

$$V_0 + (J''+1) \left[ B'' J'' - B' (J''+1) \right] cm^{-1} \quad (A)$$

$$V_0 + (J''+1) \left[ (B'' J'' + B'' - B') - B' \right] (J''+1) + B' J''^2 cm^{-1}$$

$$= V_0 + (J''+1) \left[ B'' (J''+1) - B'' - B' (J''+1) - B' \right] cm^{-1}$$

$$= V_0 + (J''+1) \left[ (J''+1)(B'' - B') - (B'' + B') \right]$$

$$= V_0 + \left[ (B'' - B') (J''+1)^2 - (B'' + B') (J''+1) \right] cm^{-1}$$

11) Vibrational structure:

In order to explain vib. etc. in a band system, we must consider contribution due to changes in vibrational energy.

$$E_{vib} = (v + \frac{1}{2}) h \nu_0 - (v + \frac{1}{2})^2 h \nu_0 x$$

Where  $\nu_0$  = fundamental vibration.

$x$  = anharmonicity constant.

the vib. energy for initial ( $v'$ ) and final ( $v''$ ) state would be

$$E'_{vib} = (v' + \frac{1}{2}) h \nu_0' - (v' + \frac{1}{2})^2 h \nu_0' x'$$

$$E''_{vib} = (v'' + \frac{1}{2}) h \nu_0'' - (v'' + \frac{1}{2})^2 h \nu_0'' x''$$

$$\therefore \nu_{vib} = \frac{E''_{vib} - E'_{vib}}{h}$$

$$= \left[ \nu_0'' \left\{ (v'' + \frac{1}{2}) - (v'' + \frac{1}{2})^2 x'' \right\} - \nu_0' \left\{ (v' + \frac{1}{2}) - \frac{(v' + \frac{1}{2})^2}{(v' + \frac{1}{2})^2 x'} \right\} \right]$$

$$\nu_{vib} = \nu_0'' (v'' + \frac{1}{2}) - \nu_0'' x'' (v'' + \frac{1}{2})^2 - \nu_0' (v' + \frac{1}{2}) + \nu_0' x' (v' + \frac{1}{2})^2$$

Adding and subtracting  $\nu_0'' \nu'$  and rearranging, we get

$$\nu_{vib} = \left[ (v'' - v') \nu_0'' + (v' + \frac{1}{2}) (\nu_0'' - \nu_0') - \left\{ (v'' + \frac{1}{2})^2 \nu_0'' x'' - (v' + \frac{1}{2})^2 \nu_0' x' \right\} \right] \text{cm}^{-1}$$

$$\bar{\nu}_{obs} = \frac{2\nu_0 \nu'}{\bar{\nu}} = \left[ \frac{(\nu_0'' - \nu_0') \nu_0''}{\bar{\nu}} + \frac{(\nu_0' + \frac{1}{2}) (\nu_0'' - \nu_0')}{\bar{\nu}} \right] - \left\{ \frac{(\nu_0'' + \frac{1}{2})^2 \nu_0'' \nu_0'}{\bar{\nu}} \right\} \text{ cm}^{-1}$$

In the above equation.

The first term of R.H side is the principal term. It will have diff. values for the diff. values of  $\nu''$  and  $\nu'$

If  $\nu'' - \nu' = \Delta\nu = 1$ . We have the fundamental vibration

$\Delta\nu = 2 \rightarrow$  first harmonic and so on. It is these diff. quantum transitions that give rise to diff. group of bands in band system.

The second term is smaller as compared to first term by keeping first term fixed and varying the value of  $\nu'$ . We obtain a number of partial bands in a particular group.

The III term of the above equation is still smaller. This term causes the unequal spacing of the band groups.

### Electronic structure:

For complete interpretation of electronic band spectrum we must take into account contribution of the frequency due to

Change in electronic energy.

