

Rotational Spectroscopy.

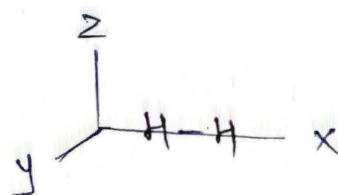
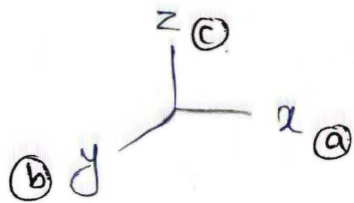
Types of rotational molecules -

1. Linear
2. Spherical tops
3. Symmetric tops \Rightarrow Prolate
 \Rightarrow Oblate
4. Asymmetric tops.

1. Linear -

$$(I_a = 0, I_b = I_c)$$

(I = moment of Inertia.)



ex. H_2 , HCl , DCS , CO_2 , O_2 , HCN .

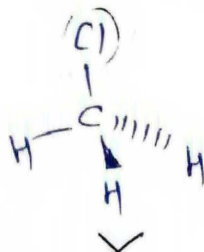
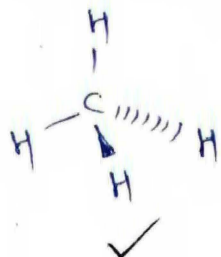
2. Spherical tops -

$$(I_a = I_b = I_c)$$

ex. Perfect T_d and O_h molecules.

(Ligands / atoms attached are same.)

ex. CH_4 , SF_6 , NH_4^+ , UF_6 , P_4



3. Symmetric tops -

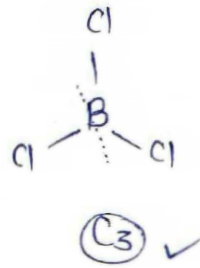
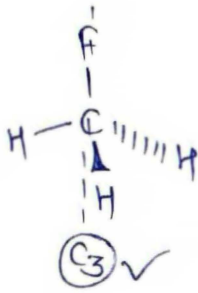
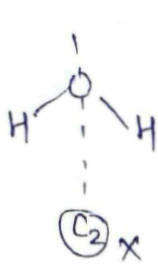
Conditions - ① $n \geq 3$

C_n -axis

ex. C_3, C_4, C_5, \dots

② C_2 -axis + S_4 -axis. \Rightarrow ex. allene

ex.



Symmetric tops

Prolate

(Shuttle cork type)

$(I_b = I_c > I_a)$


ex. CH_3F, CH_3CN

$H_3C-C \equiv CH, \text{allene}$

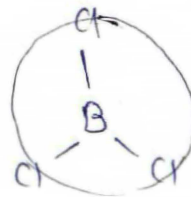
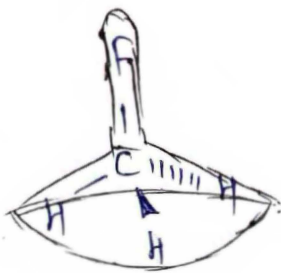
Oblate

(Disc type)

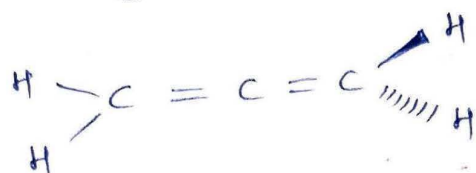
$(I_b = I_c < I_a)$

ex. $BCl_3,$ 

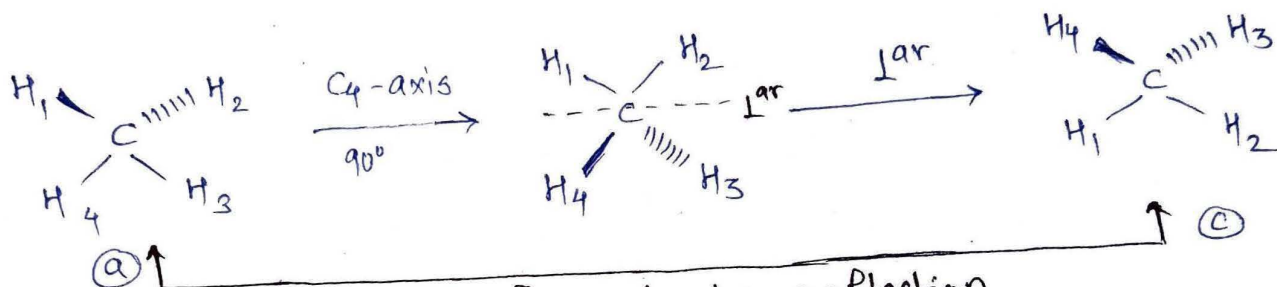
$NH_3,$ 



* Allene System -



Consider as -



Rotation followed by reflection.

a and c are equivalent.

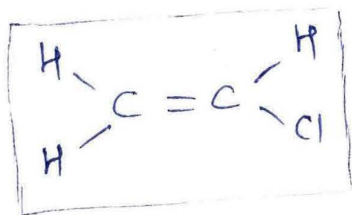
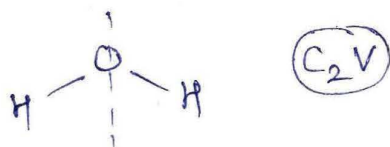
⇒ S₄-axis.

4. Asymmetric tops -

Conditions - C_{nh}, C_{2v}, C_s.

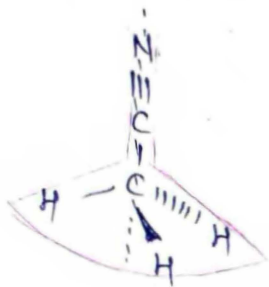
(I_a ≠ I_b ≠ I_c)

ex. H₂O, H₂C = CHCl, NO₂, H₃BO₃, anthracene.



