

GENESIS TUTORIALS

Institute for CSIR-UGC-NET/JRF, GATE & IIT-JAM

Molecular Spectroscopy

Molecular Spectroscopy

The molecular spectroscopy is the area of study which describes the interaction of electromagnetic radiations with matter. The instrument used in such studies are called spectrometers.

- Spectroscopic techniques are faster than chemical analysis, require less time less sample and are generally non-destructive
- Atomic spectrum is due to change of energy (by absorption or emission) arising from the transition of electron from one energy level to another energy level in the atom.
- The molecular spectrum involves transitions between rotational and vibrational energy levels, in addition to electronic transitions. Hence molecular spectrum is the result of change of molecular rotational and vibrational level as well as energy change due to electronic transitions from one molecular orbital to another
- In early days of investigation, molecular spectra were found in the form of broad continuous bands. Hence molecular spectra were generally known as 'Band spectra (& line spectra in case of atoms)
- But later on the bands were found to consist of closely packed lines by using the spectrometers of high resolution power. These lines are found as group of lines, called as 'Bands' the lines in each band becoming closer & closer until these merge into an edge called band head. Again a large number of bands are found clusters together forming a band-group
- The molecular spectra provide most useful information regarding the shapes and size of molecules, the bond length, strength of bonds, bond dissociation energies and bond angles.
- Molecular spectroscopy provides information about dimensions of molecules and possible molecular energy levels for the study of molecular structure and thermodynamic properties of the molecule

Origin of Molecular Spectra

→ A molecule possesses different type of energy—Translation, Rotational, Vibrational and Electronic energy

$$E_{\text{Total}} = E_{\text{Trans.}} + E_{\text{rot.}} + E_{\text{vib}} + E_{\text{ele}}$$

Order of these energies-

$$E_{\text{ele}} \gg E_{\text{vib}} \gg E_{\text{rot.}} \gg E_{\text{Trans.}}$$

→ The expressions corresponding to these energies are given by

$$E_{\text{Trans}} = \frac{n^2 h^2}{8ml^2} \quad n \rightarrow \text{Translation quantum number } n = 1, 2, 3, 4, \dots$$

$$E_{\text{rot}}(\text{joule}) = J(J + 1) \frac{h^2}{8\pi^2 I} \quad J = \text{rotational quantum number } J = 0, 1, 2, 3, \dots$$

$$E (\text{cm}^{-1}) = BJ(J + 1)$$

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

$$E_{\text{vib}} = \left(v + \frac{1}{2}\right) \frac{h}{2\pi} \sqrt{\frac{K}{\mu}}$$

$V \rightarrow$ Vibrational quantum number

$K \rightarrow$ force constant

$\mu \rightarrow$ reduced mass

$$V = 0, 1, 2, 3, \dots$$

$$E_{\text{ele}} = \frac{2\pi^2 e^4 Z^2}{(4\pi\epsilon_0)^2 n^2 h^2} n \rightarrow \text{Electronic quantum number and has value } = 1, 2, 3, 4, \dots$$

→ If a molecule is placed in an electromagnetic field (eq. light), a transfer of energy from the electromagnetic field to the molecule occurs when

$$\Delta E = h\nu$$

$H =$ Planks constant

$\nu =$ Frequency of light

$\Delta E =$ Difference in energy between two quantized states

→ The molecule absorbs energy when it is excited from the lower energy state (E_1) to a higher energy state (E_2) and emits radiations of same frequency when the molecules reverts from higher energy state to lower energy state Hence—

