

Unit I; Non-rigid Rotator

To assume that a bond is rigid is only an approximation. Actually all bonds are elastic to some extent and as the value of rotational quantum number, J , increases, due to centrifugal force tending to move the atoms apart, bond length increases.

As a result —

- (a) a molecule may have vibrational energy, and,
- (b) rotational constant 'B' and bond length vary.

Real vibrations are not simple harmonic and Schrödinger equation for a non-rigid molecule gives

$$E_J = \bar{B} \cdot hc \cdot J(J+1) - \bar{D} \cdot hc \cdot J^2(J+1)^2.$$

where, \bar{D} = centrifugal distortion constant.

and

$$\begin{aligned} \bar{D} &= \frac{E_J}{hc} \\ &= \bar{B} \cdot J(J+1) - \bar{D} \cdot J^2(J+1)^2. \end{aligned}$$

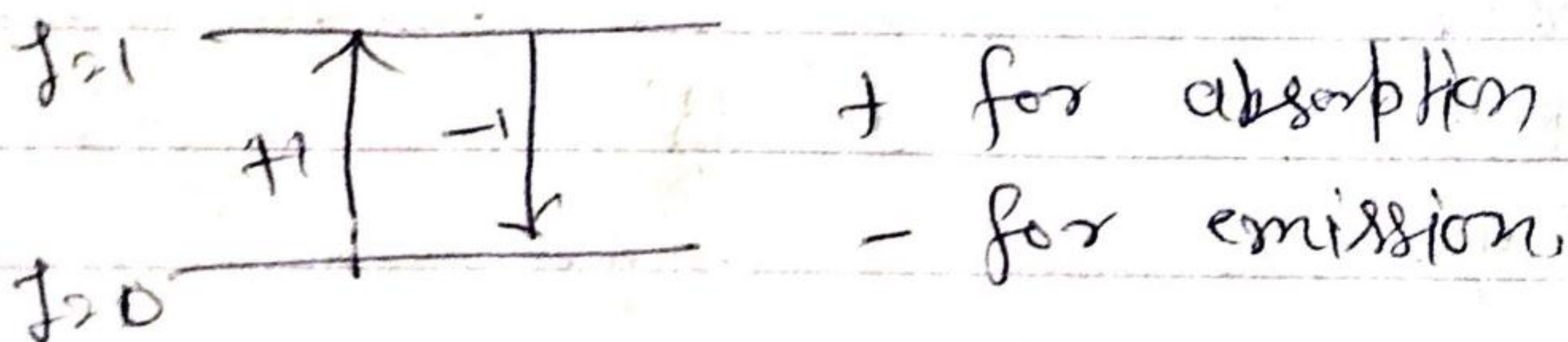
For small 'j' value distortion constant is almost negligible, and

$$\bar{\nu} = \bar{B} j(j+1).$$

selection rule —

only such transitions are possible in which —

(i) $\Delta j = \pm 1$



(ii) molecule must have permanent dipole moment.

