

CYCLE TEST PAPER

REG. NO.

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DATE _____

DEGREE _____

NAME _____

SPECIALISATION _____

COURSE _____

SEMESTER _____

Vibrational and rotational spectroscopy

The radiation of energy absorbed in IR region brings about the simultaneous changes in the rotational and vibrational energy of the molecule. This is observed in the fine structure of rotation of bands. The combined spectrum is called the vibrational-rotational spectrum.

The vibrational and rotational changes are considered as independent event and there is no interaction between them. Then the net energy change is the algebraic sum of the rotational and vibrational energy levels.

Therefore

$$\Delta E_{\text{Total}} = \Delta E_{\text{vibrational}} + \Delta E_{\text{rotational}} \rightarrow \textcircled{1}$$

The eq No ① in term of Wave Number.

$$\bar{\nu}_{J,v} = (\bar{\nu}_J + \bar{\nu}_v) \text{ cm}^{-1} \rightarrow \textcircled{2}$$

As We know that energy in term of wave number for rotational energy level (the energy of the rotation is quantised and it is given by.)

$$\bar{\nu}_J = B J(J+1) \rightarrow \textcircled{3}$$

Where J is the rotational Quantum No.

B is the rotation constant

Where $B = \frac{h^2}{8\pi^2 I c} \rightarrow \textcircled{3}$

We treat the molecule of the rotation as a rigid rotator

So the vibrational energy Quantised level is given by

$$\bar{\nu}_v = (v + \frac{1}{2}) \omega_e - (v + \frac{1}{2})^2 \omega_e x_e \rightarrow \textcircled{4}$$

This is the equation for the vibrational energy level

Where $\omega_e \rightarrow$ Angular Velocity or equilibrium

oscillation frequency

$x_e \rightarrow$ Anharmonic oscillator

ν = Vibrational Quantum No.

Total energy in term of Wave No put the values of

eq No (3) and eq No (4) in eq No (2)

$$\bar{\nu}_{J,v} = B J(J+1) + (\nu + \frac{1}{2})\omega_e - (\nu + \frac{1}{2})^2 \omega_e x_e \quad \text{--- (5)}$$

Rotational \downarrow Vibrational energy level

According to the Selection Rule.

$$\Delta \nu = \pm 1$$

$$\Delta J = \pm 1$$

for vibrational level transition of a molecule from $\nu=0$ to $\nu=1$

for rotational level transition of a molecule from $J'' - J'$

J'' is the lower Rotational energy level

J' is the higher level Rotational energy level

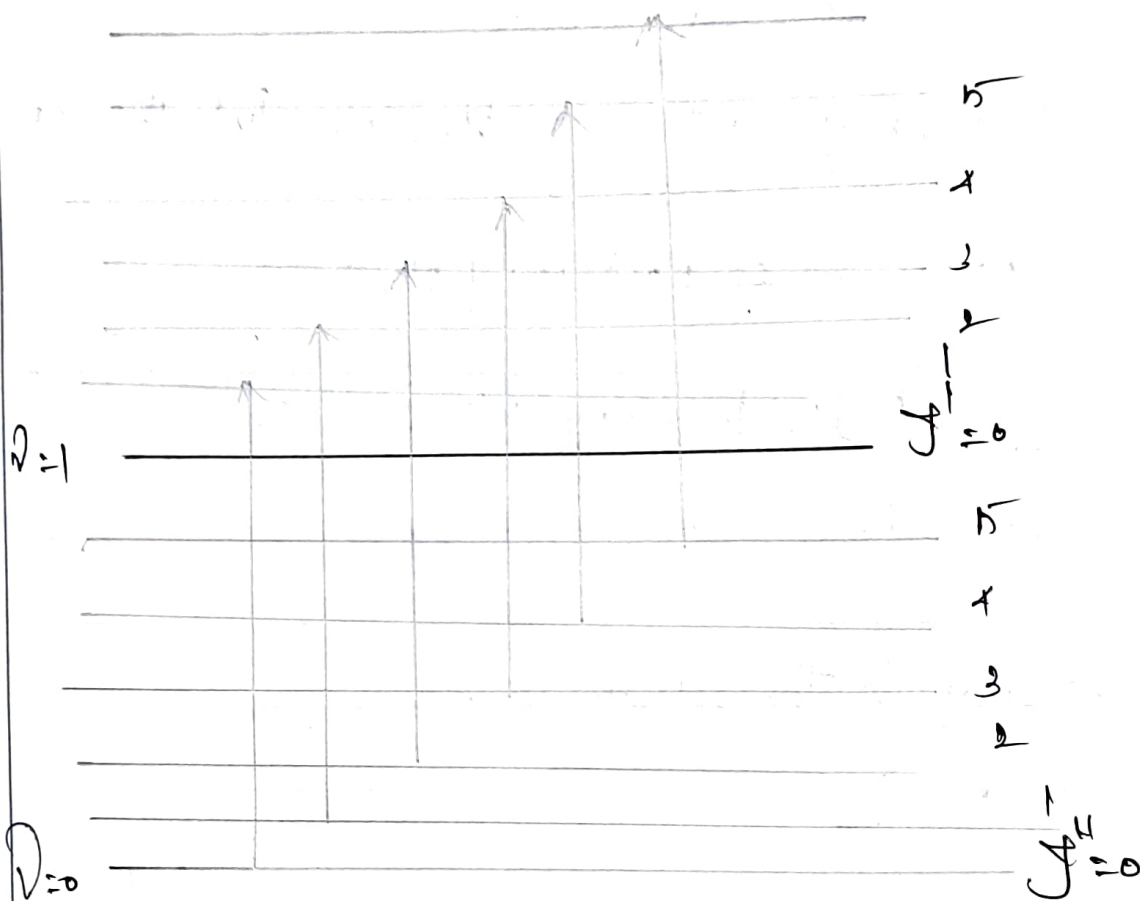
So the Selection Rule

$$\Delta \nu = \bar{\nu}_{J', \nu=1} - \bar{\nu}_{J'', \nu=0}$$

--- (6)