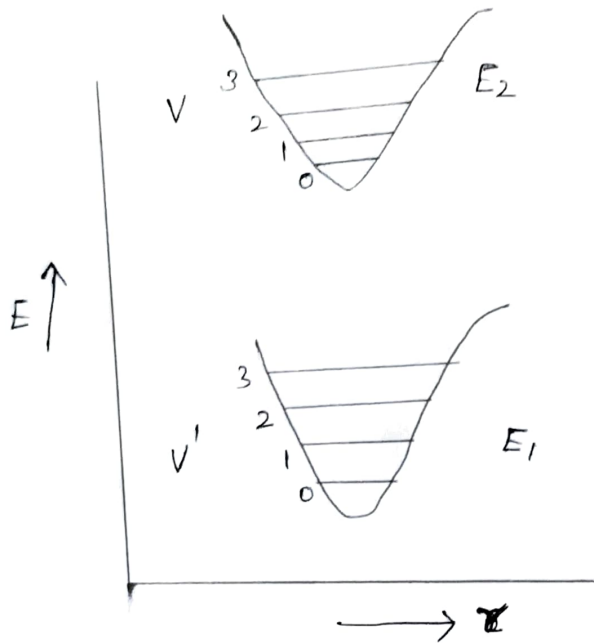
$$\bar{\nu} = \bar{\nu}_{ele} + \bar{\nu}_{vib} + \bar{\nu}_{rot}$$

the electronic frequency,  $\bar{\nu}_{ele}$  of the molecule may have several diff. values, corresponding to diff. electronic transition. The molecule can show several band system.

The e's outside the closed shells act as optical e's of the molecule responsible for the observed band spectra.

Condon principle: (or) Potential energy curves (6)

The way in which the potential energy of a diatomic molecule varies with the internuclear distance in two different electronic levels.

