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Topic — Rotational Spectra

Rotational spectrum (Far IR)

For pure rotational spectra - the molecule should have permanent dipole moment and in the gaseous form. During rotational motion, the direction of the dipole undergoes a periodic change, resulting in periodic fluctuations in the magnitude of a component of dipole as shown in the figure;
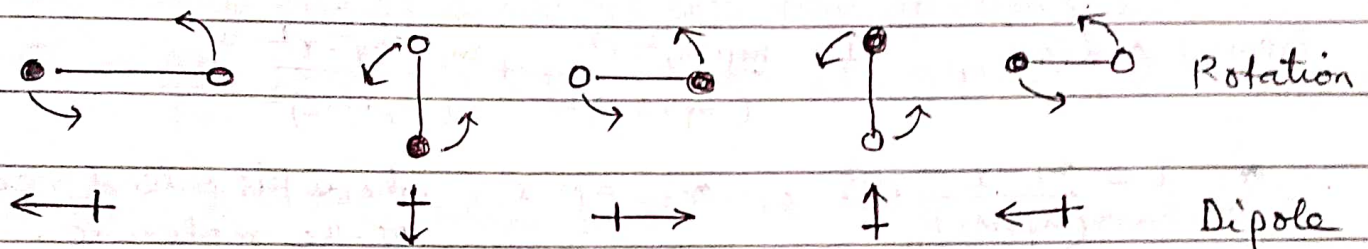
Rotation

Dipole

when frequency of EMR coincides with molecular rotation, the EMR interacts with molecular dipole and keeps pushing the molecule to a higher rotational energy level. This absorption of radiation thus gives pure rotational spectrum of molecule. The homonuclear molecules eg, H_2, N_2, Cl_2 etc don't produce rotational bands because $\mu = 0$. So they are called microwave inactive. The pure rotational (microwave) spectra occur in the spectral range $1-100 \, cm^{-1}$ ie. $10^4 \mu - 10^2 \mu$ range

Theory of pure rotational spectra -

Rigid Rotor model - By rigid rotor we mean a molecule which rotates such that its internuclear bond distance does not change during rotation. Consider a diatomic molecule to rotate as a whole about the axis through its C.G. Let the two atoms have masses m_1 and m_2 connected by a rigid rod

of length r (representing bond length). Let r_1 and r_2 be the distances of two atoms from the C.G. of the system.

(a) __Moment of inertia__ - It is given by $I = m_1 r_1^2 + m_2 r_2^2$ —(1)

Since the system is balanced about C.G.

hence, $m_1 r_1 = m_2 r_2$ —(2) and further $r = r_1 + r_2$ —(3)

From equation (2) and (3), $r_1 = \dfrac{m_2 r}{m_1 + m_2}$ and $r_2 = \dfrac{m_1 r}{m_1 + m_2}$ —(4)

From (1) and (4), $\qquad I = \dfrac{m_1 \cdot m_2^2 \cdot r^2}{(m_1 + m_2)^2} + \dfrac{m_2 \cdot m_1^2 \cdot r^2}{(m_1 + m_2)^2}$

or $\quad I = \dfrac{m_1 m_2}{(m_1 + m_2)} \cdot r^2 \qquad$ or $I = \mu \cdot r^2$ where μ is called reduced mass. of the molecule.

(b) __Kinetic energy of rotation__ - It is given by $E_{rot} = \frac{1}{2} m_1 v_1^2 + \frac{1}{2} m_2 v_2^2$

where v_1 and v_2 are linear velocities of masses m_1 and m_2 respectively. Since r_1 and r_2 are assumed to remain unchanged during rotation, we can write $\omega = \dfrac{v}{r}$ where ω = angular velocity.

