B.Sc. Sem IV

Unit III: Molecular Spectroscopy

Topic: Rotational Spectroscopy

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Rotational Spectroscopy

➢ Rotational Spectroscopy, also known as Microwave Spectroscopy as the energy absorbed/emitted between rotational states lies in the microwave region of the electromagnetic spectrum ($3 \times 10^{10} - 3 \times 10^{12}$ Hz)

➢ Molecules that have a permanent dipole moment (for e.g. HCl) are said to be microwave active i.e. they show rotational spectra

➢ Molecules that have no permanent dipole moment like homonuclear diatomic molecules (for e.g. Cl_2, H_2) are microwave inactive

➢ The rotational spectra of non-polar molecules cannot be observed by microwave spectroscopy but can be observed and measured by Raman spectroscopy.

Rotational Spectroscopy

➢ On rotation, the plus and minus charges change places periodically and the component dipole moment in a given direction fluctuates regularly

➢ It is exactly similar in form to the fluctuating electric field of radiation.

➢ Interaction can occur, energy can be absorbed or emitted, and the rotation give rises to a spectrum
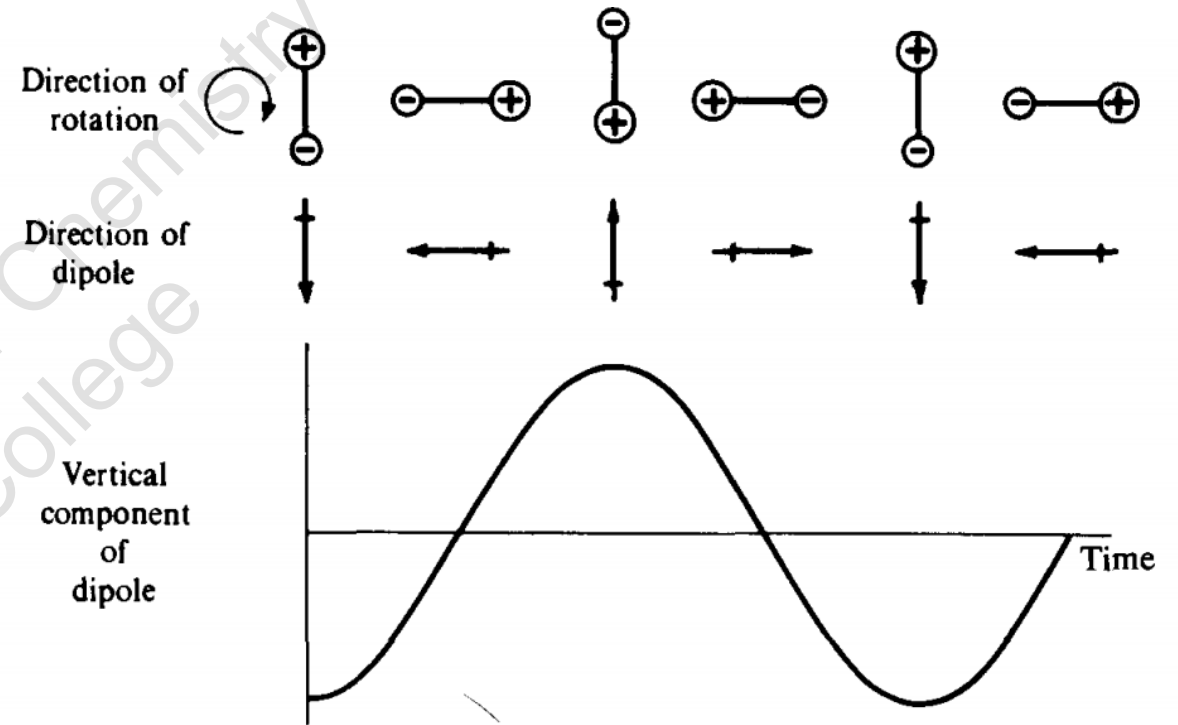
The rotation of a polar diatomic molecule, showing the fluctuation in the dipole moment measured in a particular direction

Rotational Spectra

➢ Rotational energy like all other form of energy is quantized i.e. its energy is limited to certain definite values depending on the shape and size of the molecule concerned.

➢ The permitted energy values are called rotational energy levels, calculated by Schrodinger equation

➢ For diatomic system the molecules can be considered as rigid diatomic molecules for simplicity i.e. bond length doesn't change with time.
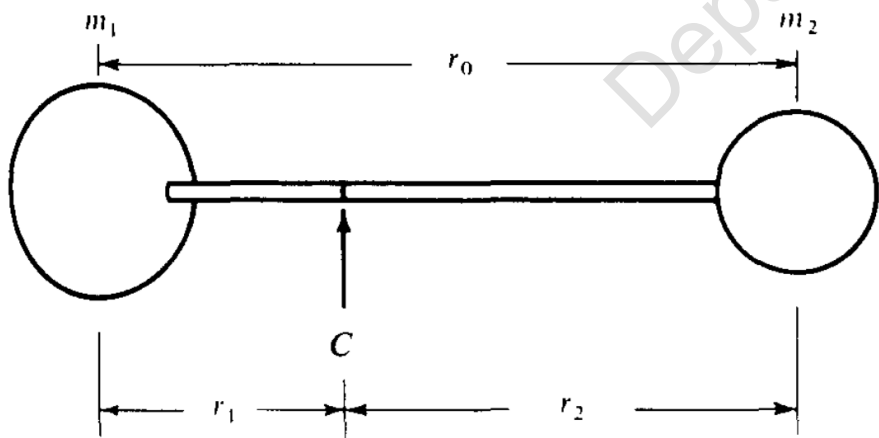
A rigid diatomic molecule treated as two masses, m_1 and m_2, joined by a rigid bar of length $r_0 = r_1 + r_2$