$$\text{For Emission } \Delta E = E_2 - E_1$$

For Absorption $\Delta E = E_1 - E_2$

→ When a molecule absorbs energy following change in the molecule takes place

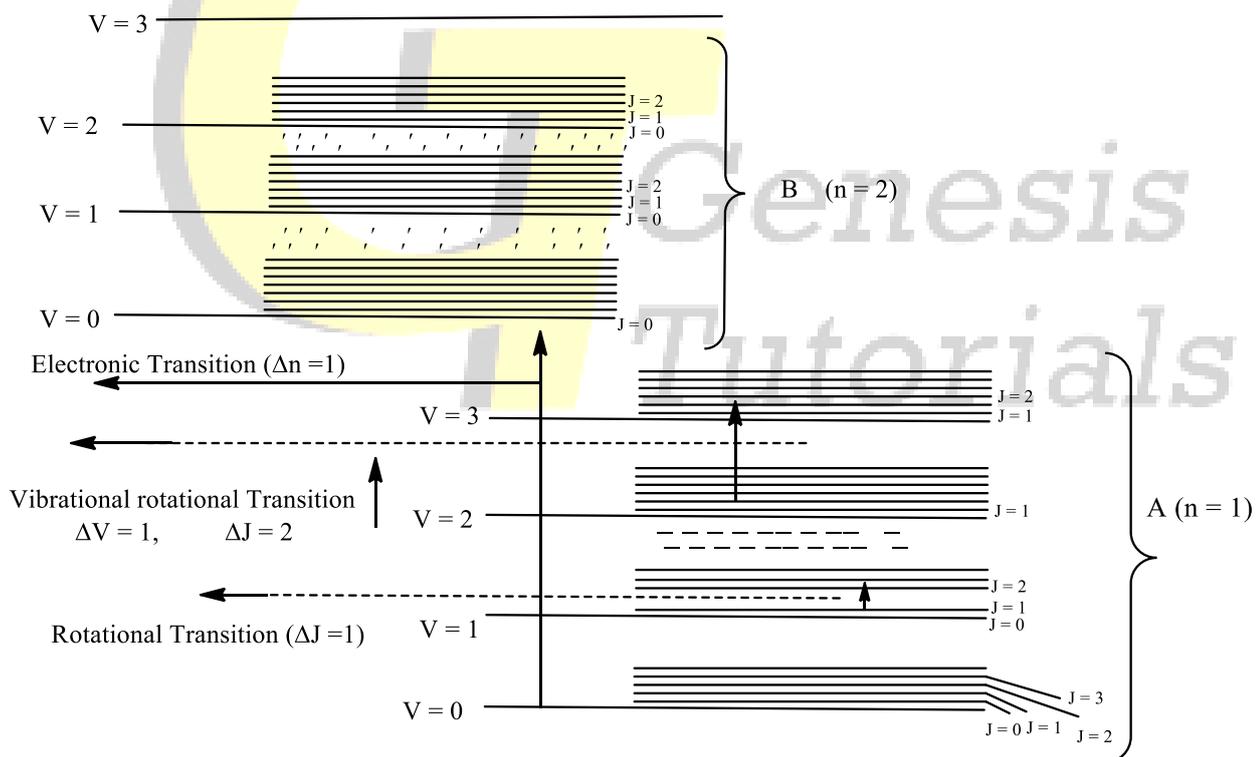
(1) Change in rotational levels

(2) Change in vibrational levels (in which rotational change are superimposed)

(3) Change in electronic state with simultaneous change in both vibrational and rotational level

→ Consider a diatomic molecule which absorbs energy & there may be a change in energy states producing many spectral lines

→ The various energy levels in a molecule are shown in figure suppose A and B are two electronic states (energy levels) of a molecule. In each electronic states, these are vibrational energy levels, indicated by vib. Quantum number $v = (0, 1, 2, 3, \dots)$. For each vibrational states, there exist several energy levels ($J = 0, 1, 2, 3, \dots$). The transition between these energy levels will lead to a change in energy value & give rise to spectral lines



Exclusion of translational Spectroscopy

The energy difference between the two successive translational levels is of the order of 10^{-60} J mol⁻¹. This separation is too small & very difficult to determine experimentally and the corresponding translational spectroscopy is completely excluded

Classification of Molecular Spectra

Corresponding to energy change in a molecule, Molecular Spectra are of following types

1. Rotational Spectra
2. Vibrational-rotational spectra
3. Electronic Spectra

1. Rotational Spectra These spectra are produced due to change of energy in rotational quantum levels within a vibrational level. Thus pure rotational spectra are the simplest molecular spectra. Rotational Spectra involve very small energy change of the order of 0.005 eV. The frequency rotational spectral line is given by

$$u = \frac{\Delta E}{h} = \frac{0.005 \times 1.6 \times 10^{-12} \text{erg}}{6.626 \times 10^{-27}}$$

$$\lambda = \frac{c}{\nu} = \frac{3 \times 10^{10} \times 6.626 \times 10^{-27}}{0.005 \times 1.6 \times 10^{-12}}$$

$$\lambda = 2484.75 \times 10^{-5} \text{cm}$$

$$\lambda = 248 \mu \quad \text{around } 250 \mu$$

→ The rotational energy levels are relatively close to each other and hence energy change taking place in rotational transitions are of small amounts. Hence pure rotational spectra appear in for IR and the microwave region ($10^4 \mu$ to $10^2 \mu$ range). Hence rotational spectroscopy is also known as microwave or far IR spectroscopy.

2. Vibrational-rotational spectra The separation of vibrational energy levels is greater as compared to rotational energy levels. The transitions between vibrational energy levels occur involving the energies of the order of 0.1 eV

$$u = \frac{\Delta E}{h}$$

$$\Delta E = \frac{hc}{\lambda}$$

$$\lambda = \frac{hc}{\Delta E} = \frac{6.626 \times 10^{-27} \text{ergs} \times 3 \times 10^{11} \text{cm s}^{-1}}{0.1 \times 1.6 \times 10^{-12} \text{erg}}$$

$$\lambda = 124.2 \times 10^{-5} \text{cm}$$

$$\lambda = 12.4 \times 10^{-4} \text{ cm}$$

$$\lambda = 12.4 \mu$$

The vibrational spectra appear in mid-IR regions ($10^2 \mu$ to 1μ range). During vibrational energy changes, rotational energy also changes

→ The energy emitted or absorbed is the sum of these two energy changes. That is why the mid IR spectrum is called vibrational-rotational spectrum

