* Vibration – Rotation Spectra of a diatomic molecule :–

According to Born-Oppenheimer approximation the molecule may be considered to extents rotation and vibration motions quite independently of each other. This follow from the fact that the vibration is much larger than the rotation energy. The total energy of the molecule excuting the vibration and vibration motion may be turns as the sum of the separate energies. i.e.

$$E = E_{rot} + E_{vib} \quad (\text{Joules})$$

$$\epsilon = \epsilon_{rot} + \epsilon_{vib} \; (cm^{-1})$$

Now putting the value of ϵ_{rot} and ϵ_{vib} in the above expression we get –

$$\epsilon = BJ(J+1) - DJ^2(J+1)^2 + HJ^3(J+1)^3 + \cdots$$
$$+ (v+\tfrac{1}{2})\bar{\omega_e} - x_e(v+\tfrac{1}{2})^2\bar{\omega_e} \; cm^{-1}$$

The centrifugation from centrifugal dissociation constant may be assumed to be neglisible through molecule is not rigid so

$$\boxed{\epsilon = BJ(J+1) + (v+\tfrac{1}{2})\bar{\omega_e} - x_e(v+\tfrac{1}{2})^2\bar{\omega_e}} \longrightarrow (1)$$

Since, the rotational constant 'B' is taken the same for all J & v values.

[Born-Oppenheimer approximation Consequence]

So, the separation between all J levels for v=0 to v=1 will be the same.

* Selection rules for Rotation-Vibration transitions:—

A molecule on absorbing the radiation corresponding to the vibrational excitation may simultaneously be accompained by the change in the rotational level. The spectrum exhibiting such transition is known as Vibration-Rotation spectrum. The selection rules for such transitions are the same as those for each separetly. Thus —

$$\Delta v = \pm 1, \pm 2, \text{ etc.}$$

$$\Delta J = \pm 1.$$

Since, $\Delta J \neq 0$ not allowed. It follows that a vibrational change will always be accompained by a simultaneous rotational change. However Δv may have zero value. But this correspond to the purely rotational transitions.

*. Expression of Vibrational-Rotational Energies:—

An analytical expression for the spectrum may be obtained by applying the selection rules i.e. $\Delta v = \pm 1, \pm 2$ & $\Delta J = \pm 1$ to the energy levels expression. —(1)

Let us consider the transition

$$v = 0 \longrightarrow v = 1$$

$$\Delta \epsilon_{J,v} = \epsilon_{J', v=1} - \epsilon_{J'', v=0}$$

$$\Delta \epsilon_{J,v} = BJ'(J'+1) + (1+\tfrac{1}{2})\bar{\omega_e} - x_e(1+\tfrac{1}{2})^2\bar{\omega_e} - \{BJ''(J''+1) + (0+\tfrac{1}{2})\bar{\omega_e} - x_e(0+\tfrac{1}{2})^2\bar{\omega_e}\}$$

$$\Delta e_{J,v} = BJ'(J'+1) + \tfrac{3}{2}\bar{\omega_e} - \tfrac{9}{4} x_e \bar{\omega_e} - \left\{ BJ''(J''+1) + \tfrac{1}{2}\bar{\omega_e} - \tfrac{1}{4} x_e \bar{\omega_e} \right\}$$

$$\Delta e_{J,v} = BJ'(J'+1) + \tfrac{3}{2}\bar{\omega_e} - \tfrac{9}{4} x_e\bar{\omega_e} - BJ''(J''+1) - \tfrac{1}{2}\bar{\omega_e} + \tfrac{1}{4} x_e\bar{\omega_e}$$

$$\Delta e_{J,v} = BJ'(J'+1) - BJ''(J''+1) + \tfrac{3}{2}\bar{\omega_e} - \tfrac{1}{2}\bar{\omega_e} - \tfrac{9}{4} x_e\bar{\omega_e} + \tfrac{1}{4} x_e\bar{\omega_e}$$

$$\Delta e_{J,v} = BJ'(J'+1) - BJ''(J''+1) + \bar{\omega_e} - 2\bar{\omega_e} x_e$$

$$\Delta e_{J,v} = BJ'(J'+1) - BJ''(J''+1) + \bar{\omega_e}(1-2x_e)$$

$$\Delta e_{J,v} = BJ'(J'+1) - BJ''(J''+1) + \bar{\omega_0}$$

[where $\bar{\omega_0} = \bar{\omega_e}(1-2x_e)$]

$$\Delta e_{J,v} = B\left\{ J'^2 + J' - J''^2 - J'' \right\} + \bar{\omega_0}$$

$$\Delta E_{J,v} = B\left\{ J'^2 - J'J'' + J'J'' - J''^2 + J' - J'' \right\} + \bar{\omega_0}$$

$$\Delta e_{J,v} = B\left\{ J'(J'-J'') + J''(J'-J'') + (J'-J'') \right\} + \bar{\omega_0}$$

$$\Delta E_{J,v} = B(J'-J'')(J'+J''+1) + \bar{\omega_0}$$

$$\boxed{\Delta E_{J,v} = \bar{\omega_0} + B(J'-J'')(J'+J''+1)}$$

Now we have—

(1). $\Delta J = \pm 1$ if $\Delta J = +1$ then—

$J' = J''+1$

or $J' - J'' = 1$

Hence, $\Delta e_{J,v} = \bar{\omega_0} + B \times 1 (J'+J')$ since, $(J' = J+1)$

$$\Delta E_{J,V} = \omega_{\bar{o}} + 2BJ'$$

Hence, $\Delta E_{J,V} = \omega_{\bar{o}} + B(2J''+2)$

$$\boxed{\Delta E_{J,V} = \omega_{\bar{o}} + 2B(J''+1)\ cm^{-1}}$$

where, $J'' = 0, 1, 2 \ldots\ldots$

(2). $\Delta J = \pm 1$ if $\Delta J = -1$ then –

$$J'' = J'+1$$

or $J' - J'' = -1$

Hence,

$$\Delta E_{J,V} = \omega_{\bar{o}} + B(-1)(J'+J'+1+1)$$

$$\boxed{\Delta E_{J,V} = \omega_{\bar{o}} - 2B(J'+1)\ cm^{-1}}$$

where, $J' = 0, 1, 2 \ldots\ldots$

These two expression may conveniently be combined in to –

$$\boxed{\Delta E_{J,V} = \omega_{\bar{o}} \pm 2Bm\ cm^{-1}}$$

$m = \pm 1, \pm 2, \ldots\ldots$

where $m = J''+1$

& $m = J'+1$

*. NOTE :-

'm' cannot be zero. Since, this would empty values of J' or J'' to be -1.

Since, $m = J''+1$ & $m = J'+1$

if $J''=0$ & where, $m = -1+1 = 0$.