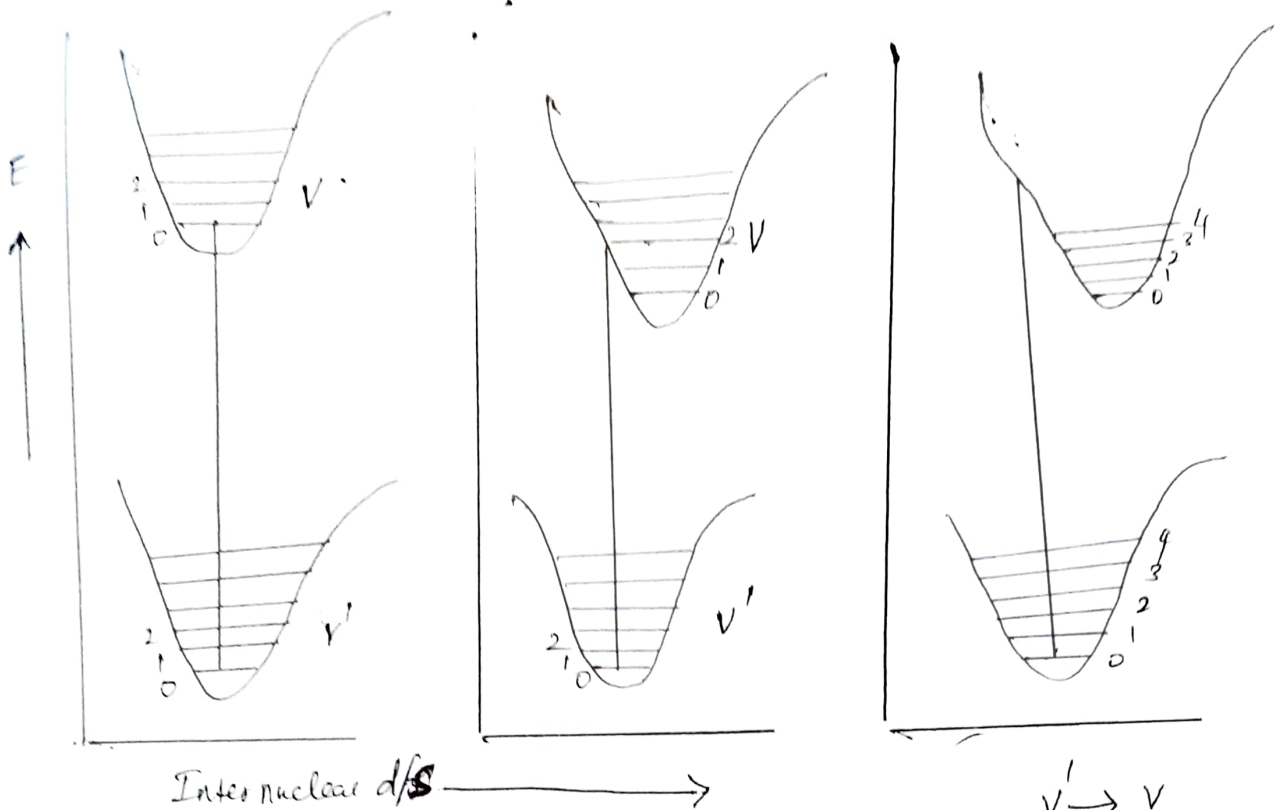


$E$  = Energy     $r$  = internuclear distance;  $E_1$  = G.S. eb. level.  
 $E_2$  = Ex. state. eb. level     $v'$  = vib. levels in the g.s. eb. level.  
 $V$  = Vib level in the e.s. electronic level     $0, 1, 2, 3, \dots$  = Vib. g. nos.

Considering transitions from one electronic level ( $E_1$ ) to the other ( $E_2$ ), three factors decide which transition takes place and from where to where.

- i) Selection rules:  $\Delta V = 0, \pm 1, \pm 2, \dots$
- ii) As an electronic transition in a molecule takes place so rapidly compared to the vibrational motion of the nuclei, that the inter-nuclear distance can be regarded as fixed during the transition. Therefore the transition occurs vertically as shown in the diagram.
- iii) Electronic transitions are more probable if they begin or end at the middle of  $v=0$  or at either end of any of the higher vib. levels.

Under the three factors given, the expected electronic transitions may be represented as in the following figures.



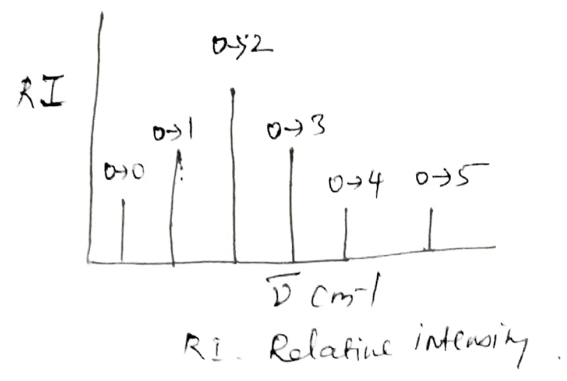
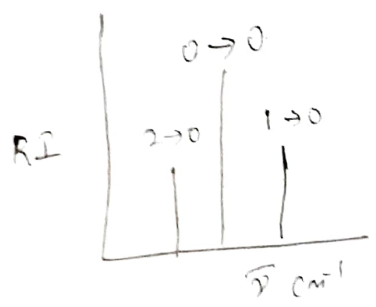
a)  $V' \rightarrow V$   
 $0 \rightarrow 0$   
 Both upper & lower energy state has same inter nuclear  $d/s$ .

b)  $V' \rightarrow V$   
 $0 \rightarrow 2$   
 upper state has slightly greater Internuclear  $d/s$

c)  $V' \rightarrow V$   
 $0 \rightarrow 4$   
 upper state has largest Internuclear  $d/s$ .

Spacial line  $(0,0)$  will be more intense than  $(1,0)$   $(2,0)$  etc.

The most probable transition is  $0 \rightarrow 1, 2, 3$  the other transitions are less probable.



RI. Relative intensity.

consider the fig (c). In this case upper electronic state has much larger inter atomic rep<sup>n</sup> than that of lower electronic state. The most stable transition leads to a state in which the excited molecule has an energy greater than that required for dissociation. The excited molecule splits up into atoms. Since the released atoms can take up any amount of kinetic energy. and result into continuous absorption band. (8)

From the above discussion based on the Franck Condon Principle it is clear that, the most intense transition from  $v' = 0$  is always that corresponding to an electronic transition from the minimum of the lower p.e curve vertically upward.