3. Electronic Spectra The electronic energy level (denoted by the quantum number n) are far apart

→ The change in electronic state is associated with a larger difference in energy of the order of 5 eV. The wavelength (λ) is given by the expression-

$$\lambda = \frac{hc}{\Delta E} = \frac{6.626 \times 10^{-27} \times 3 \times 10^{10}}{5 \times 1.6 \times 10^{-12}}$$

$$= 2.484 \times 10^{-5}$$

$$= 2.484 \times 10^{-4}$$

$$= 0.2484 \mu \cong 0.25 \mu$$

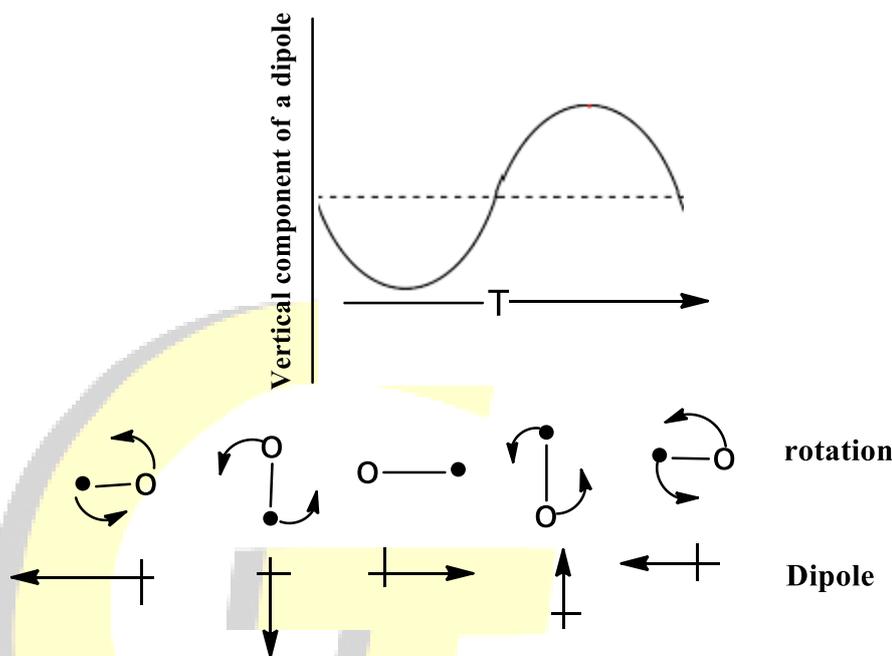
$$= 2484 \times 10^{-8} \text{ cm} = 2484 \text{ \AA}$$

$$\cong 2500 \text{ \AA}$$

→ Electronic spectra appear in visible and UV-region (1μ to 0.1μ range). That is why electronic spectroscopy is also called visible and ultraviolet spectroscopy

Rotational (Microwave) Spectroscopy

Spectroscopy in the microwave region is concerned with the study of rotating molecules. The molecules possessing permanent dipoles give rotational spectra. During rotational motion, the direction of the dipole undergoes a periodic change resulting in periodic fluctuations in the magnitude of a component of the dipole (as shown in figure)



Rotation of a diatomic molecule (●—●) possessing a permanent dipole

- When frequency of electromagnetic radiation coincides with that of molecular rotation, the electromagnetic radiation interacts with the molecular dipole and keeps pushing the molecule to a higher rotational energy level. This absorption of radiation thus gives the pure rotational spectrum of the molecule
- The emission or absorption of electromagnetic radiation in rotational energy levels occurs only if a change in dipole moment is associated with it. That is, the molecule must be polar (i.e. must possess a permanent dipole) in order to produce a rotational spectrum. e.g. HCl, CO etc. Such molecules are called microwave active. The homonuclear molecule like H₂, Cl₂, N₂ do not produce rotational bands, as their dipole moment is zero. Such molecules are called microwave inactive

Theory of the pure Rotational spectra:-

Consider a diatomic molecule that rotate about its axis about the center of gravity. The diatomic molecule can be pictured as-

- (1) Rigid Rotator Model
- (2) Non-right rotator model

(1) Rigid Rotator Model consider a diatomic molecule consisting of two atoms of masses m_1 and m_2 connected by a bond having bond length (internuclear distance) r and r_1 & r_2 are the distance of two atoms from center of gravity of the system.,

