PURE ROTATIONAL SPECTROSCOPY

The transitions among rotational energy levels of ground vibrational state, which corresponds to ground electronic state are studied under pure-rotational or microwave spectroscopy.

Rotational energy of a particle : (Rigid Rotor)

In classical mechanics, the energy of an particle which rotates around an axis is given by $E = \dfrac{1}{2}I\omega^2$

$\omega \rightarrow$ angular velocity in radian per second, $I \rightarrow$ moment of inertia.

$E = \dfrac{1}{2}\dfrac{(I\omega)^2}{I} = \dfrac{p^2}{2I}$　　　($p \rightarrow$ angular momentum)

Quantum mechanical energy :

$E = \dfrac{\hat{p}^2}{2I}$　　　　　　　$\because \hat{p} = \sqrt{J(J+1)}\hbar$　only few rotation are allowed.

$= \dfrac{(\sqrt{J(J+1)}\hbar)^2}{2I}$　　　$J \rightarrow$ rotational quantum number

$= J(J+1)\dfrac{\hbar^2}{2I}$　　　　$J = 0, 1, 2, 3,....$

$= J(J+1)\dfrac{h^2}{8\pi^2 I} = J(J+1)B$　　　　$B \rightarrow$ rotational constant ; $B = \dfrac{h^2}{8\pi^2 I}$ Joule

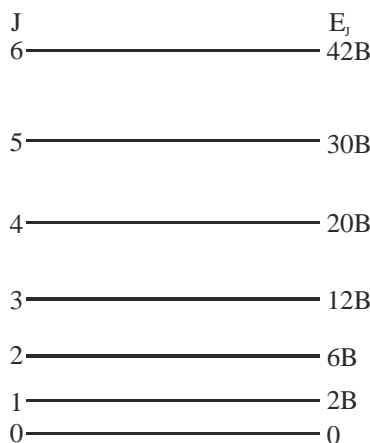| J		E_J
6	————————————	42B
5	————————————	30B
4	————————————	20B
3	————————————	12B
2	————————————	6B
1	————————————	2B
0	————————————	0

Fig. The allowed rotational energies of a rigid diatomic molecule

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

For absorption, $\Delta J = +1$ (important to study)

For emission, $\Delta J = -1$

Difference between energy levels under, $\Delta J = +1$ or position of peaks in microware spectrum.

$$\Delta E = E_{J_2} - E_{J_1} = J_2(J_2+1)B - J_1(J_1+1)B = 2B(J_1+1) \qquad (\because J_2 - J_1 = +1)$$

$$\Delta E_{0 \to 1} = 2B$$

$$\Delta E_{1 \to 2} = 4B$$

$$\Delta E_{2 \to 3} = 6B$$
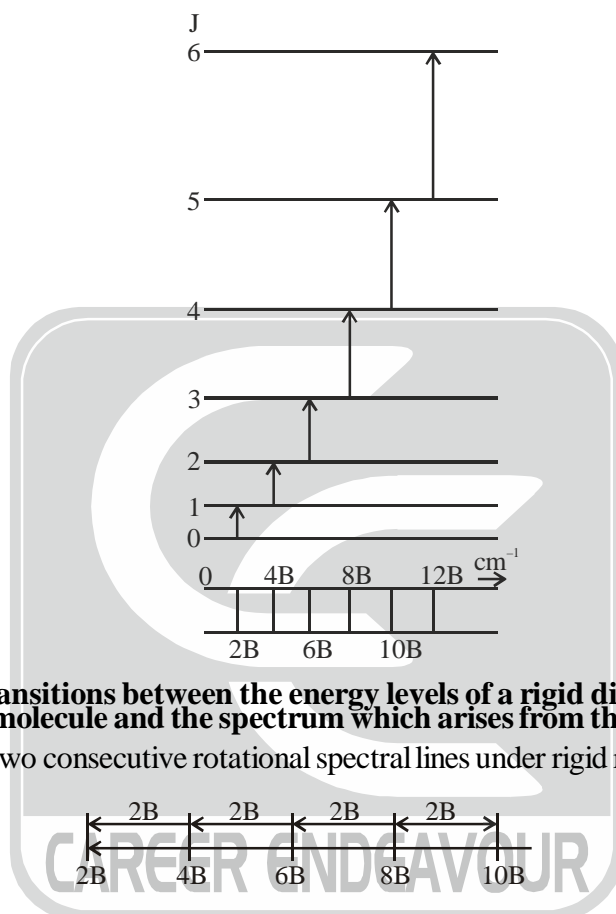
$$\vdots$$

$$\Delta E_{11 \to 12} = 24B$$

Fig. Allowed transitions between the energy levels of a rigid diatomic molecule and the spectrum which arises from them.

The difference between two consecutive rotational spectral lines under rigid rotor approximation is 2B.

