T.D.C. Part III

Physical chemistry

Characteristics of PMW Spectra

(1) It is caused by rotation of molecules around its centre of gravity.

(2) Small amount of energy change is involved.

$E = 10$ to 10^3 joule/mole

$\bar{\nu} = 1$ to 10^2 cm^{-1}

(3) Spectral range $\longrightarrow$ PMW

(4) It is characterized by rotational quantum no. (J)

$J = 0, 1, 2, 3, \ldots$

(5) For rotational energy level

$E_{rot} = \bar{B} hc\, J(J+1)$ ergs

and

$\bar{\nu} = \bar{B} J(J+1)$ cm^{-1}

(6) Frequency separation between rotational ~~lines~~ energy level

$\Delta E_{rot} = 2\overline{B}hc(J+1)$

and

$\Delta\bar{\nu} = 2\overline{B}(J+1)$

i.e. $2\overline{B}$, $4\overline{B}$, $6\overline{B}$, $8\overline{B}$

(7) Rotational energy levels are usually populated as energy difference is small

(8) probability of transitions are almost the same.

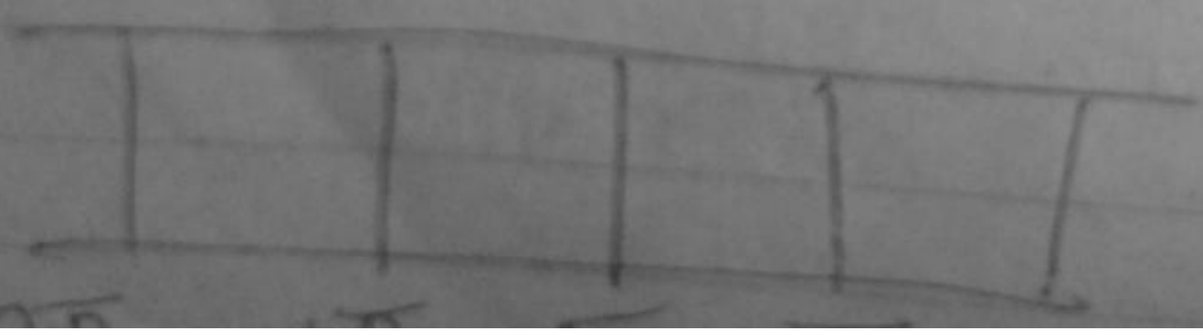
(9) Selection rule -

(a) $\Delta J = \pm 1$

(b) Molecule has permanent dipole moment

(10) Intensity of rotational lines

$2\overline{B}$, $4\overline{B}$, $6\overline{B}$, $8\overline{B}$



(11) Rotational lines are equally spaced and $\Delta\bar{\nu} = 2B$ cm^{-1}.

(12) Only molecules with permanent dipole moment are PR active. Orientation of dipole moment changes as the molecule rotates and as a result electric component of dipole moment fluctuate.

(13) PR is studied in gas phase only.

(14) Distortion of bond length occurs at J values equal to or greater than 10. ($J \geq 10$)

(15) Bond length, bond angle, moment of inertia, isotopic weight etc. can be calculated.