutive lines in the rotational spectrum of diatomic molecule are observed at 84.544 ,101.355 and 118.112 cm^{-1} .

Assign these lines to their appropriate $J^{\parallel} \rightarrow J^{\perp}$ transitions and deduce values of B and D .Hence evaluate the approximate vibrational of the molecule.

H.W(6):- The observed rotational spectrum of HF shows the $J=0 \rightarrow J=1$ absorption at 41.11cm^{-1} ,the spacing between adjacent absorptions is 40.08cm^{-1} around $J=5 \rightarrow J=6$ transition and only 37.81cm^{-1} around $J=10 \rightarrow J=11$ transition.

Calculate B and I values from these three given data.

Example(6):- The rotational constant for $\text{H}^{12}\text{C}^{14}\text{N}$ and $\text{D}^{12}\text{C}^{14}\text{N}$ are 1.4782 and 1.2077 cm^{-1} respectively. Calculate the moment of Inertia of these molecules and inter nuclear distances of C-H and $\text{C}\equiv\text{N}$ bonds.

Solution:-

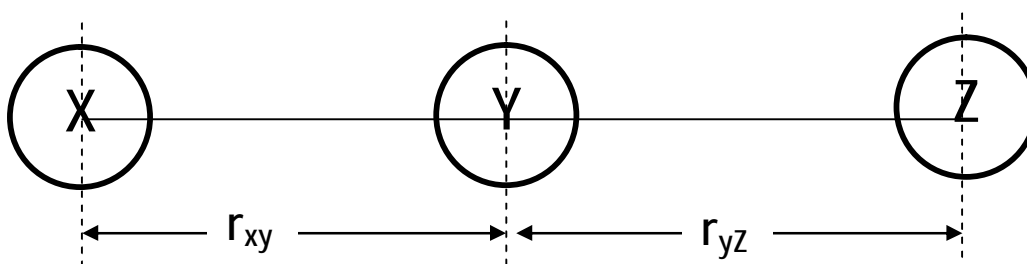
$$\begin{aligned} \text{1-For HCN } I &= \frac{h}{8\pi^2 BC} = \frac{6.625 \times 10^{-34}}{8\pi^2 \times 147.82 \times 3 \times 10^8} \\ &= 1.894 \times 10^{-46} \text{ Kg. m}^2 \end{aligned}$$

$$\begin{aligned} \text{2- For DCN } I' &= \frac{h}{8\pi^2 BC} = \frac{6.625 \times 10^{-34}}{8\pi^2 \times 120.77 \times 3 \times 10^8} \\ &= 2.3182 \times 10^{-46} \text{ Kg. m}^2 \end{aligned}$$

The moment Inertia of polyatomic molecule we can find by the following equations:-

$$I = \frac{m_x m_y r_{xy}^2 + m_y m_z r_{yz}^2 + m_x m_z (r_{xy} + r_{zy})^2}{m_x + m_y + m_z}$$

$$I' = \frac{m_x m_y r_{xy}^2 + m_y m_z r_{yz}^2 + m_x m_z (r_{xy} + r_{zy})^2}{m_x + m_y + m_z}$$



By using these equation can be found the inter nuclear distances of C-H and C≡N bonds.

$$I = \frac{m_H m_C r_{CH}^2 + m_C m_N r_{CN}^2 + m_H m_N (r_{CH} + r_{CN})^2}{m_H + m_C + m_N} \text{----- (1)}$$

$$I' = \frac{m_D m_C r_{CH}^2 + m_C m_N r_{CN}^2 + m_D m_N (r_{CH} + r_{CN})^2}{m_D + m_C + m_N} \text{----- (2)}$$

$$m_H = 1.008 \text{ , } m_D = 2.014$$

$$m_C = 12.00 \text{ , } m_N = 14.003$$

$$\text{mass} = \frac{\text{atomic weight}}{\text{Avogadro number } (6.022 \times 10^{23})}$$

$$1\text{- For H} = \frac{1.008}{6.022 \times 10^{23}} = 0.167 \times 10^{-23}$$

$$2\text{- For C} = \frac{12}{6.022 \times 10^{23}} = 1.993 \times 10^{-23}$$

$$3\text{- For D} = \frac{2.04}{6.022 \times 10^{23}} = 0.339 \times 10^{-23}$$

$$4\text{- For N} = \frac{14.003}{6.022 \times 10^{23}} = 3.325 \times 10^{-23}$$