Bond length, $$r_0 = r_1 + r_2 \qquad \text{eq. (i)}$$

The molecule rotates end-over-end about a point C, the centre of gravity. The its moment about C is given by equation,

$$m_1 r_1 = m_2 r_2 \qquad \text{eq. (ii)}$$

The moment of inertia about C is defined by:

$$
\begin{aligned}
I &= m_1 r_1^2 + m_2 r_2^2 \\
&= m_2 r_2 r_1 + m_1 r_1 r_2 \qquad \text{From eq. (ii)} \\
&= r_1 r_2 (m_1 + m_2)
\end{aligned}
$$

From eq. (i) & (ii):

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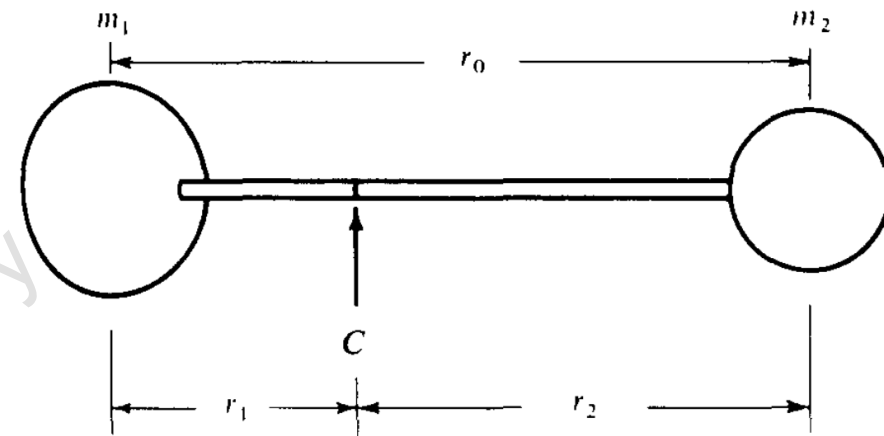
Therefore,

$$r_1 = \frac{m_2 r_0}{m_1 + m_2} \quad \text{and} \quad r_2 = \frac{m_1 r_0}{m_1 + m_2} \qquad \text{eq. (iii)}$$

Replacing eq. (iii) in eq. (ii):

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

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

Reduced mass of the system

Expression of moment of inertia in terms of atomic masses and the bond length

Energy levels

From Schrodinger equation the rotational energy level allowed to the rigid diatomic molecule are given by the expression:

$$E_J = \frac{h^2}{8\pi^2 I} J(J+1) \quad \text{joules} \quad \text{where } J = 0, 1, 2, \ldots \qquad \textit{eq. (v)}$$

J is called rotational quantum number, can take integral values from 0 upwards

eq. (v) expressed the allowed energies in joules; The rotational spectra are usually discussed

$$\varepsilon_J = \frac{E_J}{hc} = \frac{h}{8\pi^2 Ic} J(J+1) \quad \text{cm}^{-1} \quad (J = 0, 1, 2, \ldots) \qquad \textit{eq. (vi)}$$

eq. (vi) is usually abbreviated to

$$\varepsilon_J = BJ(J+1) \quad \text{cm}^{-1} \quad (J = 0, 1, 2, \ldots) \qquad \textit{eq. (vii)}$$

Where **B**, the rotational constant is given by

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

Energy level

If the molecule is raised from the J=0 state (ground rotational state, in which no rotation occurs) to J=1 state, the energy absorbed will be

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

and, therefore,

$$\bar{v}_{J=0 \rightarrow J=1} = 2B \quad \text{cm}^{-1}$$

An absorption line will appear at 2B cm^{-1}

If the molecule is raised from the J=1 state to J=2 state, the energy absorbed will be

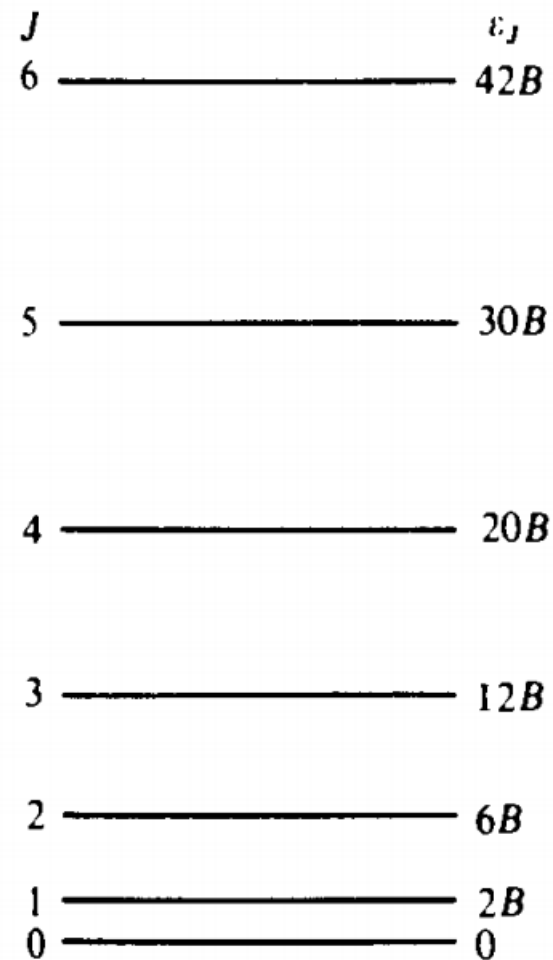$$\bar{v}_{J=1 \rightarrow J=2} = \varepsilon_{J=2} - \varepsilon_{J=1}$$