So $E_{rot} = \frac{1}{2} m_1 (\omega \cdot r_1)^2 + \frac{1}{2} m_2 (\omega \cdot r_2)^2 = \frac{1}{2} \omega^2 (m_1 r_1^2 + m_2 r_2^2)$

or $E_{rot} = \frac{1}{2} I \omega^2$

Since molecule is rigid rotor, so P.E. = 0. Thus the quantised rotational energy values are obtained by solving Schrödinger equation, $\nabla^2 \psi + \dfrac{8\pi^2 I \cdot E_{rot}}{h^2} \psi = 0$ (for rigid diatomic rotor)

which gives E_{rot}, also written as $E_J = \dfrac{h^2}{8\pi^2 I} \cdot J(J+1)$ —(5)

where J = rotational quantum number having values $0, 1, 2, 3 \cdots$.

The equation (5) gives rotational energy of the molecule in a given rotational energy level.

(c) **Quantum mechanical restriction — (selection Rule) —** The quantum mechanics permits only those rotational transitions in which there is a change of unity in rotational quantum number ie $\Delta J = \pm 1$. Since microwave spectra are usually observed as absorption spectra, hence operative part of the selection rule is $\Delta J = +1$.

(d) **Rotational spectra consists of equidistant spectral lines —**
Expressing energy in cm^{-1} we get from equation (5),

$$\bar{E}_J = \frac{E_J}{hc} = \frac{h}{8\pi^2 I c} J(J+1) \ cm^{-1} \quad (J = 0, 1, 2, 3 \cdots)$$

or $\bar{E}_J = B J(J+1)$ where $B\left(=\frac{h}{8\pi^2 I c} \ cm^{-1}\right)$ is rotational const.

Now for a transition taking place from $J \to J+1$, the rotational frequency $\bar{E}_J$ ie $\bar{v}$ is given by,

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

or $\bar{v}(J \to J+1) = 2B(J+1) \ cm^{-1}$ ———— (6)

From equation (6) we have,

$$\bar{v}(0 \to 1) = 2B \quad , \quad \bar{v}(1 \to 2) = 4B \quad , \quad \bar{v}(2 \to 3) = 6B \ etc$$

Therefore rotational spectra of a diatomic rigid rolor consists of a series of lines, equally spaced by $2B$.

(e) **Intensity of rotational spectral lines —** It is governed by relative population of various rotational levels. That is intensity first increases, reaches to a maximum and then decrease like Boltzmann distribution of molecules in the rotational energy levels. The value of J corresponding to the maximum in population is given by the equation.

$$J_{max} = \left(\frac{kT}{2hcB}\right)^{1/2} - \frac{1}{2}$$

The Jmax should be rounded off to the nearest integral value.

(f) **Isotopic effect on rotational spectra** — Since the masses of isotopic atoms are different hence the value of μ, I and $\bar{\nu}$ would be different. It has been established that $B \propto \frac{1}{\mu}$. Hence spectrum of heavier species (eg DCl comparative to HCl) will show smaller B and hence smaller seperation between the spectral lines

Q-1 Pure rot. spectra of gaseous HCl shows equally spaced lines by 20.80 cm^{-1}. Calculate r. Given atomic masses of $H = 1.673 \times 10^{-27}$ kg, $^{35}Cl = 58.06 \times 10^{-27}$ kg.

Sol- Here $2B = 20.80$ i.e. $B = 10.40$ cm^{-1}

Now $B = \dfrac{h}{8\pi^2 I c}$, So $I = \dfrac{h}{8\pi^2 B c}$

or $I = \dfrac{6.62 \times 10^{-34} \text{ J·s}}{8 \times (3.14)^2 \times (10.4 \text{ cm}^{-1}) \times (3 \times 10^{10} \text{ cm s}^{-1})}$ (note)

$= 2.689 \times 10^{-47}$ kg m^2 (Since J $=$ kg m^2 s^{-2})