The momentum of inertia of this system is given by—

$$I = \sum mir_1^2 = m_1r_1^2 + m_2r_2^2 \dots\dots\dots (1)$$

As the system is balanced about its center of gravity, then, at this point—

$$m_1r_1 = m_2r_2 \dots\dots\dots (2)$$

$$r = r_1 + r_2$$

or

$$r_1 = r - r_2 \text{ or } r_2 = r - r_1$$

Equation (2) can be written as—

$$\begin{aligned} m_1r_1 &= m_2r_2 \\ m_1r_1 &= m_2(r - r_2) \\ m_1r_1 &= m_2r - m_2r_2 \\ m_1r_1 + m_2r_2 &= m_2r \\ r_1(m_1 + m_2) &= m_2r \end{aligned}$$

$$r_1 = \frac{m_2r}{m_1 + m_2}$$

Similarly

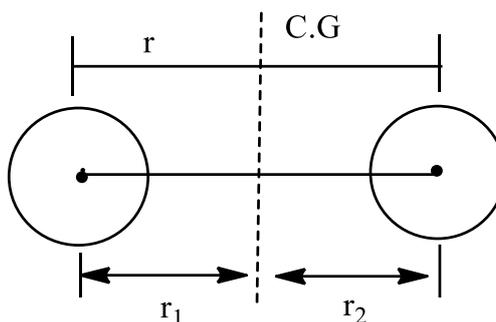
$$\begin{aligned} m_2r_2 &= m_1r_1 \\ m_2r_2 &= m_1(r - r_2) \\ m_2r_2 &= m_1r - m_1r_1 \\ m_1r_2 + m_2r_1 &= m_1r \\ r_2(m_1 + m_2) &= m_1r \\ r_2 &= \frac{m_1r}{m_1 + m_2} \end{aligned}$$

Equation (1) can be written as

$$I = m_1 \left(\frac{m_2 r}{m_1 + m_2} \right)^2 + m_2 \left(\frac{m_1 r}{m_1 + m_2} \right)^2$$

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

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



$$I = \mu r^2$$

$$\mu = \frac{m_1 m_2}{m_1 + m_2} = \text{reduced mass of the molecule}$$

→ Classically, the angular momentum is quantized is given by the expression

$$L = \sqrt{J(J+1)} \frac{h}{2\pi} \quad J = 0, 1, 2, 3$$

J → rotational quantum number

The kinetic energy of rotation of a rigid rotator is given by

$$E_{\text{rot}} = \frac{1}{2} m_1 v_1^2 + \frac{1}{2} m_2 v_2^2$$

v_1 & v_2 are the linear velocities of masses m_1 and m_2 respectively. Since r_1 and r_2 are assumed to remain unchanged during rotation. The above equation can be written as (By using the relation $v = rw$)

$$E_{\text{rot}} = \frac{1}{2} m_1 (r_1 w)^2 + \frac{1}{2} m_2 (r_2 w)^2$$

$$\frac{1}{2} w^2 (m_1 r_1^2 + m_2 r_2^2)$$

$$I = m_1 r_1^2 + m_2 r_2^2$$

$$E_{\text{rot}} = \frac{1}{2} I w^2$$

We know that — $L = Iw$

Hence the above equation can be written as

$$E_{\text{rot}} = \frac{1}{2I} I w^2 \quad (\text{multiplying and dividing by } I)$$

$$\frac{I^2 w^2}{2I} = \frac{L^2}{2I}$$

$$E_{\text{rot}} = \frac{L^2}{2I}$$

The rotational energy is quantized the molecule can have only certain permitted value of rotational energy depending on the shape and size of the molecule

The quantize rotational energy values are obtained by solving Schrodinger equation

$$E_J = \frac{h^2}{8\pi^2 I} J(J+1) \text{ (joules) or (erg)} \quad E = hc\bar{\nu}$$

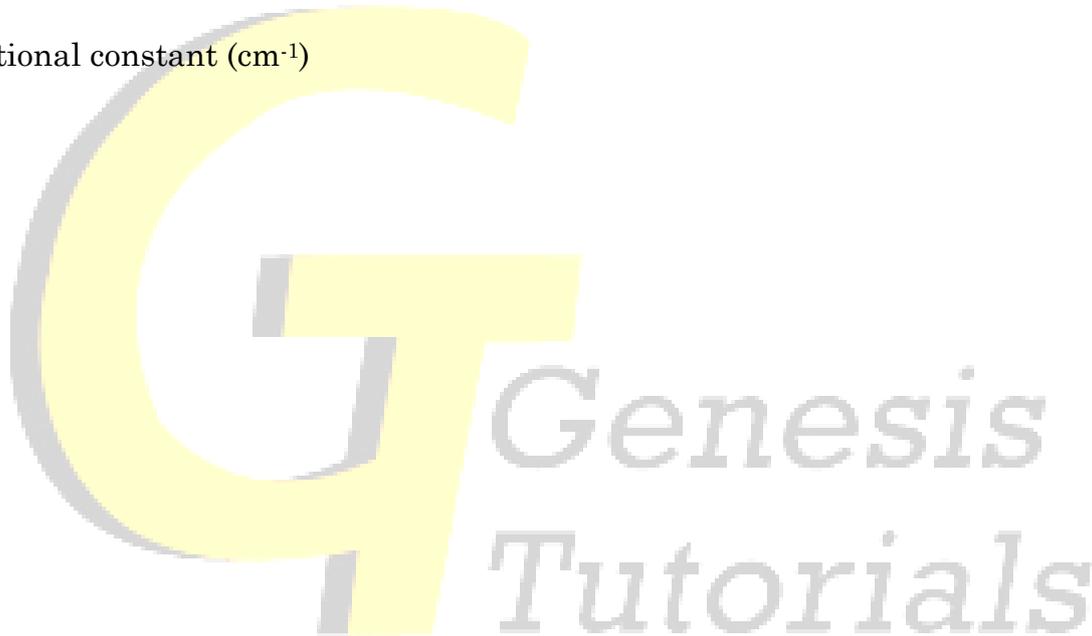
Or

$$E_J(\text{cm}^{-1}) = \frac{h^2}{8\pi^2 I} J(J+1) \quad E(\bar{\nu}) = BJ(J+1) \text{ cm}^{-1}$$

$$E_J(\text{cm}^{-1}) = \left(\frac{h}{8\pi^2 IC} \right) J(J+1) \quad \text{B}$$