$$= 6B - 2B = 4B \quad \text{cm}^{-1}$$

In general to raise the molecule from the J state to J+1 state, the energy absorbed will be

$$\bar{v}_{J \rightarrow J+1} = B(J+1)(J+2) - BJ(J+1)$$

$$= B[J^2 + 3J + 2 - (J^2 + J)]$$

or,

$$\bar{v}_{J \rightarrow J+1} = 2B(J+1) \quad \text{cm}^{-1}$$

J		ε_J
6	———————	42B
5	———————	30B
4	———————	20B
3	———————	12B
2	———————	6B
1	———————	2B
0	———————	0

The allowed rotational energies of a rigid diatomic molecule.

Rotational Spectra
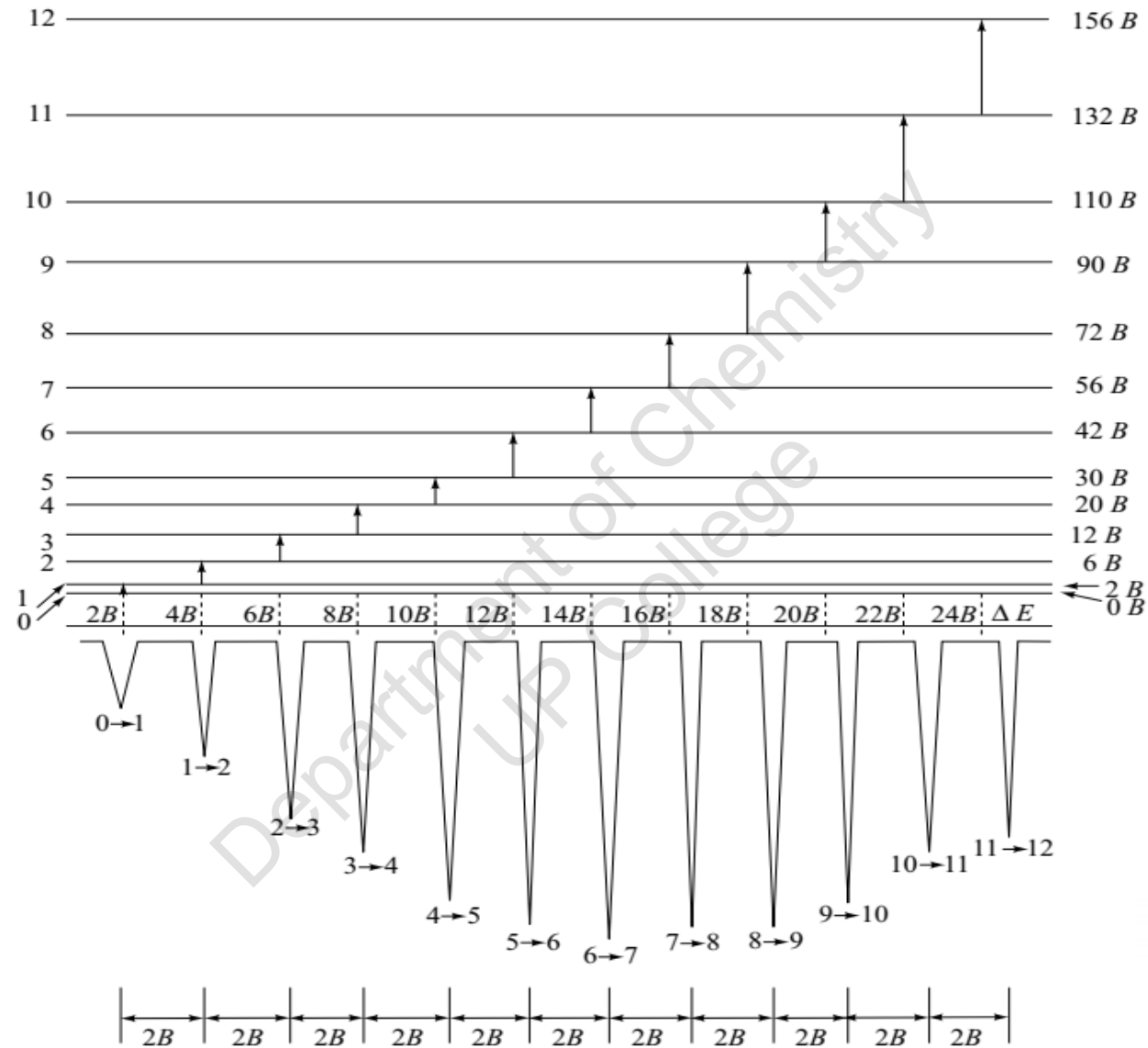

Selection rule: $\Delta J = \pm 1$

Allowed transition between the energy levels of a rigid diatomic molecule and the spectrum which arise from them

Intensities of Spectral lines

$\Delta J = \pm 2, \pm 3, ..$ are forbidden the transition probability for all these changes is zero.

