

## Micro wave Spectra

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### Molecular Requirements:

1. Spectroscopy in the microwave region concerned with the study of rotating molecules.
2. Only molecules that have a permanent dipole moment can absorb or emit electromagnetic radiation in such transitions.
3. For ex: in  $\text{HCl}$ , which is a heteronuclear diatomic molecule, such transitions can occur, energy can be absorbed or emitted and the rotation gives rise to a spectrum.
4. In homonuclear molecules like  $\text{N}_2$ ,  $\text{O}_2$ , no change occur in dipole moment during the rotation.
5. Hence, linear diatomic molecules are rotationally inactive for rotation about the bond axis.

Atomic & molecular spectrum are obtained because of the transition taking place between energy levels. These transitions can occur only between definite energy levels and not between any two energy levels. The restrictions that<sup>are</sup> applied on the transitions

are governed by certain rules known as selection rules. If a transition is taking place according to these rules, the transition is known as allowed transitions and if these are not followed, they are called forbidden transitions.

The selection rules are generally expressed in terms of change in quantum numbers for the allowed transition.

For pure rotational transition, the selection rule is  $\Delta J = \pm 1$  where  $J$  represents rotational quantum no.  $\Delta J = +1$  corresponds to absorption &  $\Delta J = -1$  corresponds to emission.

Acc. to the sel. rule  $\Delta J = \pm 1$ , the value of  $J$  changes only one unit. (In mol. spectroscopy only absorption  $\Delta J = +1$  is concerned)

i.e. Transition occurs from  $J=0 \rightarrow J=1$ ;  $J=1 \rightarrow J=2$  and so on. Transitions from  $J=0 \rightarrow J=2$  (or)  $J=1 \rightarrow J=3$  are forbidden.

M.W spectra are measured only in gaseous molecules under very low press. Since, in the condensed phase no well defined rotational levels



exist, the M.W spectra are difficult to be observed in case of liq. & solids.

HCl, HBr, NO, CO - M.W Active

H<sub>2</sub>, Cl<sub>2</sub>, Br<sub>2</sub>, N<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>2</sub> - M.W inactive.

### RIGID ROTOR MODEL

Let us consider a diatomic molecule which may be regarded as a rigid rotor. i.e. a rigid dumb bell joined along its line of centres by a bond equal in length to the distance  $r$  between the two nuclei. Since, the molecule is rigid, the pot. energy  $V = 0$ . The quantised energy levels of rotation may be obtained by solving Schrodinger eqn/.

$$\frac{\nabla^2}{2} \psi + \frac{8\pi^2 M E}{h^2} \psi = 0.$$

The soln. for the above eqn/ is

$$E_J = \frac{h^2}{8\pi^2 I} J(J+1) \text{ joules where } J = 0, 1, 2, 3, \dots$$

where  $h$  - Planck's constant

$J$  - Rotational quantum no/.

$I$  - Moment of Inertia

$E_J$  - Rotational Energy.

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The moment of inertia can be calculated as follows

If  $r_1$  &  $r_2$  be the distances of the two atoms from the centre of gravity of the system, then

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

$m_1$  &  $m_2$  - atomic masses of the two atoms.

W.K.T  $m_1 r_1 = m_2 r_2$

$$r_1 = \frac{m_2}{m_1 + m_2} r \quad \& \quad r_2 = \frac{m_1}{m_1 + m_2} r$$

Sub. the values of  $r_1$  &  $r_2$  in the eqn.

$$I = \left[ \frac{m_1 m_2}{m_1 + m_2} \right] r^2 = \mu r^2$$

where  $\mu = \frac{m_1 m_2}{m_1 + m_2}$

Now, suppose there is a transition from rotation level of quantum no.  $J'$  to that of higher quantum no.  $J$ , the energy diff. will be given by

$$\begin{aligned} \Delta E_J &= E_J - E_{J'} \\ &= \frac{h^2}{8\pi^2 I} J(J+1) - \frac{h^2}{8\pi^2 I} J'(J'+1) \end{aligned}$$

$$\Delta E_J = \frac{h^2}{8\pi^2 I} [J(J+1) - J'(J'+1)]$$

The corresponding freq. or wave no. is given by

$$\nu = \Delta E_J / h \quad \text{or} \quad \bar{\nu} = \Delta E_J / hc$$



In the rotational region, spectra, are usually studied in terms of wave no.  $\bar{\nu}$ .

$$\therefore \bar{\nu} = \frac{\Delta E_J}{hc} = \frac{h}{8\pi^2 I c} J(J+1) \text{ cm}^{-1} (J=0, 1, 2, \dots)$$

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

$B$  - constant.

It is clear that rotational energy depends on moment of inertia & the rot. quantum no.  $J$ .

Since, even at room temp., the molecules would be distributed over a large no. of rotational levels, a no. of transitions would be possible, if appropriate energies are made available to the system. Thus, if all transitions takes place, the absorption spectrum would consist of a series of lines at  $2B, 4B, 6B, \dots$ . This clearly indicates that the rot. spectrum of a diatomic molecule consists of a series of lines with freq. separation  $2B \text{ cm}^{-1}$ . Thus the splitting between the successive lines is equal to  $2B$ . This is known as freq. separation.

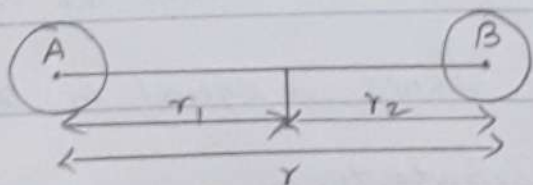
It should be noted that situation corresponding to  $J=0$  is non-rotating state of the molecule. For  $J=0$  we have  $E_J=0$ .

When a molecule undergoes transition from ground rot. state i.e.  $J=0$ , which is non-rotating state to an excited  $J=1$  state by absorption of radiation, the energy absorbed is given

by  $E_{J=1} - E_{J=0} = 2B - 0 = 2B \text{ cm}^{-1}$ .

For  $E_{J=2} - E_{J=1} = 6B - 2B = 4B$ .

For a rigid diatomic rotor, the selection rule is  $\Delta J = \pm 1$  and the spectrum will be observed only if the molecule is asymmetric & hetero nuclear, because if it is homo nuclear, there will be no change in the dipole moment during the rotation and hence there will be no interaction with radiation.



Rigid Rotor model for a diatomic molecule.