

Rotational or Microwave Spectra

Molecular spectra in far IR and beyond is known as rotational or MW spectra. It is produced in the frequency range $\bar{\nu} = 1$ to 10^2 cm^{-1} .

Rotational energy of a molecule is quantized. It depends on shape and size of the molecule. Rotational energy levels are characterized and determined by the rotational quantum no.

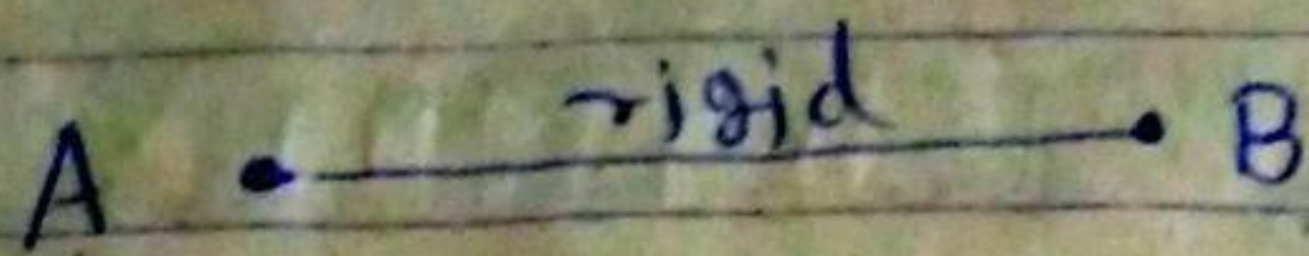
(J)

$$J = 0, 1, 2, 3, \dots$$

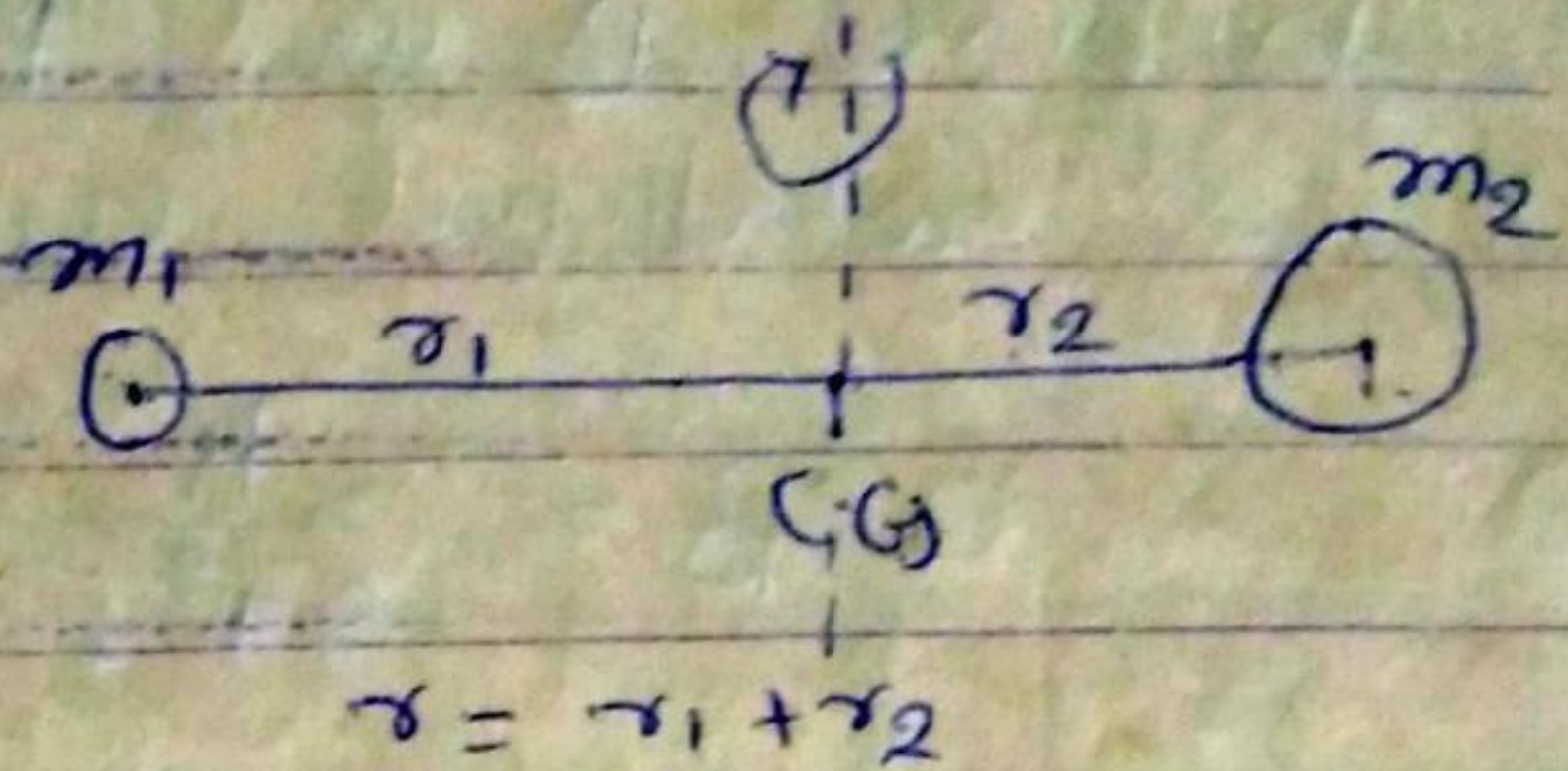
Rigid diatomic molecule

In a rigid rotator two rotating ~~system~~ ~~rotator~~ on a rigid rotator two mass points are connected by a massless rigid bar.