➢ However all the spectral lines due to $\Delta J = \pm 1$ are not equally intense.

➢ The relative intensities of the spectral lines will depend upon the relative population of the energy levels.

➢ Population of a rotational energy level with quantum number J relative to that of the ground level for which J=0 is given according to Boltzmann distribution law,

$$N_J/N_0 = \exp(-E_J/kT)$$
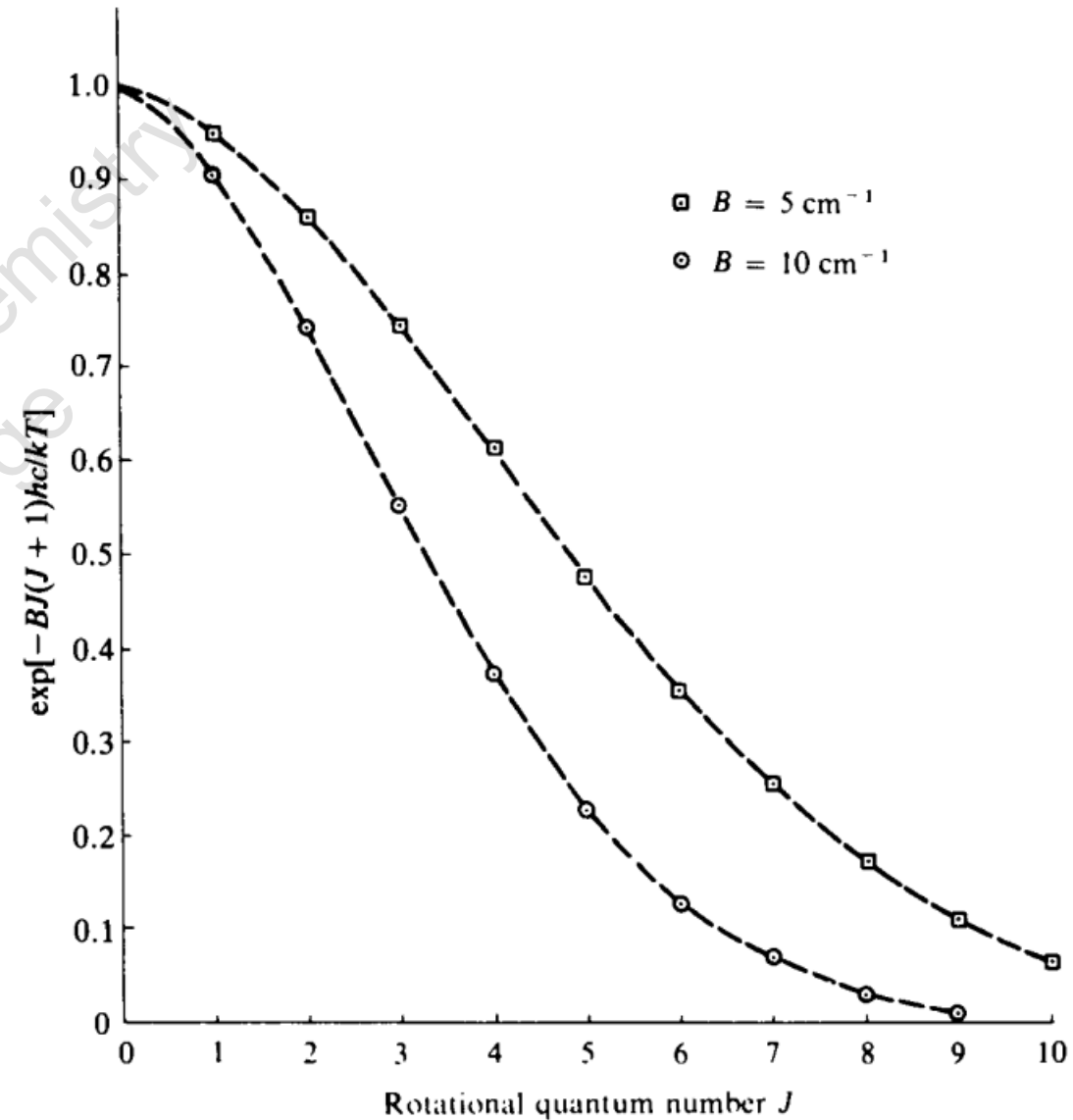
Boltzmann population of the rotational energy levels