Transition \rightarrow
for the transition

$$j+1 \leftarrow j.$$

$$\Delta \bar{\nu} = \bar{\nu}_{j+1} - \bar{\nu}_j.$$

$$\bar{\nu}_{j+1} = \bar{B}(j+1)(j+1+1) - \bar{D}(j+1)^2(j+2)^2$$

$$\bar{\nu}_j = \bar{B}j(j+1) - \bar{D}j^2(j+1)^2$$

$$\Delta\bar{\nu} = \bar{\nu}_{j+1} - \bar{\nu}_j$$

$$= \bar{B}(j+1)(j+2) - \bar{D}(j+1)^2(j+2)^2$$

$$- \{ \bar{B}j(j+1) - \bar{D}j^2(j+1)^2 \}$$

$$= \{ \bar{B}(j+1)(j+2) - \bar{B}j(j+1) \}$$

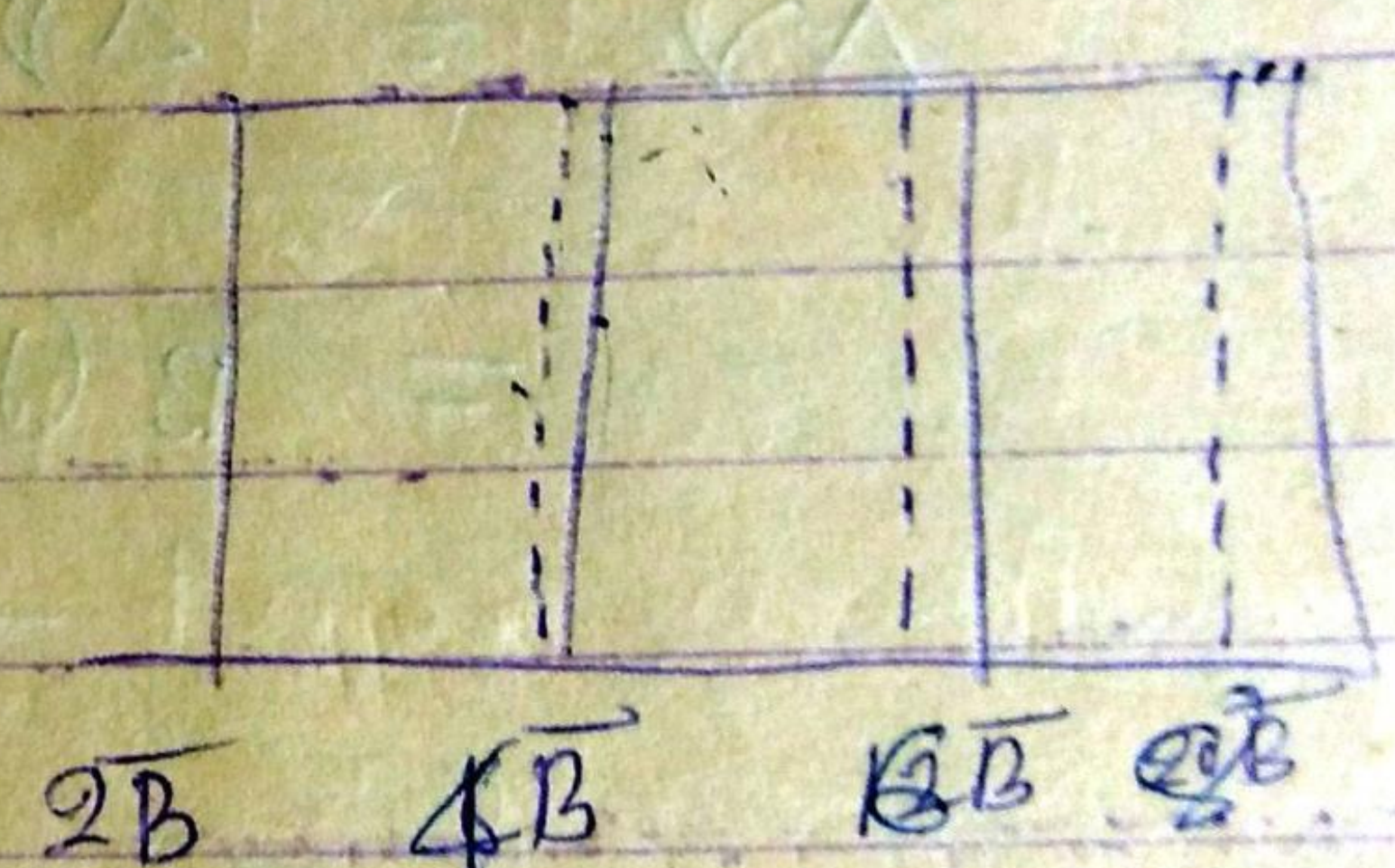
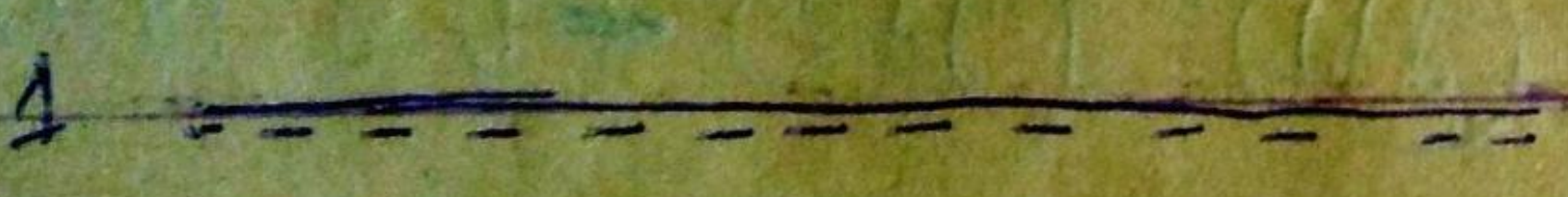
