

## Non Rigid Rotator

The Schrodinger wave equation may be set up for a non-rigid molecule and the rotational energy levels are found to be

$$E_J = \frac{h^2}{8\pi^2 I} J(J+1) - \frac{h^4}{32\pi^4 I^2 r^2 k} J^2 (J+1)^2$$

$$\text{or } \epsilon_j = \frac{E_J}{hc} = B J(J+1) - D J^2 (J+1)^2 \text{ cm}^{-1} \quad (1)$$

$$\text{where } B = \frac{h}{8\pi^2 I} \text{ cm}^{-1}$$

$J$  = rotational quantum number

$D$  is called centrifugal distortion constant

$$D = \frac{h^3}{32\pi^4 I^2 r^2 k} \text{ cm}^{-1} \quad (2)$$

which is a positive quantity. Equation (1) applies for a simple harmonic force field only; if the force field is anharmonic, the expression become

$$\epsilon_j = B J(J+1) - D J^2 (J+1)^2 + H J^3 (J+1)^3 + K J^4 (J+1)^4 \dots \text{ cm}^{-1} \quad (3)$$

where  $H, K$  etc are small constants depend upon the geometry of the molecule. They are however, negligible compared with  $D$  and most modern spectroscopic data are adequately fitted by equation (1)

$$\cancel{D = \frac{h^3}{32\pi^4 I^2 r^2 k} \text{ cm}^{-1}}$$

The order of  $D$ , being of the order  $10^{-3} \text{ cm}^{-1}$ , is very small compared with  $B$ . Thus the term  $D J^2 (J+1)^2$  almost negligible compared to  $B$ .

The selection rule for the Non-rigid rotor  $\Delta J = \pm 1$

Thus, analytical expression for the transition

$$\begin{aligned} \epsilon_{J+1} - \epsilon_J &= \bar{\nu}_J = B [(J+1)(J+2) - J(J+1)] \\ &\quad - D [(J+1)^2 (J+2)^2 - J^2 (J+1)^2] \\ &= 2B(J+1) - 4D(J+1)^3 \text{ cm}^{-1} \quad \text{--- (4)} \end{aligned}$$

where  $\bar{\nu}_J$  represents equally the upward transition from  $J$  to  $J+1$  or the downward transition from  $J+1$  to  $J$ .