Intensities of Spectral lines

A second factor is also required, the possibility of degeneracy(two or more energy states having same energy) in the energy states.
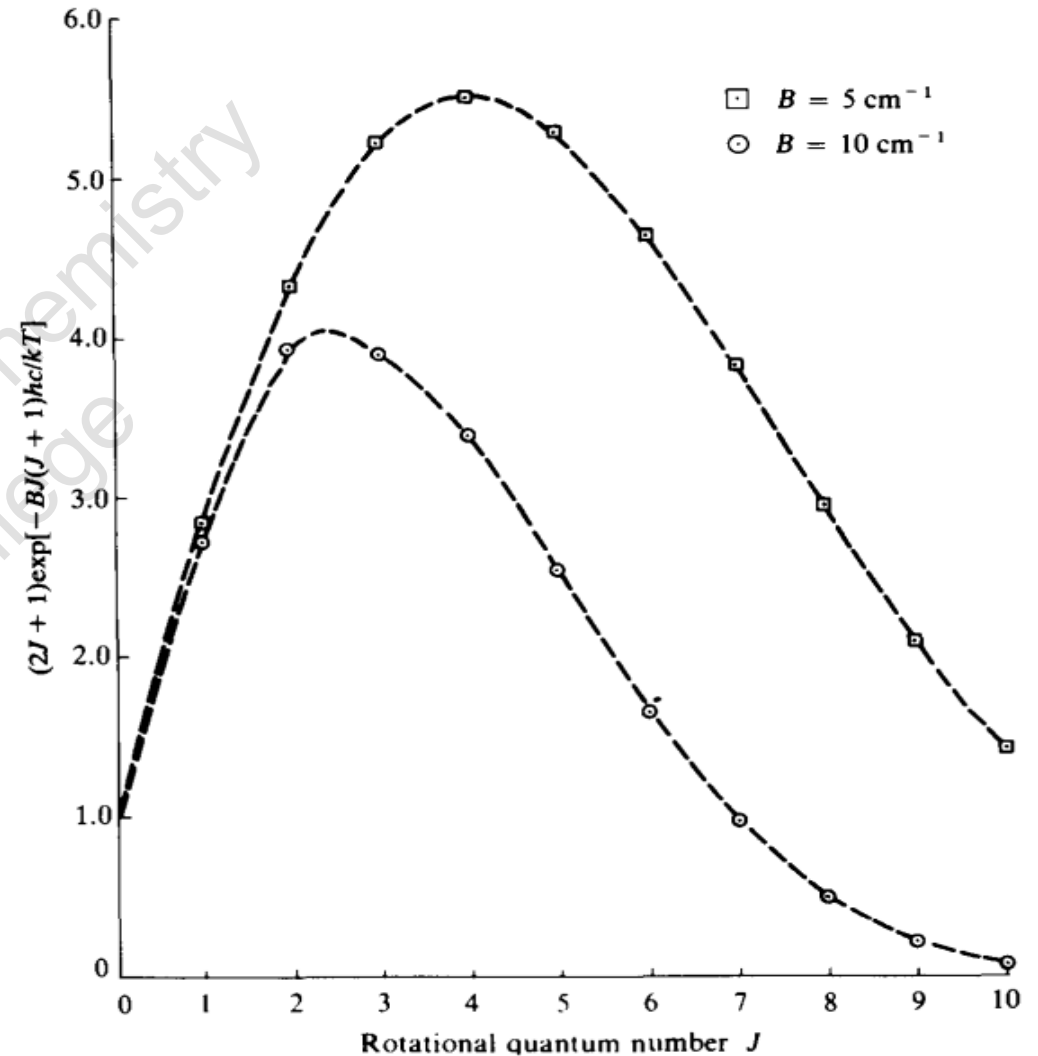
The total relative population of an energy E_J will be:

$$\text{Population} \propto (2J + 1) \exp(-E_J/kT)$$

Population rises to a maximum then diminishes

Maximimum population:

$$J = \sqrt{\frac{kT}{2hcB}} - \frac{1}{2}$$

Relative population including degeneracy

Finding J_{max} → Maximum populated energy level

$$\frac{dn_J}{dJ} = \frac{d\{g_J \exp(-E_J/kT\}}{dJ} = 0$$

This gives

$$\frac{d}{dJ}\{(2J+1)\exp(-BhcJ(J+1)/kT)\} = 0$$

or $\quad 2\exp(-BhcJ(J+1)/kT)$

$$-(2J+1)\frac{Bhc}{kT}(2J+1)\exp(-BhcJ(J+1)/kT) = 0$$

or $\quad 2-(2J+1)^2\dfrac{Bhc}{kT} = 0$

or $\quad J = \sqrt{\dfrac{kT}{2Bhc}} - \dfrac{1}{2}$

For CO at 298 K, the value of J is equal to

$$\left\{\frac{1}{2}\frac{(1.38\times10^{-23}\ \text{J K}^{-1})(298\ \text{K})}{(3.83\times10^{-23}\ \text{J})}\right\}^{1/2} - \frac{1}{2} = 7.34 - 0.5 = 6.84 \simeq 7$$

The rotational spectrum can be used to determine the bond distance of a diatomic molecule. Take, for example, the case of CO molecule; the first line in the spectrum is found to be at $3.842\ 4\ cm^{-1}$. This is equal to $2B$. Thus, we have

$$\tilde{v}_{J'=1\leftarrow J''=0} = 2B = 3.842\ 4\ cm^{-1}$$

Thus $\qquad B = 1.921\ 2\ cm^{-1} = 1.921\ 2 \times 10^2\ m^{-1}$

Since $\quad B = \dfrac{h}{8\pi^2 Ic}\quad$ therefore $\quad I = \dfrac{h}{8\pi^2 Bc}$