In Non-rigid rotator two ~~points~~ mass points are connected by a massless spring.



For a rigid diatomic molecule \Rightarrow



$$\text{Reduced mass } (\mu) = \frac{m_1 m_2}{m_1 + m_2}$$

The molecule has a natural rot. about the axis through its centre of gravity.

$$\therefore \text{Moment of inertia } (I) = \mu r^2$$

$$\text{Angular momentum } (P) = I \omega$$

$$P = I \omega = \sqrt{j(j+1)} \cdot \frac{h}{2\pi}$$

on calculation by Schrödinger equation.

$$\begin{aligned} \text{Rotational energy } (E) &= \frac{1}{2} I \omega^2 \\ &= \frac{1}{2I} I^2 \omega^2 = \frac{1}{2} I P^2 \\ &= \frac{1}{2I} \cdot \frac{h^2}{4\pi^2} (j(j+1))^2 \\ &= \frac{h^2}{8\pi^2 I} j(j+1) \\ &= B h j(j+1) \end{aligned}$$

$$\text{or } E = B h J(J+1) \\ = B h c J(J+1)$$

where B and \bar{B} is known as rotational constant

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

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

Frequency of spectral line

$$E = h \nu$$

$$\therefore \nu = E/h \text{ sec}^{-1}$$

$$\text{sec}^{-1} = \frac{B h J(J+1)}{h} = B J(J+1) \text{ sec}^{-1} \\ = B c J(J+1) =$$

$$E = h c \bar{\nu}$$

$$\therefore \bar{\nu} = \frac{E}{h c}$$

$$\text{cm}^{-1} = \frac{B h J(J+1)}{h c}$$

$$= \frac{B}{c} J(J+1)$$

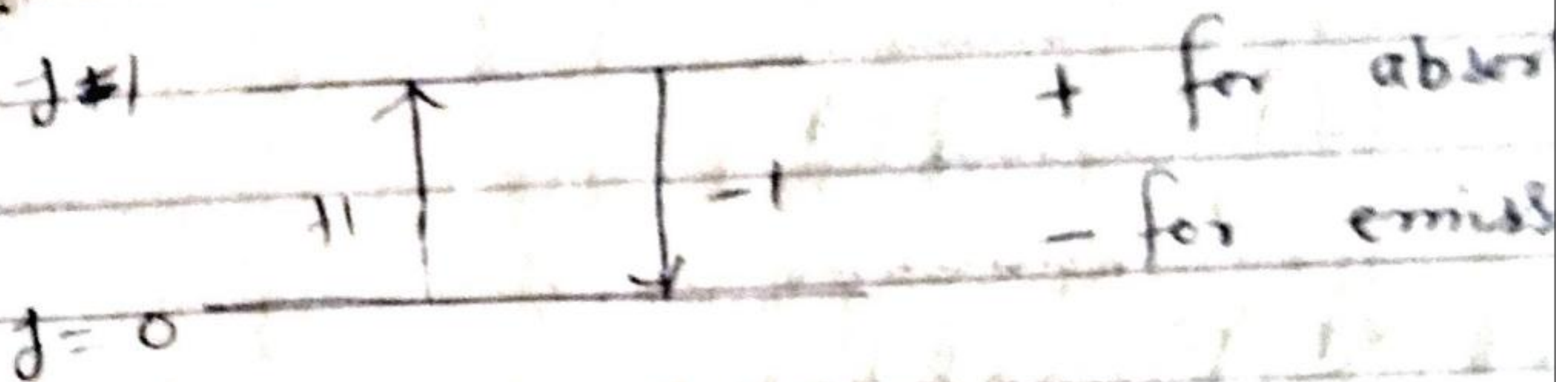
$$= B J(J+1)$$

$$B = \frac{h^2}{8\pi^2 I}$$

Selection Rule —

only such transitions allowed

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



(ii) in which the molecule has a dipole moment. e.g. HCl , CO etc. are polar and O_2 , CO_2 , $(\mu=0)$ etc. are non-polar.