Gross selection rule :

The molecule with permanent dipole moment will be rotational or microwave active.

All Heteronuclear diatomic molecules are microwaves active e.g., HCl, CO, NO, HBr

All Homonunclear diatomic molecules are microwave inactive. e.g., H_2, Cl_2, Br_2, N_2

Triatomic and Polyatomic molecules with permanent dipole moment will be microwave active
e.g. H_2O, N_2O, OCS, NH_3, $CHCl_3$

The Intensities of Spectral Lines:

We want now to consider briefly the relative intensities of the spectral lines, for this a prime requirement is plainly a knowledge of the relative probabilities of transition between the various energy level. Does, for instance, a molecule have more or less chance of making the transition $J = 0 \to J = 1$ than the transition $J = 1 \to J = 2$? We mentioned above that a change of $\Delta J = \pm 2, \pm 3$ etc. was for bidden in other words, the transition probability for all these changes is zero. Precisely similar calculations show that the probability of all changes with $\Delta J = \pm 1$ is almost the same all, to a good approximation are equally likely to occur.

This does not mean, however, that all spectral lines will be equally intense. Although the intrinsic probability that a single molecule in the $J = 0$ state, say will move to $J = 1$ is the same as that of a single molecule moving from $J = 1$ to $J = 2$, in an assemblage of molecules, such as in a normal gas sample, there will be different number of molecules in each level to begin with, and therefore different total numbers of molecules will carry out transitions between the various levels. In fact, since the intrinsic probabilities are identical, the line intensities will be directly proportional to the initial number of molecules in each level.

The first factor governing the population of the levels is the Boltzmann distribution. Here we know that the rotational energy in the lowest level is zero, since $J = 0$, so, if we have no molecules in this state, the number in any higher state is given by:

$$N_J / N_0 = \exp(-E_J / kT) = \exp[-BhcJ(J+1)/kT] \qquad \dots \text{(i)}$$

Where, we must remember, is the velocity of light in cm s^{-1} when B is in cm^{-1}. A very simple calculation shows how N$_J$ varies with J; for example, taking a typical value of B = 2cm^{-1}, and room temperature (say T = 300 K), the relative population in the J = 1 state is

$$\frac{N_1}{N_0} = \exp\left(-\frac{2 \times 6.63 \times 10^{-34} \times 3 \times 10^{10} \times 1 \times 2}{1.38 \times 10^{-23} \times 300}\right) = \exp(-0.019) \approx 0.98$$

and we see that there are almost as many molecules in the $J = 1$ state, at equilibrium, as in the $J = 0$.

A second factor is also required-the possibility of degeneracy in the energy states. Degeneracy is the existence of two or more energy states which have exactly the same energy.

Thus we see that, although the molecular population in each level decreases exponentially, the number of degeneracy levels available increases rapidly with J. The total relative population at any energy E$_J$ will plainly be

$$\text{Population } \alpha (2J+1)\exp(-E_J / kT) \qquad \dots \text{(ii)}$$

When this is plotted against J the points fall on a curve, indicating that the population rises to a maximum and then diminishes. Differentiation of equation (ii) shows that the population is a maximum at the nearest integral J value to

$$\text{Maximum population } J = \sqrt{\frac{kT}{2hcB}} - \frac{1}{2} \qquad \dots \text{(iii)}$$

We have seen that line intensities are directly proportional to the populations of the rotational levels; hence it is plain that transitions between levels with very high J values will have small intensities while the intensity will be a maximum at or near J value by Eq. (iii).
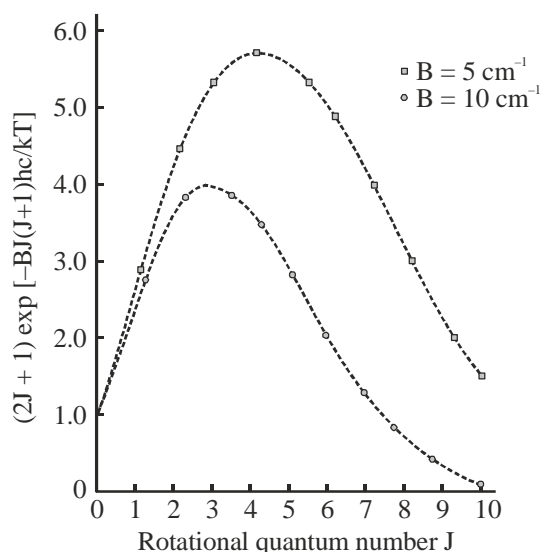
Break down of rigid rotor approximation:
(Non-rigid rotor - Bond length between atom in molecule change):

$E = BJ(J+1) + P.E.$

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

where H is deformation constant $H\psi = \varepsilon\psi$; $(H_0 + H_1)\psi = \varepsilon\psi$

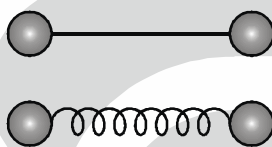where B is rotational constant, and D is deformation constant.