بتعويض قيم *mass* وبتطبيق المعادلتين (1) و(2) نحصل على

$$11.406 \times 10^{-20} = 0.44r_{CH}^2 + 6.22r_{CN}^2 + 6.522(r_{CH} + r_{CN})^2 \text{----- (3)}$$

$$13.96 \times 10^{-20} = 0.862r_{CH}^2 + 5.997r_{CN}^2 + 1.006(r_{CH} + r_{CN})^2 \text{----- (4)}$$

وبحل المعادلتين نحصل على

$$r_{\text{CH}}=1.06 \text{ \AA} , r_{\text{CN}}=1.157 \text{ \AA}$$

Micro wave application :-

- 1-From B value can be determine or calculate the length of bonds and the angle of simple molecules .
- 2- Calculation of moment of inertia for different molecule and then determine the equilibrium Distance re by graphs the relation between B and V(Vibration level).
- 3- Study of molecule fluctuation to rigid rotator condition by calculate the constant of distortion.
- 4- Study the stark effect which was helped the researchers by calculate the values of Dipole moment .
- 5-Study of the molecular symmetry especially the molecule (cyclorentadiene , Thiophene)

Notes:-

The rotation spectrum:-

- 1-The energy or wave number of rotation energy levels can be calculated from the equation $\nu(J) = B(J + 1)$
 $J= 0,1,2,3,4,-----$ and B rotation constant.
- 2-When $J=0$ then $\nu(J) = 0$ at this point no rotation of molecule.
- 3-When the molecule absorbed radiation leads to the molecule arise to first excited level ($J=1$), and the absorption energy equal to the difference between two levels ($J=1$ and $J=0$) the

$$\epsilon_{J=1} - \epsilon_{J=0} = B(1) + (1 + 1) - B(0)(0 + 1) = 2B$$

This means the first absorption spectrum at the value **2B**.

4-When the molecule absorbed another quantity of energy this leads arise the molecule to $J=2$ and the energy equal to difference energy levels between $J=2$, and $J=1$