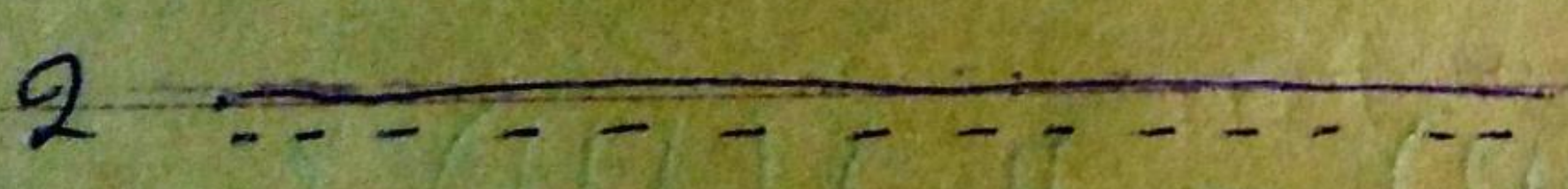
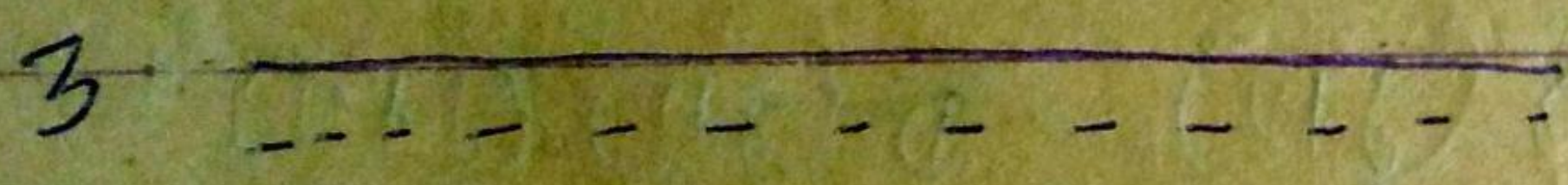
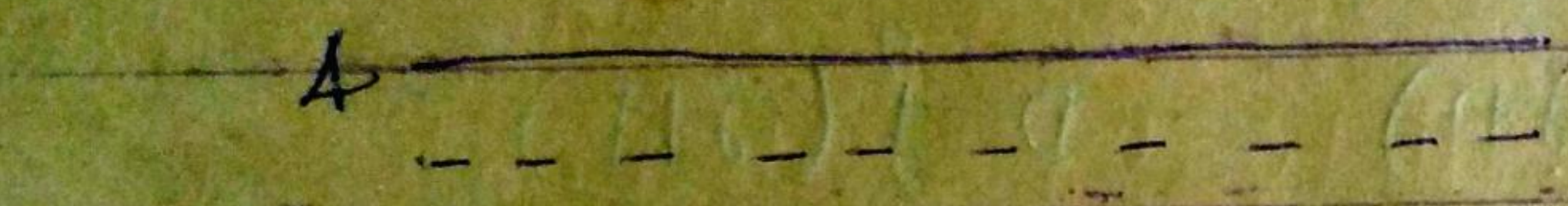
$$- \{ \bar{D}(j+1)^2(j+2)^2 - \bar{D}j^2(j+1)^2 \}$$

$$= 2\bar{B}(j+1) - \bar{D}(j+1)^2 \cdot 4(j+1)$$

$$= 2\bar{B}(j+1) - 4\bar{D}(j+1)^3 \quad \text{cm}^{-1}$$

Thus, the rotational spectrum of elastic rotator is similar to that of a rigid rotator except that each rotational line is displaced slightly to low frequency.

Dot Spectrum



$2B$ $4B$ $6B$ $8B$
 --- for non-rigid rotator
 — for rigid rotator