$B = \dfrac{h^2}{8\pi^2 I}$ (in joule)

$B = \dfrac{h}{8\pi^2 Ic}$ (in cm^{-1})

$D = \dfrac{h^4}{32\pi^2 I^2 r^2 k}$ (in joule)

$D = \dfrac{h^3}{32\pi^4 \mu^2 r^4 kc}$ (in cm^{-1})

This D decreases the energy of the molecule this energy is decreases due to the vibration. This vibration have potential energy and this potential energy effect the rotational energy.

$E = BJ(J+1) - \underset{\substack{\downarrow \\ \text{1st order} \\ \text{perturbation}}}{DJ^2(J+1)^2} + \underset{\substack{\downarrow \\ \text{2nd order} \\ \text{perturbation}}}{HJ^4(J+1)^4} + \cdots$

We neglect other terms because their values are small.

$D = \dfrac{h^3}{32\pi^4 I^2 r^2 kc}$ (in cm^{-1})

$\boxed{\dfrac{4B^3}{\overline{v}^2}} \Rightarrow \boxed{\overline{v} = \dfrac{1}{2\pi c}\sqrt{\dfrac{K}{\mu}}}$ ($\overline{v}$ is vibrational number)

$\nu = \dfrac{1}{2\pi}\sqrt{\dfrac{k}{\mu}} \Rightarrow c\overline{v} = \dfrac{1}{2\pi}\sqrt{\dfrac{k}{\mu}} \Rightarrow \overline{v} = \dfrac{1}{2\pi c}\sqrt{\dfrac{k}{\mu}}$

$D \approx 0.01\%$ of B

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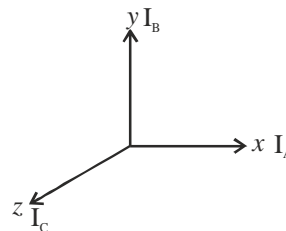
$\Delta J = \pm 1$

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

$E_{J'} = BJ'(J'+1) - DJ'^2(J'+1)^2$

$E_{J''} = BJ''(J''+1) - DJ''^2(J''+1)^2$

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

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

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

Polyatomic Molecules:

1...   **Linear molecule:** All molecules are arrange in straight line.

For example: HCl, OCS; $\boxed{I_C = I_B \neq I_A, \ I_A = 0}$

If a molecule has C_∞ axis, then molecule is linear.

2...   **Symmetric top molecule:**

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

(i) Prolate symmetric top molecule: (Prolate means elongated along poles)

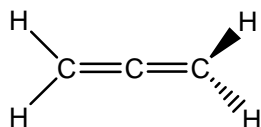$$I_c = I_b \neq I_a, \ I_a \neq 0$$
$$I_c = I_b > I_a, \ I_a \neq 0$$

E.g.: CH_3Cl, CH_3I, $CHCl_3$, NH_3, NF_3

(ii) Oblate symmetric top molecules: (Oblate means elongated along axis)

$$I_c = I_b < I_a \ \text{ or } \ I_a = I_b < I_c$$

If a molecule has one C_n or S_n $(n \geq 3)$ axis, then the molecules is symmetric top molecule.
Example: Allene S_4-axis.

Prolate symmetric top molecule.
If value of moment of inertia along different axis is lesser than other two axes, molecule is prolate symmetric top and its vice-versa.

3...   **Spherically symmetric molecule:**

$$I_a = I_b = I_c$$

Example: CH_4, SF_6

Molecules with Td, Oh, Ih (Icosahedron) point group has two or more than two non-coincidental C_n or S_n $(n \geq 3)$ axis then these molecule are spherically symmetric molecules.

4...   **Assymetric molecules:** $I_a \neq I_b \neq I_c$

H_2O, CH_2O (Formaldehyde)

C_{2v}, C_s, C_{2h} – point group.