$$\epsilon_{J=2} - \epsilon_{J=1} = B2(2 + 1) - B(1)(1 + 1) = 6B - 2B = 4$$

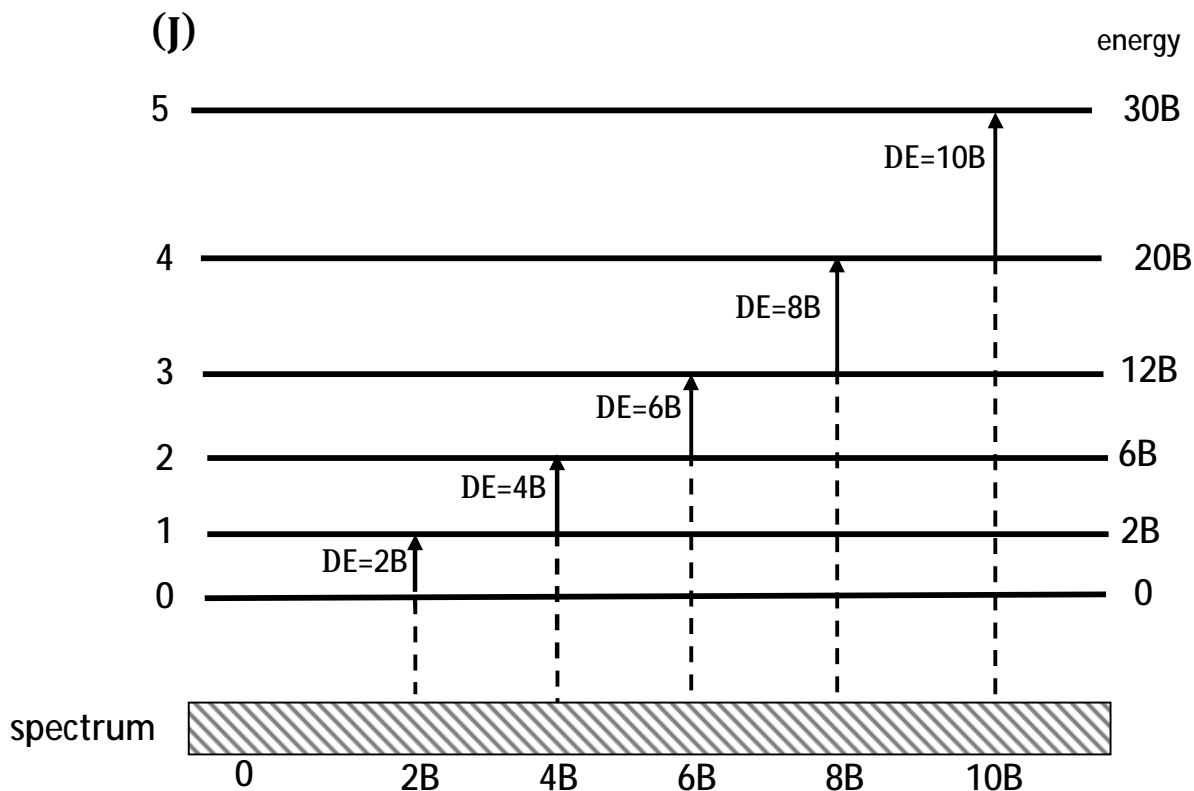
This means the second absorption line at **4B**.

In general we can need for arise the molecule from level J to level J+1

$$\epsilon_J = B_J(J + 1)$$

$$\epsilon_J - \epsilon_{J+1} = B(J + 1)(J + 2) - BJ(J + 2) = 2B(J + 1)$$

This equation gives us the separation energy levels or separation between consecutive spectrum lines, As shows in the following figure.



From the above we can know the separation between two levels equal to $2B$.

5-When one can be study the linear diatomic molecules which have permanent dipole moment in microwave region appear spectrum contain series from consecutive lines $2B, 4B, 6B, 8B, \dots$ and the separation distance between them $2B$.

6-when we can study the spectrum with more accuracy and more carefully we can show that the separation distance between lines not fixed and this distance decrease when J increase, and the reason of this behavior due to centrifugal distortion effect on the bond (between atom) as result to increase of angular velocity and this effect on I and the B value is decrease .

اي ان الفاصلة بين الخطوط ليست ثابتة على قيمة $2B$ وانما تقل هذه الفاصلة بزيادة قيمة J بسبب وجود التأثير اللامركزي الذي يؤثر على الاصرة نتيجة زيادة السرعة الزاوية وهذا يؤدي الى زيادة I وبالتالي نقص في قيمة B كلما زاد J .

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

D:- Centrifugal distortion and $D \ll B$.

In most calculation (D neglect)

7-In adsorption process the radiation interact with dipole moment and when molecule emit electromagnetic radiation this due to ration of electric moment.

8- In poly atomic molecule like CO_2 , HCN ,----- these molecule are big and then have high moment of inertia comparison with diatomic molecule like CO , HCl ----- as a result to this the energy levels nearest together and the frequency of rotation line is small or low.

9- Population of rotational Energy Level

The allowed rotation levels obey to selection rules $\Delta J = \pm 1$

Then

$$\frac{N_J}{N_0} = (2J + 1)e^{-(E_J - E_0)/KT} \text{ --- (1)}$$

N_J = No. of molecule in rotation level E_J at T .

N_0 = No. of molecule in rotation level $J=0$ (stable state) .

$2J+1$ = the order of degenerate of level J .

K = Boltzman constant = $1.38 \times 10^{-23} \text{ J.k}^{-1} = 1.38 \times 10^{-16} \text{ erg deg}^{-1}$

$E_0 = 0$ because $J=0$

$E_J = BhcJ(J+1)$

\therefore eq. (1) become

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

N_J depend of J