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

B → rotational constant (cm^{-1})



Quantum Mechanical Restrictions:

Selection Rule for Rotational spectra for a molecule to show rotational spectra, it must have a dipole moment but all transition involving orbitarily any two rotational levels are not permissible. The quantum mechanics permits only those rotational transitions in which there is an increase quantum number

Mathematically__

$$J^{\text{II}} - J^{\text{I}} = \Delta J = \pm 1$$

This is called selection rule for a transition for a rigid diatomic molecule

→ Consider the transition of molecule from lower rotational level to higher rotational level. The difference of rotational energy between these two rotational energy level (from $J \rightarrow J + 1$)

$$\Delta E_{J \rightarrow J+1} = E_{(J+1)} - E_J$$

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

$$= B(J^2 + 2J + J + 2) - BJ(J+1)$$

$$BJ^2 + 3BJ + 2B - [BJ^2 + BJ]$$

$$= 2BJ + 2B$$

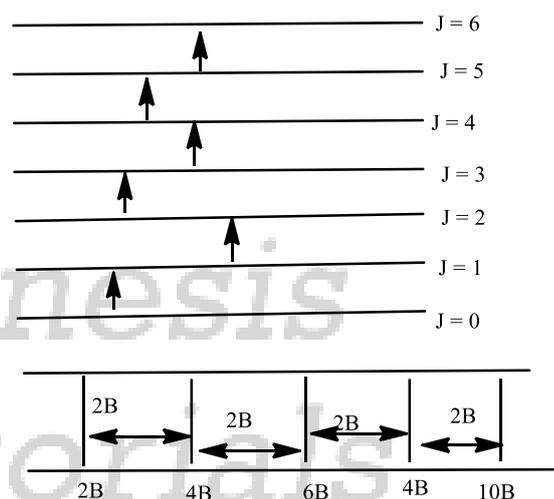
$$\Delta E_{J \rightarrow J+1} = 2B(J+1)\text{cm}^{-1}$$

$$\Delta E (J = 0 \text{ to } J = 1) = 2B$$

$$\Delta E (J = 1 \text{ to } J = 2) = 4B$$

$$\Delta E (J = 2 \rightarrow J = 3) = 6B$$

$$\Delta E (J = 3 \rightarrow J = 4) = 8B \text{ etc}$$



These lines are equally spaced by an amount of $2B$. The amount of $2B$ is called frequency separation

Intensity of Rotational Spectral lines

The intensity of the spectral lines is governed by the relative of molecules i.e. relative population of various rotational levels. Therefore the intensity of spectral lines would show a variation similar to that shown by the population

→ Intensity first increase, reaches to a maximum and then decreases. The position of the most intense spectral line is given by the expression that is derived as follow

$$\text{Intensity} \propto \frac{N_J}{N_0} = g_J e^{-\frac{E_J}{k_B T}} \quad \text{Where } E_J = hc B J(J+1)$$

$$g_J = 2J + 1 \quad \square$$

To get the maximum density, we apply the condition of maxima—

$$\frac{d}{dJ} \left(\frac{N_J}{N_0} \right) = \frac{d}{dJ} \left[(2J + 1) e^{-\frac{E_J}{k_B T}} \right] = 0$$

$$(2J + 1) \frac{d}{dJ} e^{-\frac{hcBJ(J+1)}{k_B T}} + e^{-\frac{hcBJ(J+1)}{k_B T}} \frac{d}{dJ} (2J + 1) = 0$$

$$(2J + 1) e^{-\frac{hcBJ(J+1)}{k_B T}} \frac{d}{dJ} \left(-\frac{hcB(J+1)}{k_B T} \right) + 2 e^{-\frac{hcBJ(J+1)}{k_B T}} = 0$$

On solving the above equation, we get

$$\frac{hcB}{k_B T} (2J + 1)^2 = 2$$

$$(2J + 1)^2 = \frac{hcB}{k_B T}$$

$$(2J + 1) = \sqrt{\frac{2k_B T}{hcB}} = 1$$

$$J = \frac{\sqrt{\frac{2k_B T}{hcB}} - 1}{2} \quad J = J_{\max}$$

$$J_{\max} = \sqrt{\frac{2k_B T}{4hcB}} - \frac{1}{2}$$

$$J_{\max} = \sqrt{\frac{k_B T}{2hcB}} - \frac{1}{2}$$

J_{\max} should be rounded off to the nearest integral value

QUESTION Calculate J_{\max} for a rigid diatomic molecule for which at 300K, the rotational constant is 1.56 cm^{-1}