Symmetric Top molecule:

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

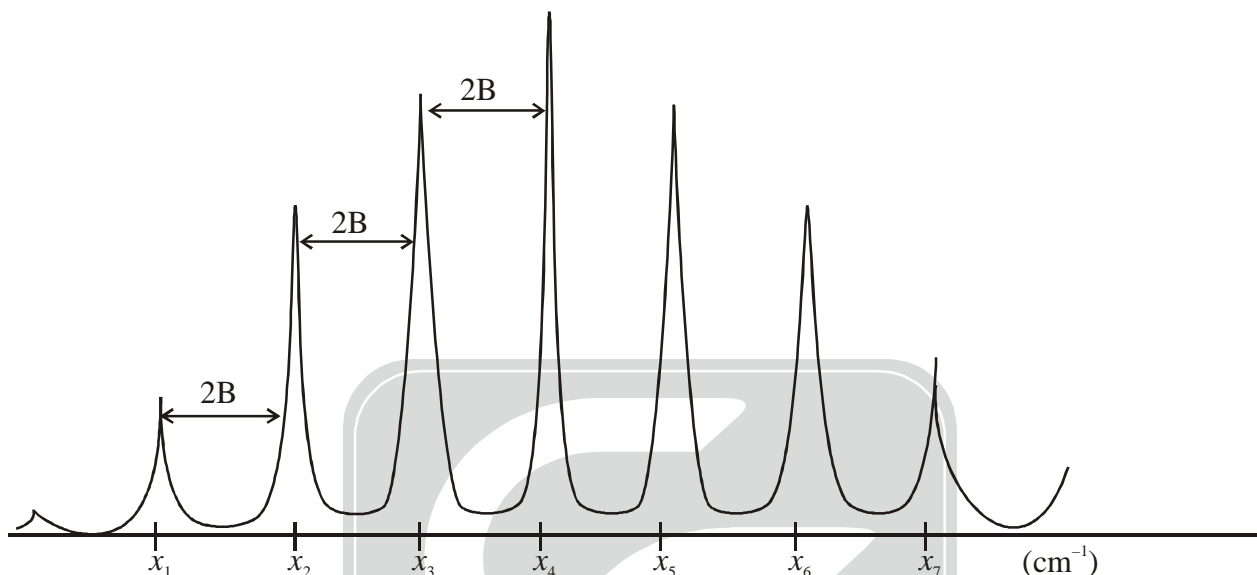$$\varepsilon_{J,K} = E_{J,K}/hc = BJ(J+1) + (A-B)K^2 \ \text{cm}^{-1}$$

where, $B = \dfrac{h}{8\pi^2 I_B c}$ and $A = \dfrac{h}{8\pi^2 I_A c}$

$\Delta J = \pm 1$ and $\Delta K = 0$

$\varepsilon_{J+1,K} - \varepsilon_{J,K} = \bar{v}_{J,K} = B(J+1)(J+2) + (A-B)K^2 - \left[BJ(J+1) + (A-B)K^2 \right]$

$\qquad\qquad\qquad\qquad = 2B(J+1) \qquad cm^{-1}$

Application of microwave spectroscopy :

(i)   To determine average bond length.

B can be calculated from the microwave spectra $2B = x_2 - x_1$

$B = \dfrac{h}{8\pi^2 Ic} \Rightarrow I = \dfrac{h}{8\pi^2 Bc} \qquad \because I = \mu r^2 \Rightarrow r = \sqrt{\dfrac{I}{\mu}}$

$r \rightarrow$ bond length

(ii) To calculate mass of isotopically substituted nuclei.

Rotational constant $(B) = \dfrac{h}{8\pi^2 Ic}$

$\therefore B \propto \dfrac{1}{I} \Rightarrow B \propto \dfrac{1}{\mu}$ (after isotopic substitution B will decrease)

$\therefore \dfrac{B}{B'} = \dfrac{\mu'}{\mu} \Rightarrow \mu' = \dfrac{B}{B'} \times \mu$, $\mu' \rightarrow$ reduced mass after isotopic substitution

(iii) To determine classical rotational frequency and periods.

Kinetic energy $= \dfrac{1}{2} I \omega^2$

$BJ(J+1) = \dfrac{1}{2} I \omega^2 = \dfrac{1}{2} I (2\pi v)^2 \Rightarrow v^2 = \dfrac{h^2}{16\pi^4 I^2} J(J+1)$

$$v = \frac{h}{4\pi^2 I}\sqrt{J(J+1)}$$

$$v = 2B\sqrt{J(J+1)}$$

$v \rightarrow$ classical rotational frequency

$$\therefore \text{ Time period } (T) = \frac{1}{v} = \frac{1}{2B\sqrt{J(J+1)}}$$

SOLVED PROBLEMS

1. Among the following molecules which one shows pure rotation spectra?

    (a) N_2 (b) H_2S (c) CO_2 (d) CH_4

Soln. A molecule having no permanent dipole moment does not generate the oscillating electrical field on rotation and hence cannot interact with the radiation. Such a molecule does not exhibit the rotational spectrum. Thus, the essential criterion for a molecule to exhibit rotational spectrum is that it must have a permanent dipole moment. The molecules with permanent dipole moment are known as microwave active molecules.

$$\mu_{H_2S} \neq 0$$

So, H_2S is active in rotation spectra

Correct option is (b)