Excited state level

Ground state level



sub eq No (6) in eq No (5)

$$\bar{A}\bar{v} = [B J' (J' + 1) + (1 + \frac{1}{2}) \bar{w}_e - (1 + \frac{1}{2})^2 \bar{w}_e x_e] -$$

$$B J'' (J'' + 1) + (0 + \frac{1}{2}) \bar{w}_e - (0 + \frac{1}{2})^2 \bar{w}_e x_e]$$

$$\bar{A}\bar{v} = [B J' (J' + 1) + \frac{3}{2} \bar{w}_e - \frac{9}{4} \bar{w}_e x_e] - [B J'' (J'' + 1) + \frac{1}{2} \bar{w}_e - \frac{1}{4} \bar{w}_e x_e]$$

$$\bar{A}\bar{v} = [B J' (J' + 1) - B J'' (J'' + 1) + \frac{3}{2} \bar{w}_e - \frac{1}{2} \bar{w}_e - \frac{9}{4} \bar{w}_e x_e + \frac{1}{4} \bar{w}_e x_e]$$

$$\bar{A}D = B J' (J' + 1) - B J'' (J'' + 1) + W_e - 2W_e x_e$$

$$\text{Let } W_e - 2W_e x_e = W_0$$

$$\bar{A}D = B J' (J' + 1) - B J'' (J'' + 1) + W_0 \quad \text{--- (8)}$$

Now we have two cases selection rule $\Delta J = \pm 1$

$$\left. \begin{aligned} \Delta J = J' - J'' = +1 \\ \text{or } J' = 1 + J'' \end{aligned} \right\} \rightarrow \text{--- (9)}$$

sub this eq No (9) in (8)

$$\bar{A}D = B(1) [1 + J'' + J'' + 1] + W_0$$

$$\bar{A}D = B [2J'' + 2] + W_0$$

$$= W_0 + 2B(J'' + 1) \quad \text{where } (M = J'' + 1)$$

$$\therefore \bar{A}D = W_0 + 2BM \rightarrow \text{--- (9)}$$

When $\Delta J = -1$

$$\left. \begin{aligned} \Delta J = J' - J'' = -1 \\ J'' = J' + 1 \end{aligned} \right\} \rightarrow \text{--- (10)}$$

sub eq No (10) in eq No (8)

$$\bar{\Delta v} = [B(-1)(2J'+2)] + \omega_0$$

$$\bar{\Delta v} = -B(2J'+1)$$

$$\omega_0 - 2B(J'+1) \quad [\text{where } M = -(J'+1)]$$

$$\boxed{\bar{\Delta v} = \omega_0 - 2BM}$$

It says that for vibrational and rotational frequency

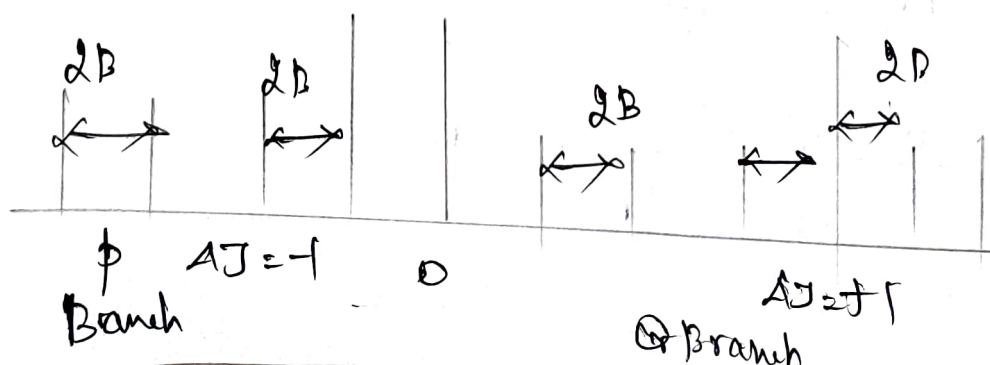
$$\bar{\Delta v} = \omega_0 + 2B \quad (\text{when } m=1)$$

$$\bar{\Delta v} = \omega_0 - 2B \quad (\text{when } m=-1)$$

$$\bar{\Delta v} = \omega_0 + 4B \quad (\text{when } m=+2)$$

$$\bar{\Delta v} = \omega_0 - 4B \quad (\text{when } m=-2)$$

Separation between the two spectral line is equally spacing is $2B$.



The vibrational rotational spectrum would consist of a series of lines with equal spacing of $2B$ cm⁻¹ on either side of the band origin ω_0 .

The line corresponding to the $-1/2$ value of m at lower freq side of ω_0 are called P branch line and at higher freq side of ω_0 are called R branch line. Middle freq called Q Branch.