If atomic masses are given then $\mu = \dfrac{m_1 m_2}{(m_1 + m_2)}$

$= 1.626 \times 10^{-27}$ kg

Since $I = \mu r^2$, So $r = \left(\dfrac{I}{\mu}\right)^{1/2} = \left(\dfrac{2.689 \times 10^{-47} \text{ kg m}^2}{1.626 \times 10^{-27} \text{ kg}}\right)^{1/2}$

$= 1.29 \times 10^{-10}$ m $= 1.29$ A$^\circ$

Q.2 The bond length of CO is $1.13 A°$. Calculate the energy (in Joules and eV) and angular velocity of this molecule in first excited rotational level. Given atomic weights of $C^{12} = 12.011$ and $O^{16} = 15.999$.

Sol- Here $r = 1.13 A° = 1.13 \times 10^{-10} m$

The reduced mass $= \dfrac{m_1 m_2}{(m_1 + m_2) N_A}$ where N_A = Avogadro number

So $\mu = \dfrac{12.011 \times 15.999}{28.010 \times 6.02 \times 10^{23}} = 1.0737 \times 10^{-23} g = 1.0737 \times 10^{-26} kg$

Now $I = \mu . r^2 = 1.0737 \times 10^{-26} kg \times (1.13 \times 10^{-10})^2 = 1.371 \times 10^{-46} kg m^2$

we know $E_J = \dfrac{h^2}{8 \pi^2 I} J(J+1)$ Joules

For first excited rotational level $J = 1$, Hence

$E_1 = \dfrac{h^2}{8\pi^2 I} \times 1 \times (1+1) = \dfrac{h^2}{4\pi^2 I} = \dfrac{(6.626 \times 10^{-34} JS)^2}{4 \times (3.14)^2 \times 1.371 \times 10^{-46} kg m^2}$

or $E_1 = 7.61 \times 10^{-23}$ Joules

Since $1 eV = 1.6 \times 10^{-19}$ Joules   So $E_1 = \dfrac{7.61 \times 10^{-23}}{1.6 \times 10^{-19}} = 4.76 \times 10^{-4} eV$

Since $E_J = \dfrac{1}{2} I \omega^2$ So $\omega = \sqrt{\dfrac{2 E_J}{I}} = 3.23 \times 10^{11}$ rad s^{-1}

Q.3. Calculate J_{max} for a rigid diatomic molecule for which at $300 K$ the rotational const. is $1.566 cm^{-1}$.

Sol. $J_{max} = \left(\dfrac{kT}{2hcB} \right)^{1/2} - \dfrac{1}{2} = \left[\dfrac{(1.38 \times 10^{-23} JK^{-1})(300K)}{2 \times (6.62 \times 10^{-34} JS)(3 \times 10^{10} cm s^{-1})(1.566 cm^{-1})} \right]^{1/2} - \dfrac{1}{2}$

$= 8$ (Nearest integral value)

Relative intensities of rotational spectral lines — It is observed that many of the diatomic molecules are present in the excited state energy levels even at room temperature. The relative intensities of spectral lines depends upon relative population of the energy levels which is given by Boltzmann distribution.
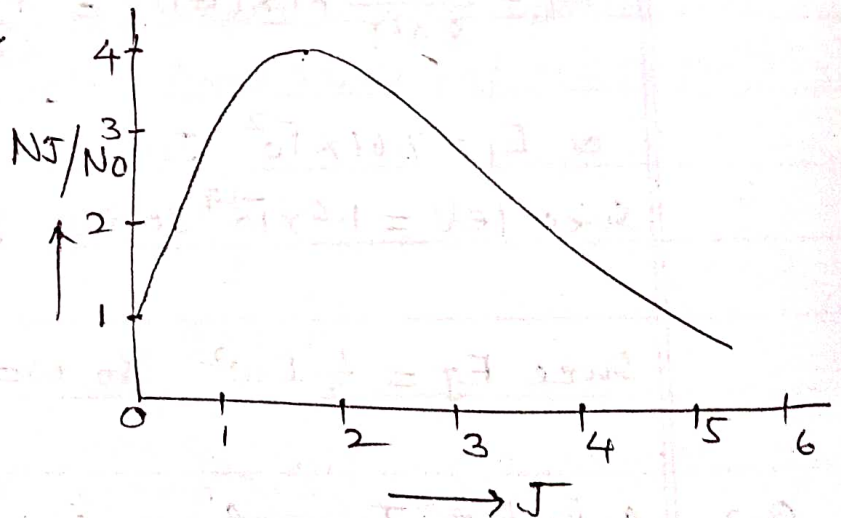
So Intensity $\propto N_J/N_0 = \bar{e}^{E_J/kT}$