2. Quantized rotational energy of molecule is given as

    (a) $v(r) = D_e\left[1 - \exp\left(\beta(r - r_e)\right)\right]^2$ (b) $\mu_s = -g \times e / 2m_e c \times \frac{h}{2\pi}\sqrt{S(S+1)}$

    (c) $\varepsilon_J = J(J+1)h^2 / 8\pi^2 I$ (d) $v = \frac{\Delta E}{h} = \frac{\varepsilon_{upper} - \varepsilon_{lower}}{h}$

Soln. Quantized rotational energy of molecule is given as

$$E_J = J(J+1)h^2 / 8\pi^2 I$$

$J = 0, 1, 2, 3,...$ (only few rotational energy levels are allowed)

Correct option is (c)

3. Centrifugal forces due to rotation of molecule about any given axis tend to

    (a) increase the moment of inertia about the axis

    (b) decrease the effective rotational constant

    (c) both (a) and (b)   (d) None of these

Soln. The molecule is rotating perpendicular to its principle axis experiences an outward force than this force is called the centrifugal force. Due to centrifugal force bond length of the molecule increases. So moment of inertia of molecule increase $(\because I \propto r^2)$ and rotational constant decrease $\left(\because B \propto \dfrac{1}{I}\right)$.

Correct option is (c)

4. The third lowest microwave absorption frequency for $^{13}C\,^{16}O$ is 330567 MHz. The second lowest absorption frequency for $^{12}C\,^{16}O$ should be at

    (a) 220378 MHz   (b) 230542 MHz   (c) 345813 MHz   (d) 205032 MHz

Soln. The third lowest microwave absorption frequency appears at = 6B

Second lowest microwave absorption frequency appears at = 4B

$\therefore$ $6B(^{13}C^{16}O) = 330567$ MHz

$4B(^{12}C^{16}O) = ?$ $\quad \because B \propto \dfrac{1}{\mu}$

$\dfrac{B(^{12}C^{16}O)}{B(^{13}C^{16}O)} = \dfrac{\mu^{13}C^{16}O}{\mu^{12}C^{16}O}$ $\Rightarrow B(^{12}C^{16}O) = \dfrac{330567}{6} \times \dfrac{13 \times 16}{29} \times \dfrac{28}{12 \times 16} = 57{,}627.58$ MHz

$\therefore$ $4B(^{12}C^{16}O) = 230510$ MHz

Correct option is (c)

5. HI and DI are made to undergo the same transition from $J = 0 \rightarrow J = 1$. The light frequency causing the transition for HI equals v. Approximately which frequency would you expect to induce the same transition in DI?

   (a) $2v$ (b) $\sqrt{2}v$ (c) $v/2$ (d) $v/\sqrt{2}$

Soln. Energy associated with $J = 0 \rightarrow J = 1$ transition, $\Delta E_{HI} = hv$

Also, $\Delta E_{0 \rightarrow 1} = 2B = \dfrac{2 \times h^2}{8\pi^2 I}$; $\Delta E_{0 \rightarrow 1} \propto \dfrac{1}{I}$; $\Delta E_{0 \rightarrow 1} \propto \dfrac{1}{\mu}$

$\therefore$ $\dfrac{\Delta E_{DI}}{\Delta E_{HI}} = \dfrac{\mu_{HI}}{\mu_{DI}} = \dfrac{1}{2}$

$\because$ Frequency, $v = \dfrac{\Delta E}{h} \Rightarrow v = \dfrac{\Delta E_{DI}}{h} = \dfrac{(\Delta E_{HI}/2)}{h} = \dfrac{hv}{2h} = \dfrac{v}{2}$

Correct option is (c)

6. Which of the following molecule will show pure rotational spectrum?
   (a) CH_4 (b) H_2O (c) C_6H_6 (d) Cl_2

Soln. A molecule having no permanent dipole moment does not generate the oscillating electrical field on rotation and hence cannot interact with the radiation. Such a molecule does not exhibit the rotational spectrum. Thus, the essential criterion for a molecule to exhibit rotational spectrum is that it must have a permanent dipole moment. The molecules with permanent dipole moment are known as microwave active molecules.

$\mu_{H_2O} \neq 0$ (So H_2O is microwave active molecule)

Correct option is (b)

6. Rotational spectra are observed in the
   (a) near infrared region   (b) visible region
   (c) far infrared region   (d) UV region

Soln. The infrared portion of the electromagnetic spectrum is usually divided into three regions; the near-, mid- and far-infrared, named for their relation to the visible spectrum. The higher energy near-IR, approximately 1400-4000 cm^{-1} (0.7-2.5 μm wavelength) can excite overtone or harmonic vibrations. The mid-infrared, approximately 4000-400 cm^{-1} (2.5-25 μm) may be used to study the fundamental vibrations and associated rotational-vibrational structure. The far-infrared, approximately 400-10 cm^{-1} (25-1000 μm), lying adjacent to the microwave region, has low energy and may be used for rotational spectroscopy.