Substituting the values, we have

$$I = \frac{(6.626 \times 10^{-34}\ J\ s)}{8(3.14)^2\ (1.921\ 2 \times 10^2\ m^{-1})(2.998 \times 10^8\ m\ s^-)}$$

$$= 1.458 \times 10^{-46}\ kg\ m^2$$

Now $\quad I = \mu r^2\quad$ therefore $\quad r = (I/\mu)^{1/2}$

The values of μ for CO molecule is

$$\mu = \frac{m_1 m_2}{m_1 + m_2} = \frac{\{(0.012\ kg)/(6.022 \times 10^{23})\}\{(0.016\ kg)/(6.022 \times 10^{23})\}}{\{(0.012\ kg)/(6.022 \times 10^{23})\} + \{(0.016\ kg)/6.022 \times 10^{23})\}}$$

$$= \frac{0.012 \times 0.016}{0.028 \times 6.022 \times 10^{23}}\ kg = 1.14 \times 10^{-26}\ kg$$

Hence $\quad r = \left(\dfrac{I}{\mu}\right)^{1/2} = \left(\dfrac{1.458 \times 10^{-46}\ kg\ m^2}{1.14 \times 10^{-26}\ kg}\right)^{1/2}$

$$= 1.13 \times 10^{-10}\ m = 1.13 \times 10^{-8}\ cm = 113\ pm$$

Effect of isotopic substitution

➢ When a particular atom in a molecule is replaced by its isotope, the resultant molecule is found to be chemically identical to the original molecule.

➢ The internuclear distance and the electron distribution of the molecule do not change by the isotopic substitution and thus its dipole moment remains unaltered.

➢ There occurs an increase in the moment of inertia of the molecule.

➢ Since I appears in the denominator of the expression of B, An increase in the value of I leads to a decrease in the value of B.

➢ As a result, the energies of various rotational levels decreases and the energy levels become closer to one another.
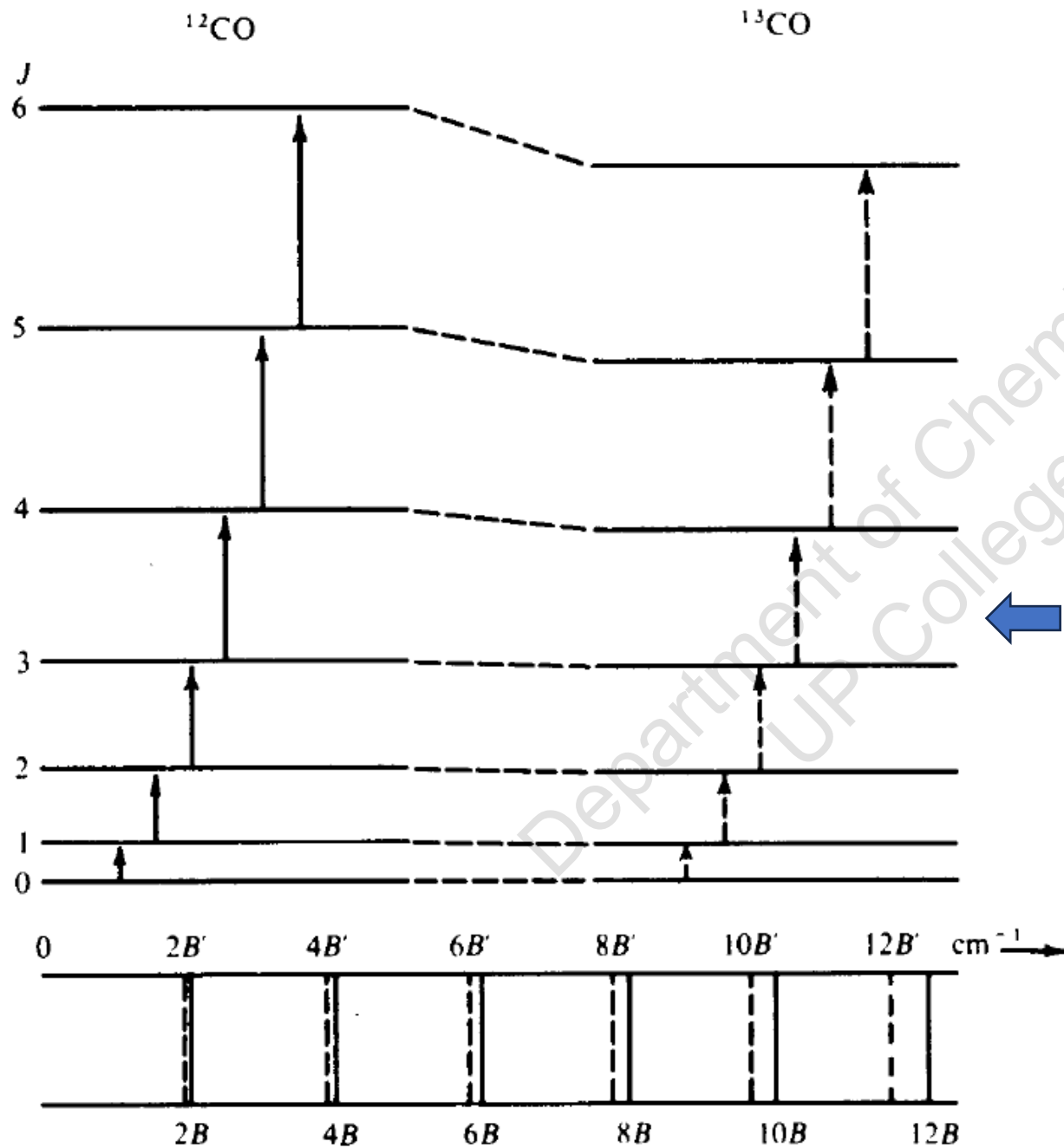
The effect of isotopic substitution on the energy levels and rotational spectrum of a diatomic molecule such as carbon monoxide.