SOLUTION $J_{\max} = \left(\frac{2k_B T}{2hcB} \right)^{\frac{1}{2}} - \frac{1}{2}$

$$J_{\max} = \left(\frac{1.38 \times 10^{-23} \times 300}{2 \times 6.626 \times 10^{-34} \times 3 \times 10^{10} \times 1.566} \right)^{\frac{1}{2}} - \frac{1}{2}$$

$$J_{\max} = 7.65 \cong 8$$

Effect of isotopic substitution

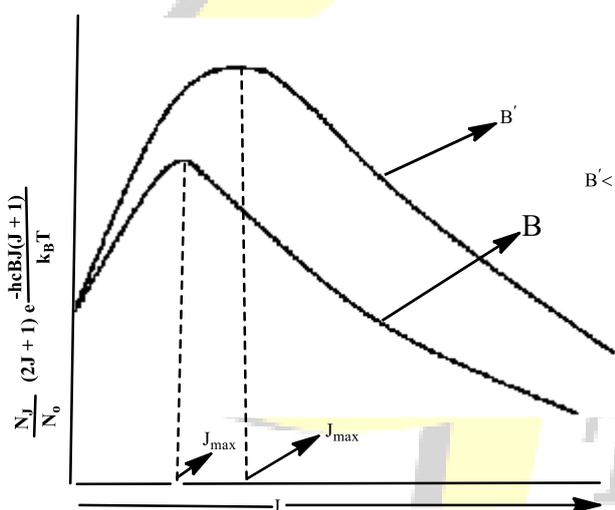
When a particular atom in a molecule is replaced by its isotope (an element identical in every way except for its atomic mass), the resulting substance is identical chemistry with the original.

→ There is no appreciable change in internuclear distance on isotopic substitution. There is a change in total mass and in the moment of inertia and B value for the molecule

→ considering carbon monoxide as an example on going $^{12}\text{C}^{16}\text{O}$ to $^{13}\text{C}^{16}\text{O}$ there is a mass increase and decrease in the B value. If we designate the ^{13}C molecule a prime then $B^1 < B$. This change is reflected in rotational energy levels of the molecule

→ The spectrum of heavier species will show a smaller separation between the lines ($2B^1$) than that of lighter one ($2B$)

→ On plotting a graph between $\frac{N_J}{N_0}$ vs J we get →



$$J_{\max} = \sqrt{\frac{k_B T}{2hCB}} - \frac{1}{2}$$

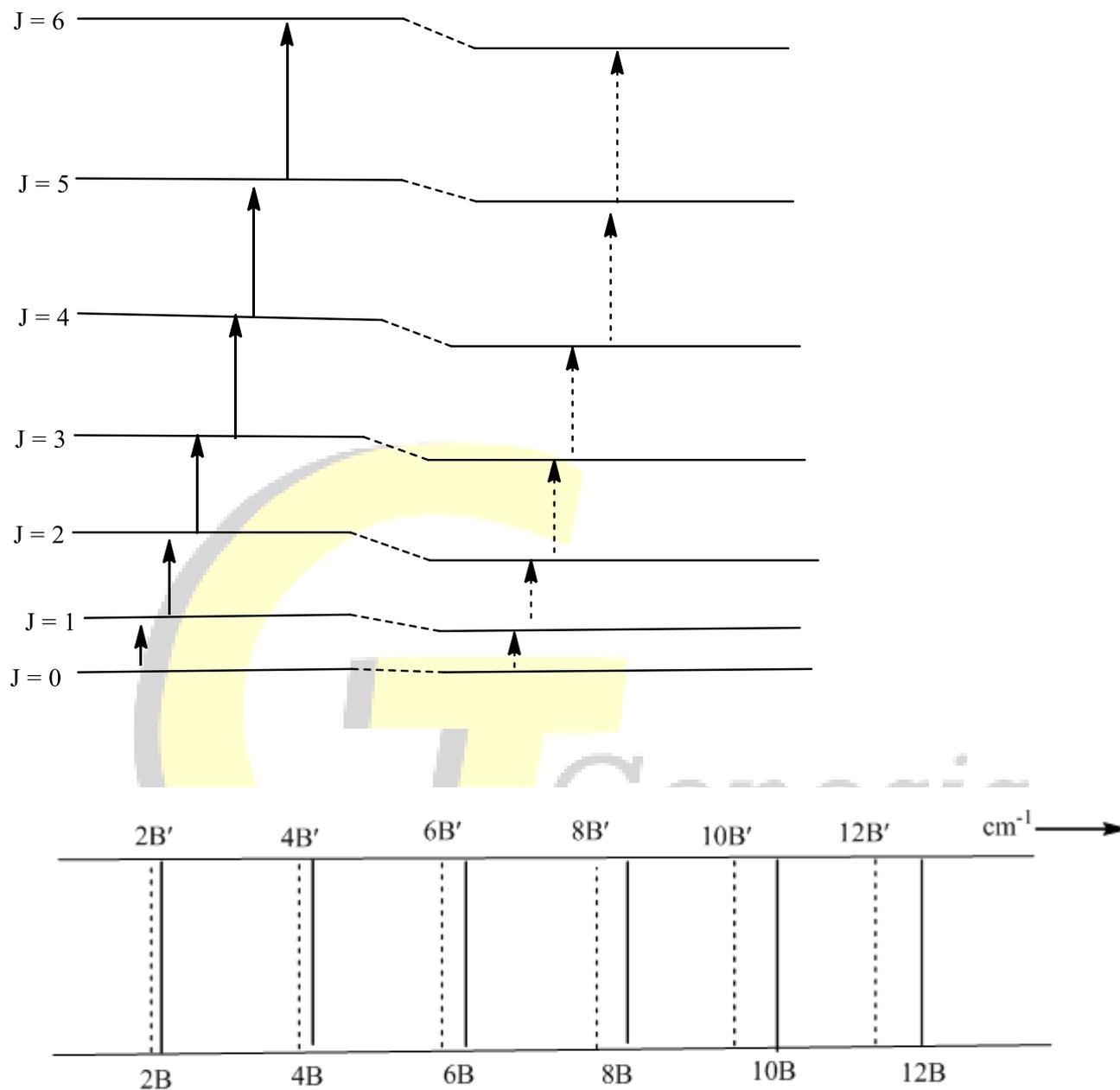
→ Gilliam et al found the first rotational absorption of $^{12}\text{C}^{16}\text{O}$ to be at $3.84\ 235\ \text{cm}^{-1}$, while that of $^{13}\text{C}^{16}\text{O}$ was at $3.67\ 337\ \text{cm}^{-1}$.