Correct option is (c)

7. In the hydrogen molecule, when hydrogen is replaced by deuterium. What will happen to the rotational constant B?
   (a) Increase   (b) Becomes zero   (c) Decreases   (d) Remains same

Soln. When hydrogen replaced by deuterium in a hydrogen molecule then reduced mass of molecule will increase.

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

So more energy required for the rotation of the molecule at the same rotational level. Hence rotational constant of molecule decrease.

Correct option is (c)

8. The moment of inertia of the CO molecule is $1.46 \times 10^{-46} \ kg - m^2$. Calculate the energy (in eV) and the angular velocity in the second lowest rotational energy level of the CO molecule (J = 1).

Soln. The quantum-mechanical energy of a rotating diatomic molecule is given by

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

where, I is the moment of inertia of the molecule about the axis of rotation. The second lowest rotational energy level corresponds to $J = 1$, and for this level in CO

$$E_{J=1} = \frac{h^2 \times 2}{8\pi^2 I} = \frac{h^2}{4\pi^2 I}$$

Substituting the value of h in M.K.S. units and the given value of I, we have

$$E_{J=1} = \frac{\left(6.62 \times 10^{-34} J - \sec\right)^2}{4 \times (3.14)^2 \times \left(1.46 \times 10^{-46} \ kg.m^2\right)}$$

$$= \frac{6.62 \times 10^{-34} \times 6.62 \times 10^{-34}}{4 \times 3.14 \times 3.14 \times 1.46 \times 10^{-46}}$$

$$= 7.61 \times 10^{-23} J$$

But 1 eV = $1.6 \times 10^{-19} J$

$$\therefore \qquad E_{J=1} = \frac{7.61 \times 10^{-23}}{1.6 \times 10^{-19}}$$

$$= 4.75 \times 10^{-4} \ eV$$

The angular velocity of the CO molecule (when J = 1) is
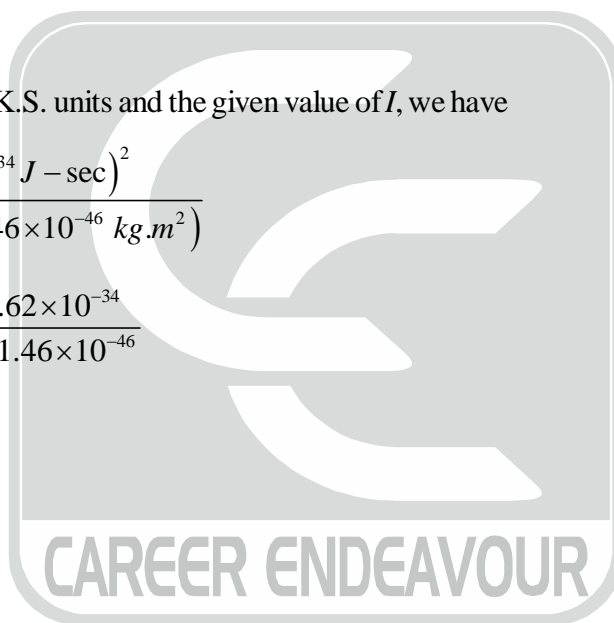
$$\omega = \sqrt{\frac{2E}{I}} \qquad \left(\because E = \frac{1}{2} I \omega^2\right)$$

$$= \sqrt{\frac{2 \times 7.61 \times 10^{-23}}{1.46 \times 10^{-46}}}$$

$$= 10.2 \times 10^{11} \ \text{rad/sec}$$

9. The $J = 0 \to J = 1$ absorption line in CO occurs at a frequency of 1.153×10^{11} cycles/sec. Calculate the moment of inertia and internuclear separation of CO.

$$\left(h = 6.62 \times 10^{-27} \ erg - \sec, \ N_A = 6.023 \times 10^{23}\right)$$

Soln. The rotational energy of a diatomic molecule is given by

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

The energy separation between $J = 0$ and $J = 1$ levels is:

$$\Delta E = E_{J=1} - E_{J=0} = \frac{h^2}{4\pi^2 I}$$

The frequency $\bar{v}$ absorbed in transition $J = 0 \rightarrow J = 1$ is:

$$v' = \frac{\Delta E}{h} = \frac{h}{4\pi^2 I}$$

$$\Rightarrow \quad I = \frac{h}{4\pi^2 v'} = \frac{6.62 \times 10^{-27} \, erg-\sec}{4 \times (3.14)^2 \times (1.153 \times 10^{11} \sec^{-1})}$$

$$= 1.46 \times 10^{-39} \, gm-cm^2$$

The reduced mass of the CO molecule is given by

$$\mu_{CO} = \frac{M_C M_O}{M_C + M_O}$$

$$= \frac{(12 \times 16)/(6.023 \times 10^{23})^2}{(12+16)/(6.023 \times 10^{23})}$$

$$= \frac{12 \times 16}{28 \times (6.023 \times 10^{23})} = 1.14 \times 10^{-23} \, g$$