Allowed rotational state or rotational levels: \rightarrow

For the transition

$$j+1 \leftarrow j$$

$$E_{(j+1)} = Bhc (j+1)(j+1+1)$$

and $E_{(j+1)} = Bhc (j+1)(j+2)$

$$E_j = Bhc j(j+1)$$

$$\therefore \Delta E = Bhc (j+1) \times 2$$

$j=0$

where $J = \text{lower value}$

Thus,

J	E_J	$\bar{\nu} \text{ (cm}^{-1}\text{)}$	$\Delta\bar{\nu}$	Frequency separation between the lines rotational lines.
0	0	0	0	
1	$2\bar{B}hc$	$2\bar{B}$	$2\bar{B}$	$2\bar{B}$
2	$6\bar{B}hc$	$6\bar{B}$	$4\bar{B}$	$2\bar{B}$
3	$12\bar{B}hc$	$12\bar{B}$	$6\bar{B}$	$2\bar{B}$
4	$20\bar{B}hc$	$20\bar{B}$	$8\bar{B}$	$2\bar{B}$
5	$30\bar{B}hc$	$30\bar{B}$	$10\bar{B}$	

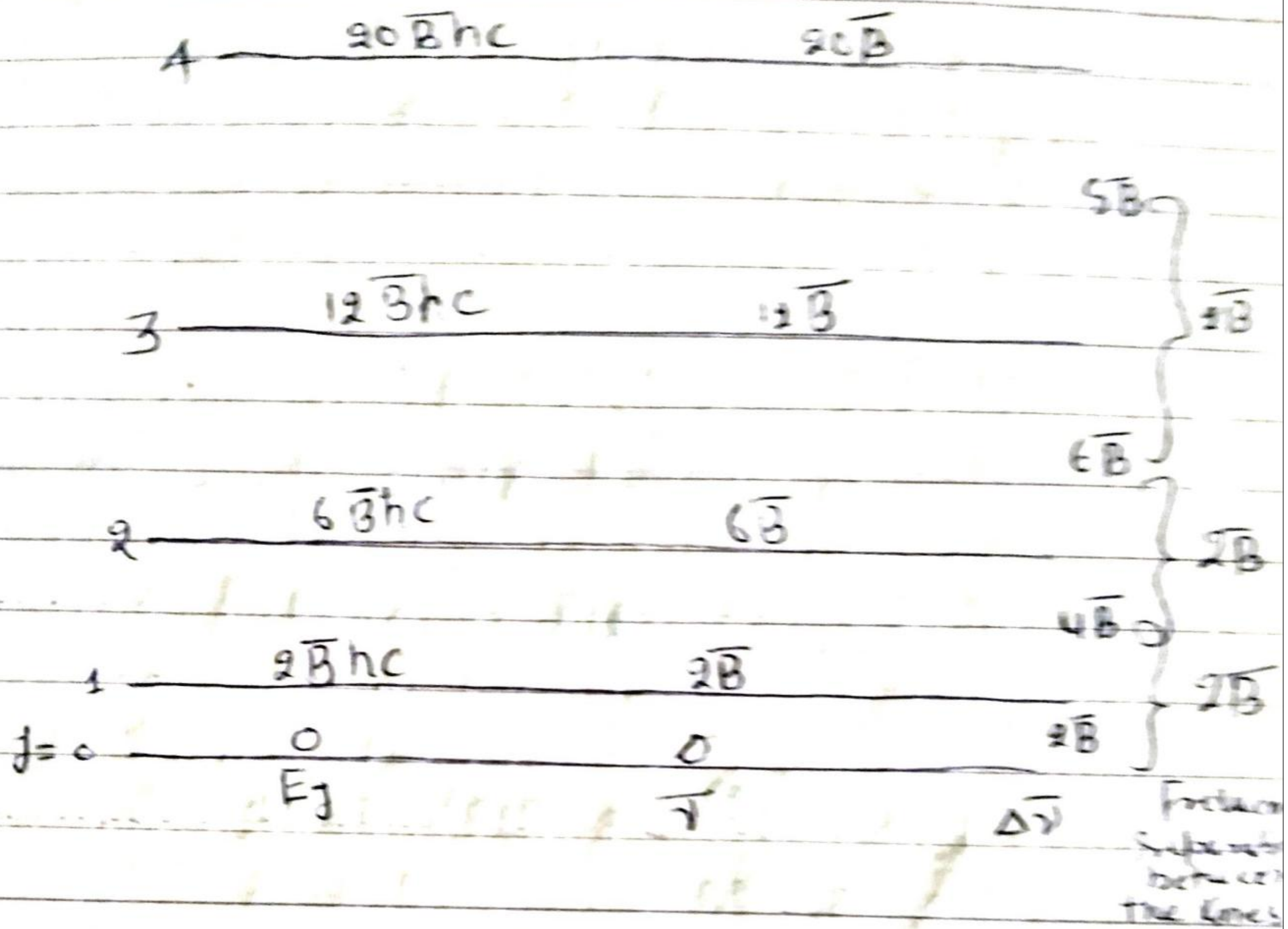
For the transition

$$J+1 \leftarrow J$$

$$\bar{\nu}_{J+1} = \bar{B}(J+1)(J+2)$$

$$\bar{\nu}_J = \bar{B}J(J+1)$$

$$\Delta\bar{\nu} = 2\bar{B}(J+1)$$



Rotational Spectra of a rigid diatomic molecule \rightarrow