The value of B from these figures—

$B = 1.92118\ \text{cm}^{-1}$ and $B^1 = 1.83669\ \text{cm}^{-1}$ prime refers heavier molecule-

$$\frac{B}{B^1} = \frac{h}{8\pi^2 I C} \frac{8\pi^2 I' C}{h} = \frac{I'}{I} = \frac{\mu'}{\mu} = 1.046$$

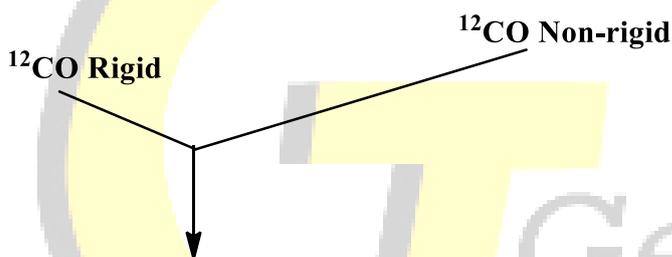
Effect of isotopic substitution on the energy levels and rotational spectrum of CO.



Microwave studies can be used for determining the atomic weight precisely and give an estimate of the abundance of isotopes by comparison of absorption intensities

Non-Rigid Rotator:-

- It is evident from the experimental data that the separation between successive lines (and hence the apparent B value) decreases steadily with increasing J
- The reason for this decrease may be seen if we calculate internuclear distance from the B values. The bond length increases with J and we can see that our assumption of the rigid bond is only an approximation
- All the bonds are elastic to some extent and the increases in length with J reflect the fact that the more quickly a diatomic molecule rotates, greater is the centrifugal force tending to move apart
- Hence the value of rotation all constant from the initial of rotational constant from the initial spectral lines will be higher than of high energy spectral lines
- For a non-rigid rotation, the rotational energy level as well as rotational spectral line will be slightly closer than rigid rotation



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

D is centrifugal distortion constant and is of the order of $10^{-4}B$. It is a small positive quantity and is given by the expression –

$$D = \frac{4B^3}{(\bar{\nu}_0)^2} \text{ cm}^{-1}$$

$$\bar{\nu}_0 = \text{fundamental vibration frequency}$$

$\bar{\nu}_0$ is always very much greater than B Hence D will be much smaller than B.

→ The energy expression for the transitions

$$\Delta E = E_{(J+1)} - E_J = B[(J + 1)(J + 2) - J(J + 1)] - D[(J + 1)^2(J + 2)^2 - J^2(J + 1)^2] \text{ cm}^{-1}$$

$$\Delta E = 2B(J + 1) - D(4J^3 + 12J + 4)$$

$$\Delta E = B(J + 1)[J + 2 - J] - D(J + 1)^2[J^2 + 4 + 4J - J^2]$$

$$2B(J + 1) - 4D(J + 1)^2[J + 1]$$

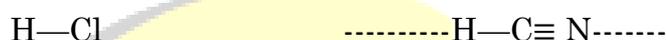
$$\Delta E = 2B(J + 1) - 4D(J + 1)^3$$

Types of molecules undergoing rotation:

The rotation of a three dimensional body may be quite complex and it is convenient about three mutually perpendicular directions through the centre of gravity. This a body has three principal moments of inertia, one about each axis, usually represented by I_A , I_B , & I_C

→ Molecule may be classified into different groups on the basis of relative values of their three principal moments of intertie.