Therefore, the internuclear separation (bond length) r is

$$r = \sqrt{\frac{I}{\mu}} \qquad (\because \ I = \mu r^2)$$

$$= \sqrt{\frac{1.46 \times 10^{-39} \, gm-cm^2}{1.14 \times 10^{-23} \, gm}}$$

$$= 1.13 \times 10^{-8} \, cm = 1.13 \, \mathring{A}$$

10. The OH – radical has a moment of inertia of $1.48 \times 10^{-40} \, gm-cm^2$. Calculate its internuclear distance. Also calculate, for $J = 5$, its angular momentum and angular velocity. Determine the energy absorbed in the $J = 6 \rightarrow J = 5$ transition in cm^{-1} and erg/molecule.

Soln. The reduced mass of the OH-radical is given by

$$\mu_{OH} = \frac{M_O M_H}{M_O + M_H}$$

$$= \frac{(1 \times 16)(6.023 \times 10^{23})}{(1+16)(6.023 \times 10^{23})^2} = \frac{16}{17 \times (6.023 \times 10^{23})} = 1.56 \times 10^{-24} \, gm$$

If I is the moment of inertia, then the internuclear distanec r is

$$r = \sqrt{\frac{I}{\mu}} = \sqrt{\frac{1.48 \times 10^{-40} \, gm-cm^2}{1.56 \times 10^{-24} \, gm}}$$

$$= 0.97 \times 10^{-8} \, cm = 0.97 \, \mathring{A}$$

The angular momentum is given by

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

For J = 5, we have

$$L = \sqrt{30} \times \frac{6.62 \times 10^{-27}}{2 \times 3.14} \, erg - sec = 5.77 \times 10^{-27} \, erg - sec$$

The corresponding angular velocity is:

$$\omega = \frac{L}{I}$$

$$= \frac{5.77 \times 10^{-27} \, erg - sec}{1.48 \times 10^{-40} \, gm - cm^2} = 3.90 \times 10^{13} \, sec^{-1}$$

The wave number of the radiation absorbed (absorbed energy in cm^{-1}) in transition from J to J+1 is given by

$$v = 2B(J+1)$$

where, J refers to the lower state. Therefore, for the transition $J = 6 \rightarrow J = 5$, we have

$$v = 2B(5+1) = 12B$$

But $\qquad B = \dfrac{h}{8\pi^2 Ic} \qquad\qquad \therefore \qquad v = \dfrac{12h}{8\pi^2 Ic}$

$$= \frac{12 \times (6.62 \times 10^{27} \, erg - sec)}{8 \times (3.14)^2 \times (1.48 \times 10^{-40} \, gm - cm^2)(3 \times 10^{10} \, cm - sec^{-1})}$$

$$= 227 \, cm^{-1}$$

The corresponding energy E in erg/molecule is obtained by

$$E = vhc$$

$$= (227 \, cm^{-1})(6.62 \times 10^{-27} \, erg - sec)(3 \times 10^{10} \, cm - sec^{-1})$$

$$= 4.50 \times 10^{-14} \, erg / \text{molecule}$$

11. The transition J = 3 to J = 4 in HCl molecule is associated with radiation of $83.03 \, cm^{-1}$. Use the rigid-rotator approximation to calculate the moment of inertia and internuclear distance (bond length) of HCl.

Soln. The wave number of absorbed radiation in rotational transition $J \rightarrow (J+1)$ is given by

$$v = 2B(J+1) \, cm^{-1}, \text{ where, J refers to the lower state.}$$

For $J = 3 \rightarrow J = 4$, we have

$$v = 2B(3+1) = 8B$$

But $\qquad v = 83.03 \, cm^{-1} \, (\text{given})$

$\therefore \qquad 8B = 83.03 \, cm^{-1}$

$$B = 10.38 \, cm^{-1}$$

The rotational constant B is given by

$$B = \frac{h}{8\pi^2 Ic}$$

Therefore, the moment of inertia of the molecule is

$$I = \frac{h}{8\pi^2 Bc} = \frac{6.62 \times 10^{-27} \, erg - sec}{8 \times (3.14)^2 \times (10.38 \, cm^{-1})(3 \times 10^{10} \, cm - sec^{-1})}$$

$$= 2.7 \times 10^{-40} \, gm - cm^2$$

The reduced mass of HCl molecule is

$$\mu_{HCl} = \frac{M_H M_{Cl}}{M_H + M_{Cl}}$$

$$= \frac{(1 \times 35)(6.023 \times 10^{23})^2}{(1 + 35)(6.023 \times 10^{23})}$$

$$= 1.61 \times 10^{-24} \, gm$$

The internuclear distance (bond length) is therefore

$$r = \sqrt{\frac{I}{\mu}} = \sqrt{\frac{2.7 \times 10^{-40} \, gm - cm^2}{1.61 \times 10^{-24} \, gm}} = 1.29 \times 10^{-8} \, cm = 1.29 Å$$