Applications of isotopic substitution in Microwave Spectroscopy

➢ Extremely precise determination of atomic weights of isotopic atoms.

➢ The abundance of isotopes can be estimated by comparing absorption intensities.

The first rotational absorption of $^{12}C^{16}O$ is found to occur at 3.842 4 cm^{-1} while that of $^{13}C^{16}O$ at 3.673 4 cm^{-1}. Assuming the molar masses of ^{16}O and ^{12}C as 15.999 4 g mol^{-1} and 12.0000 g mol^{-1} respectively, calculate the molar mass of ^{13}C.

We are given that

$$2\,B_{^{12}C^{16}O} = 3.842\ 4\ \text{cm}^{-1} \qquad \text{and} \qquad 2\,B_{^{13}C^{16}O} = 3.673\ 4\ \text{cm}^{-1}$$

Thus

$$B_{^{12}C^{16}O} = 1.921\ 2\ \text{cm}^{-1} \qquad \text{and} \qquad B_{^{13}C^{16}O} = 1.836\ 7\ \text{cm}^{-1}$$

Taking the ratio of the two Bs, we have

$$\frac{B_{^{12}C^{16}O}}{B_{^{13}C^{16}O}} = \frac{h/8\pi^2 I_{^{12}C^{16}O}\,c}{h/8\pi^2 I_{^{13}C^{16}O}\,c} = \frac{I_{^{13}C^{16}O}}{I_{^{12}C^{16}O}} = \frac{\mu_{^{13}C^{16}O}}{\mu_{^{12}C^{16}O}}$$

$$= \frac{m_{^{13}C}\,m_{^{16}O}}{(m_{^{13}C} + m_{^{16}O})} \times \frac{(m_{^{12}C} + m_{^{16}O})}{m_{^{12}C}\,m_{^{16}O}}$$

$$= \frac{m_{^{13}C}(m_{^{12}C} + m_{^{16}O})}{m_{^{12}C}(m_{^{13}C} + m_{^{16}O})} = \frac{M_{^{13}C}(M_{^{12}C} + M_{^{16}O})}{M_{^{12}C}(M_{^{13}C} + M_{^{16}O})}$$

Thus

$$\frac{1.921\ 2\ \text{cm}^{-1}}{1.836\ 7\ \text{cm}^{-1}} = \frac{M_{^{13}C}(12.000\ 0 + 15.999\ 4)}{(12.000\ 0)(M_{^{13}C} + 15.999\ 4\ \text{g mol}^{-1})}$$
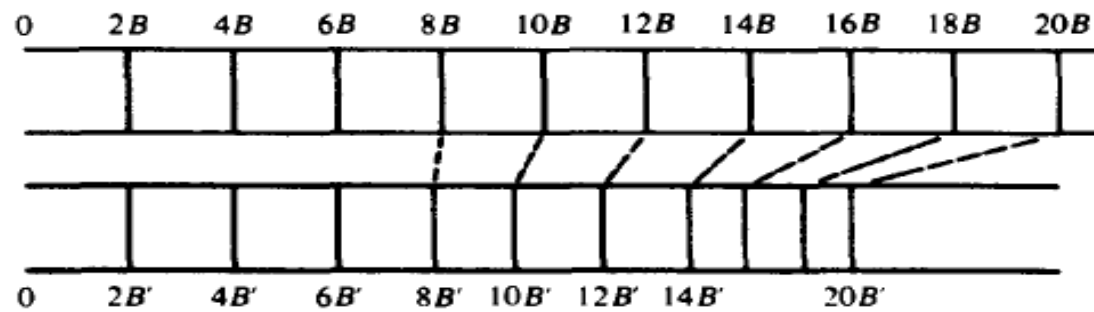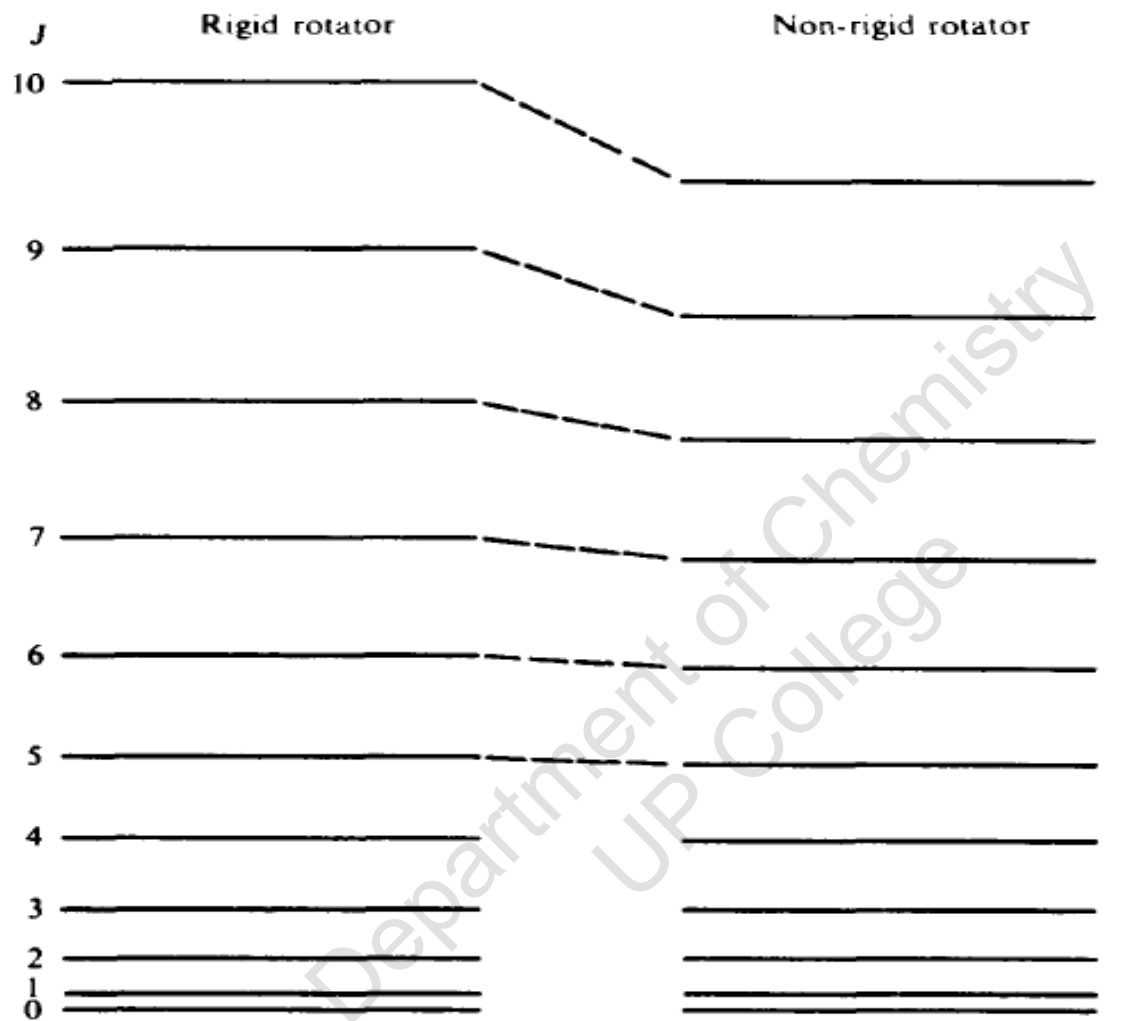
Solving for $M_{^{13}C}$, we get