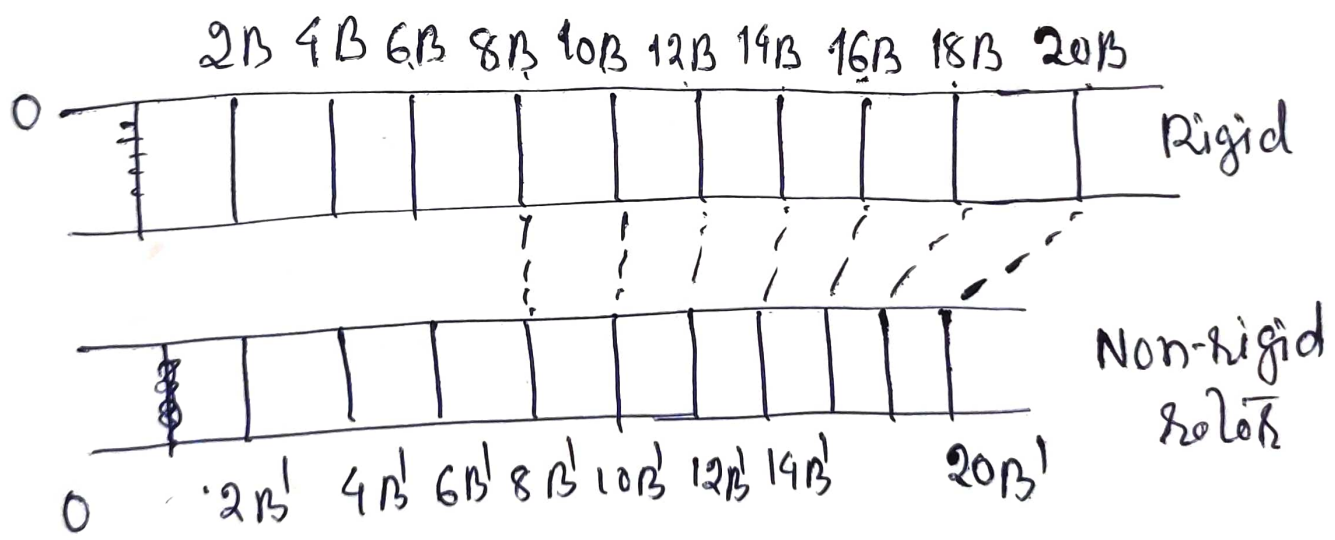
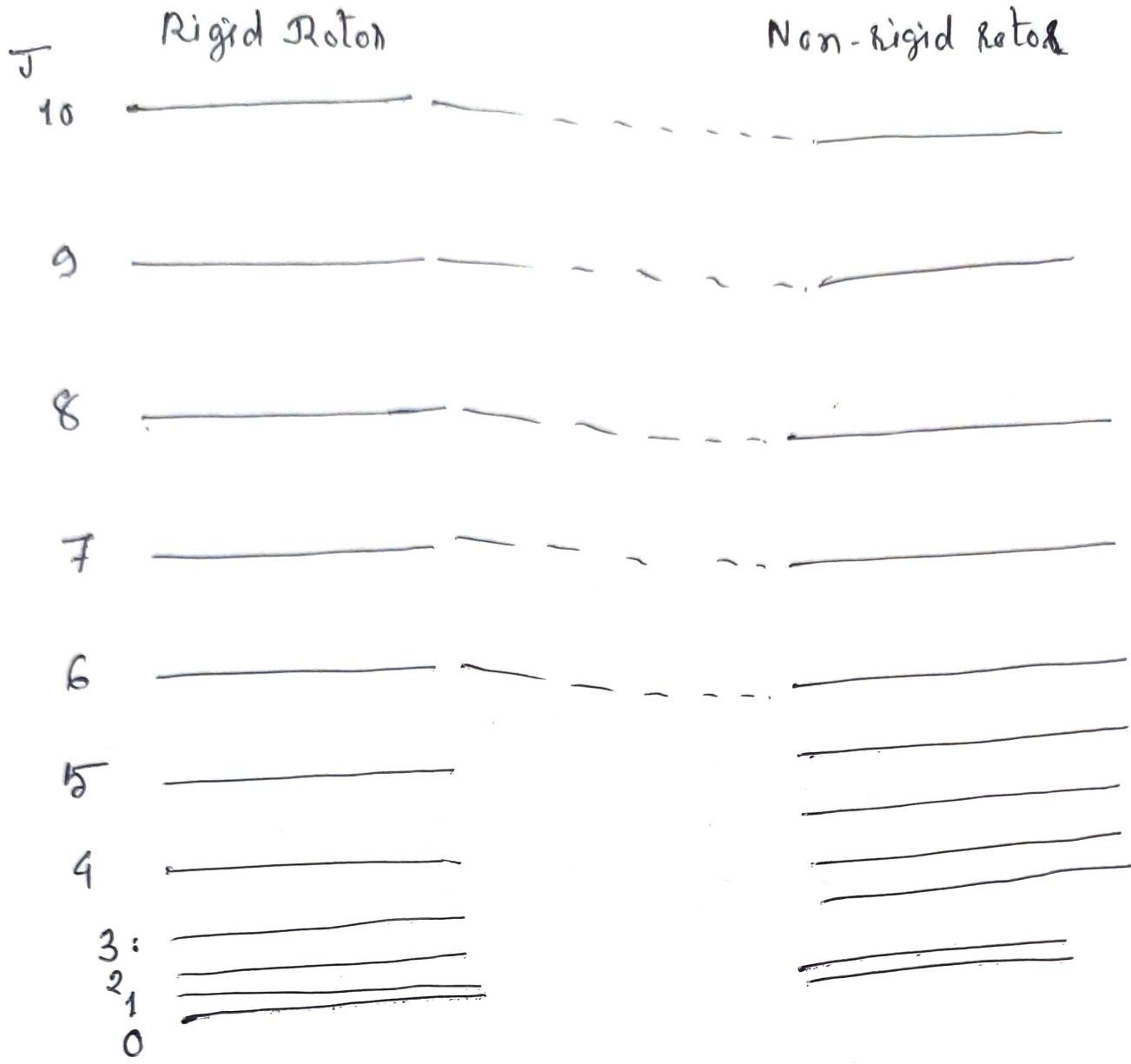


Figure The change in rotational energy levels and spectrum when passing from a rigid to non rigid diatomic molecule. Energy levels are calculated using  $D = 10^{-3} B$ .