12. The molecule that will exhibit a pure rotational absorption spectrum out of this

   (a) CH_4 (b) CO_2 (c) O_2 (d) NF_3

Soln. Only molecule that exhibit a permanent dipole moment exhibit a pure rotational spectrum.

Out of all molecules only NF_3 has dipole moment.

Correct option is (d)

13. In a rigid rotator, the energy of fourth excited state is 10 meV, then the energy of second excited state is

   (a) 1.5 meV   (b) 2 meV   (c) 2.5 meV   (d) 3 meV

Soln. Energy of a rigid rotator ;

$$E = \frac{\hbar^2}{2I} J(J+1), \qquad \qquad ...(A)$$

where $J = 0, 1, 2, ...$

So, energy of fourth excited state $= 10$ meV

$$10 \, meV = \frac{\hbar^2}{2I} 4(4+1) \implies 10 \, meV = \frac{\hbar^2}{2I} \times 20$$

$$\implies \quad \frac{\hbar^2}{I} = 1 \, meV \qquad \qquad ...(1)$$

So, energy of second excited state $= \frac{\hbar^2}{2I} 2(2+1)$

$$E_2 = \frac{\hbar^2}{2I} \times 6 \implies E_2 = \frac{3\hbar^2}{I} \qquad \qquad ...(2)$$

Put value of $\hbar^2/I$ from Eq. (1) into Eq. (2).

$$E_2 = 3(1 \, meV) \qquad E_2 = 3 \, meV.$$

Correct option is (d)

14. The H_2 molecule has a reduced mass $M = 8.35 \times 10^{-28}$ kg and an equilibrium internuclear distance $R = 0.742$ $\times 10^{-10}$ m. The rotational energy in terms of the rotational quantum number J is :

(a) $E_{rot}(J) = 7J(J-1)$ meV

(b) $E_{rot}(J) = \dfrac{5}{2}J(J+1)$ meV

(c) $E_{rot}(J) = 7J(J+1)$ meV

(d) $E_{rot}(J) = \dfrac{5}{2}J(J-1)$ meV

Soln. Rotation energy of a molecule is $E = \dfrac{\hbar^2}{2I}J(J+1)$, where I is moment of inertia and $I = \mu R^2$.

μ = reduced mass and R = equilibrium intermolecular distance

$\Rightarrow \quad E = \dfrac{\hbar^2}{2\mu R^2}J(J+1)$

Here we have to final value of $\hbar^2/2\mu R^2$

$\Rightarrow \quad \dfrac{h^2}{8\pi^2 \mu R^2} = \dfrac{(6.6 \times 10^{-34}) \times (6.6 \times 10^{-34})}{8 \times 3.14 \times 3.14 \times 8.35 \times 10^{-28} \times 0.742 \times 10^{-10} \times 0.742 \times 10^{-10}}$

$\qquad\qquad = \dfrac{12 \times 10^{-22}}{1.6 \times 10^{-19}}$ eV $= 7.5 \times 10^{-3}$ eV $= 7.5$ meV.

Correct option is (c)

15. Which of the following molecules give pure rotational spectra?
(a) O_2, CH_4 (b) H_2, HCl   (c) H_2, CO   (d) HCl, CO
Soln. HCl, CO having permanent dipole moment. So, give pure rotational spectrum.
Correct option is (d)

16. Spectroscopic transitions leading to rotation of molecules will appear at which region of the electromagnetic spectrum?
(a) Ultraviolet   (b) Radiofrequency   (c) Infra-red   (d) Microwave
Soln. Rotational of molecule lies in the region of microwave.
Correct option is (d)

17. The microwave spectrum of a rigid diatomic molecule shows first three lines at 2.65682 cm⁻¹, 5.31364 cm⁻¹, and 7.97046 cm⁻¹. What is the rotational constant of this molecule?
(a) 1.82118 cm⁻¹   (b) 3.64236 cm⁻¹   (c) 1.32841cm⁻¹   (d) 0.91059 cm⁻¹

Soln. Three lines $\rightarrow$ 2.65682, 5.31364, 7.97046

Difference in rotational spectral lines $\rightarrow 2B = 5.31364 - 2.65682 \Rightarrow 2B = 2.65682$

$\therefore \qquad B = 1.32841\ cm^{-1}$

Correct option is (c)