The degeneracy of rotational energy levels (g_J) for a diatomic molecule being given by, $g_J = 2J+1$ ie. for a given value of J, the energy level is $(2J+1)$ fold degenerate.

So Intensity $= (2J+1)\,\bar{e}^{E_J/kT}$

So $N_J/N_0 = (2J+1)\,\bar{e}^{BJ(J+1)hc/kT}$ (Since $\bar{E}_J = BJ(J+1)$ and $E_J = hc\bar{E}_J$)

The plot of N_J/N_0 v/s J for a rigid diatomic molecule at room temperature is shown in figure.

The value of J corresponding to maximum in population is given by,

$$J_{max} = \left(\frac{kT}{2hcB}\right)^{1/2} - \frac{1}{2}$$

Non-rigid rotator model – The const. separation of $2B$ between consecutive rotational spectral lines is true only at lower value of J. At higher value of J, velocity of rotation increases and there is a tendency of bond to stretch and also the value of I increases. So the rigid character of rotor is affected.

So a better model is considered where masses m_1 and m_2 are connected by a massless spring instead of rod. This is called non-rigid rotator model. The energy of rotation is expressed as, $E_J = BJ(J+1) - DJ^2(J+1)^2$ where D is the centrifugal distortion const. of the order of $10^4 B$. It takes into account the increase in bond length due to rotation of the molecule.

The selection rule is valid, $\Delta J = \pm 1$ whether the rotor is rigid or non-rigid. From the improved equation given above,

$$\overline{\nu}_{rot}_{(J \to J+1)} = 2B(J+1) - 4D(J+1)^3 \ cm^{-1}$$

From the above equation $\overline{\nu}_{(0 \to 1)} = (2B - 4D) \ cm^{-1}$

$\overline{\nu}_{(1 \to 2)} = (4B - 32D) \ cm^{-1}$, $\overline{\nu}_{(2 \to 3)} = (6B - 108D) \ cm^{-1}$

Thus the spectral lines are no longer equidistant but their separation distance decreases with increasing value of J.

Applications of microwave spectroscopy — The spectra helps in Calculation of moment of inertia I and internuclear distance r of diatomic molecule of the molecules having permanent dipole moment. Polyatomic molecules (linear) have several internuclear distances, hence these quantities can't be determined by single value of B. For this isotopic subst eg. $O^{16}-C^{12}-S^{32}$ and $O^{16}-C^{12}-S^{34}$ can give two B values and both the bond distances can be determined. Further condensed phases have no well-defined rotational energy levels. So this spectra is not useful for solids and liquids. This has application in gaseous phase because the rotation of molecule is free. The other applications are conformational analysis and detection of isotopes in a mixture.

Q.4 Calculate frequency and wave number of radiation 400nm.

Sol. $\nu = \dfrac{c}{\lambda} = \dfrac{3\times10^{10}\ cm\ \bar{s}^1}{(400\times 10^{-9}m)\times 10^2\ cm\ \bar{m}^1} = 7.5\times10^{14}$ cycle per sec

wave number $\bar{\nu} = \dfrac{1}{\lambda\,(in\ cm)} = \dfrac{1}{4\times10^5\ cm} = 25000\ cm^{-1}$