(1) **Linear Molecules:-** These are the molecules in which all the atoms are arranged in a straight lines such as HCl, HCN



The three directions of rotation may be taken as

- about the bond axis
- end-over-end rotation in plnae of paper
- end over end rotation at right angle (perpendicular) to the plane

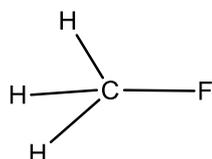
The value of I_B & I_C are same ($I_B = I_C$) while that of (a) is zero ($I_A = 0$)

Thus for Linear molecule

$$I_A = 0 \quad I_B = I_C$$

$I_B = I_C > I_A \quad I_A = 0$

(2) **Symmetric tops:-** Consider molecules such as methyl fluoride, where the three hydrogen atoms are bonded tetrahedrally to the carbon, as shown below



Similar to linear molecules, end over end rotation in and out of the plane are still identical i.e. $I_B = I_C$. The moment of inertia about C–F bond axis (Chosen as the main rotational axis since the center of gravity lies along it) is now not negligible. It involves the rotation of 3 hydrogen atom about this C–F bond axis

Such a molecule spinning about this axis can be imagined as a top

For symmetric tops:-

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

These are two subdivision of this class

(i) Molecule having $I_A, I_B & I_C$ in the relation

$$I_B = I_C > I_A$$

Such molecule are called prolate

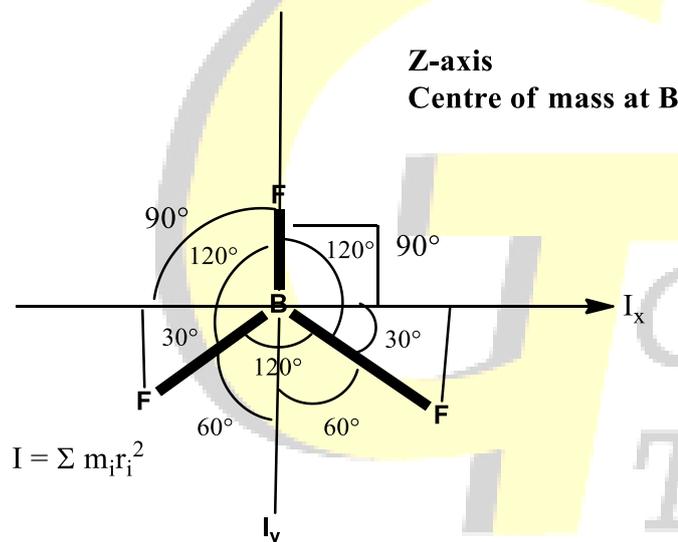
example CH_3F

(ii) Molecule having $I_A, I_B & I_C$ in the relation

$$I_B = I_C < I_A$$

Benzene, XeF_4 , BCl_3

Such molecule are called oblate



$$I_Z = 3m_F r_{B,F}^2$$

$$\sin 30^\circ = \frac{P}{r_{B-F}}$$

$$\frac{1}{2} = \frac{P}{r_{B-F}} \Rightarrow P = \frac{r_{B-F}}{2}$$

$$P = \frac{r_{B-F}}{2}$$

$$I_x = m_F r_{B,F}^2 + 2 m_F \left(\frac{r_{B-F}}{2} \right)^2$$

$$I_x = \frac{3}{2} m_F r_{B,F}^2$$

I_y (y pass through B & F)

$$\sin 60^\circ = \frac{P}{r_{B-F}}$$

$$\frac{\sqrt{3}}{2} = \frac{P}{r_{B-F}}$$

$$P = \frac{\sqrt{3}}{2} r_{B-F}$$

$$I_y = m_F \left(\frac{\sqrt{3} r_{B-F}}{2} \right)^2 + m_F \left(\frac{\sqrt{3}}{2} r_{B-F} \right)^2$$

$$\frac{3}{4} m_F \cdot r_{B-F}^2 + \frac{3}{4} m_F \cdot r_{B-F}^2$$

$$I_y = \frac{3}{4} m_F \cdot r_{B-F}^2$$

It is equal to the value of I_x

$$I_x = I_y$$

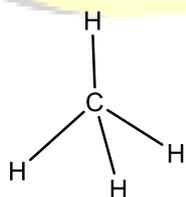
$$I_z = I_y = 3m_F \cdot r_{B-F}^2$$

$$I_z > I_x = I_y$$

Or

$$I_z = 2I_x = 2I_y$$

3. Spherical tops When a molecule has all three moments of inertia identical it is called a spherical top. A simple example is tetrahedral molecule methane CH_4



Spherical tops:- $I_A = I_B = I_C$

These molecules do not have no net dipole moment. Hence no rotational spectrum is observed

4. Asymmetric tops: Majority of the substance belong to this category. These molecules have all three moments of inertia different

$$I_A \neq I_B \neq I_C$$

Example H_2O and vinyl chloride