$$M_{^{13}C} = 13.000\ 7\ \text{g mol}^{-1}$$

Microwave Oven

➢ It is the water molecules only that absorb the radiation and so become raised into high rotational states. The biological molecules in food are far too large to be able to rotate.

➢ The lifetime of an excited rotational state is long. The excited molecules make many collisions with the surrounding molecules.

➢ With each collision, the excess rotational energy of the water molecules is re-emitted as heat and the food becomes cooked.

➢ The efficiency of the oven lies in the fact that this heating is internal.

➢ Water molecules throughout the whole bulk of the food are simultaneously excited and heated, so cooking times are drastically reduced.

Limitations of Rigid Rotor model

➢ According to the rigid rotor model, spectral lines should be equispaced

➢ But the experiment shows that with the increase in the rotational quantum number J, spacing between two successive spectral line decreases

➢ With an increase in J, rotational Kinetic energy as well as angular velocity increases. The centrifugal force also increases, resulting in distortion of the bond.

➢ So, the bond is a non rigid rotor with centrifugal distortion.

➢ With increase in J, bond length increases. So the effective rotational constant decreases.

➢ The spacing between two successive rotational spectral line decreases.

Rigid rotator   Non-rigid rotator

J

10
9
8
7
6
5
4
3
2
1
0

0   2B 4B 6B 8B 10B 12B 14B 16B 18B 20B

Rigid

Non-rigid

0   2B' 4B' 6B' 8B' 10B' 12B' 14B' 20B'

Non Rigid Rotator model

The Schrodinger wave equation may be set up for a non-rigid molecule, and the rotational energy levels are found to be:

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

$$\varepsilon_J = E_J/hc = BJ(J+1) - DJ^2(J+1)^2 \quad cm^{-1}$$

where the rotational constant, B, is as defined previously, and the *centrifugal distortion constant, D,* is given by:

$$D = \frac{h^3}{32\pi^4 I^2 r^2 kc} \quad cm^{-1} \qquad\qquad D = \frac{16B^3\pi^2\mu c^2}{k} = \frac{4B^3}{\bar{\omega}^2}$$

where $\bar{\omega}$ is the vibrational frequency of the bond and k is the force constant

Non Rigid Rotator model

➤ The value of B was found to be of the order of 10cm^{-1}. However the value of D was found to be of the order of 10^{-3}cm^{-1} which is very small compared with B.

➤ For small J, therefore, the correction term DJ^2(J+ 1)^2 is almost negligible, while for J values of 10 or more it may become appreciable.

➤ The selection rule is still $\Delta J = \pm 1$

➤ Spacing between two successive energy levels

$$\varepsilon_{J+1} - \varepsilon_J = \bar{v}_J = B[(J+1)(J+2) - J(J+1)]$$
$$- D[(J+1)^2(J+2)^2 - J^2(J+1)^2]$$
$$= 2B(J+1) - 4D(J+1)^3 \quad \text{cm}^{-1}$$