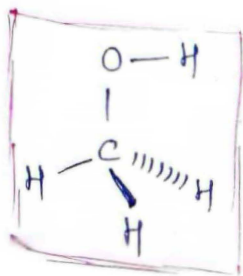
← plane of symmetry.
(C_s)

Que. What is the type of molecules -
 CH_3CN , CH_3OH



(C_3)

Symmetric Top
(Prolate)



(C_s)

Asymmetric Top.

Radiation used in rotational spectroscopy -

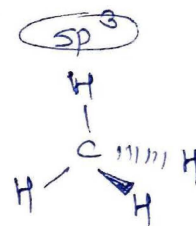
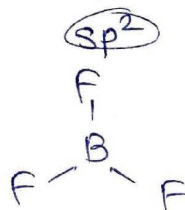
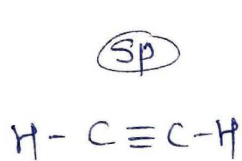
Microwave

Microwave active molecules -

⇒ dipole moment $\neq 0$.

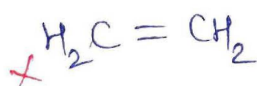
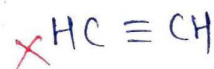
⇒ Perfect molecules are inactive in microwave.

↳ All ligands/atoms attached must be same.
No presence of lone pair.



microwave inactive.

Que. Which of the following are ^{microwave} active?



Rotational spectroscopy of diatomic molecules -

$$E = \frac{h^2}{8\pi^2 I} J(J+1) \quad \text{Joules.}$$

J = energy levels.

0, 1, 2, 3, ..., n

I = moment of inertia.

Conversion - $J \rightarrow \text{cm}^{-1}$

$$\frac{J}{h \cdot c} = \frac{J}{I \cdot 8 \times 10^{10} \text{ cm} \cdot \text{s}^{-1}} = \text{cm}^{-1}$$

$6.626 \times 10^{-34} \text{ Js}$ $3 \times 10^{10} \text{ cm} \cdot \text{s}^{-1}$

$$\Rightarrow \frac{E}{hc} = E' = \frac{h^2}{8\pi^2 I \times hc} \cdot J(J+1) \quad \text{cm}^{-1}$$

$$E' = \frac{h}{8\pi^2 I c} J(J+1) \quad \text{cm}^{-1}.$$

B = rotational constant.

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

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

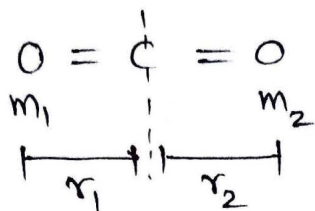
$$E' = B \cdot J(J+1) \quad \text{cm}^{-1}$$

or

$$E = B \cdot J(J+1) \quad \text{Joules.}$$

Moment of Inertia-

① Case I



Here, $m_1 = m_2$

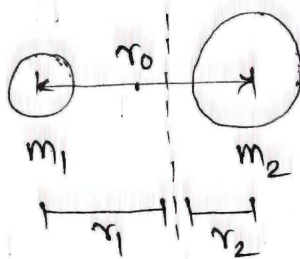
$r_1 = r_2$

$$\text{Moment of inertia (I)} = m_1 r_1^2 + m_2 r_2^2$$
$$= m_1 r_1^2 + m_1 r_1^2$$

$$\boxed{I = 2m_1 r_1^2}$$

② Case II

H-CI



$$\boxed{I = \mu r_0^2}$$

$$\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2}$$

$$\boxed{\mu = \frac{m_1 m_2}{m_1 + m_2}}$$

Rigid Rotator case -

Here, we consider value of B is constant.
Value of B is same at each ene. level.

Energy level diagram -

$$E = \frac{h}{8\pi^2 I c} J(J+1) \text{ cm}^{-1}$$

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

Rotational quantum number (J) = 0, 1, 2, ..., n .

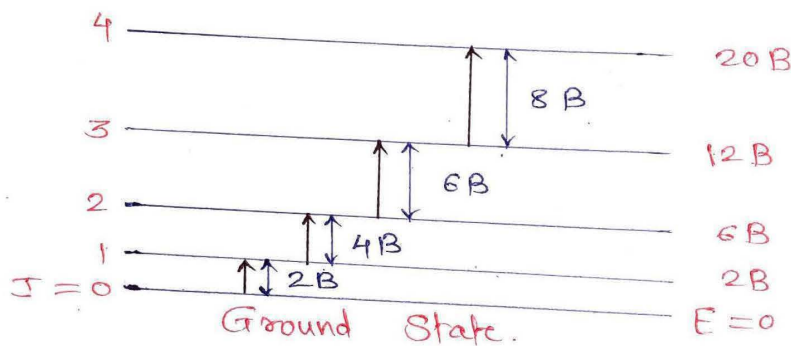
At $J=0$, $E=0$

$J=1$, $E_1 = B(1)(1+1) = 2B$

$J=2$, $E_2 = B(2)(2+1) = 6B$

$J=3$, $E_3 = B(3)(3+1) = 12B$

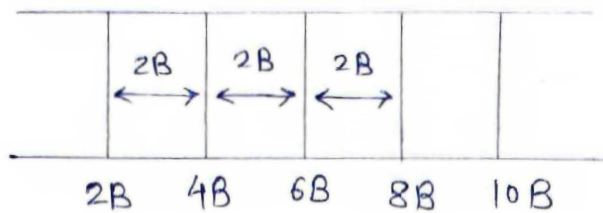
$J=4$, $E_4 = B(4)(4+1) = 20B$



Theoretically, as value of J increases, ene. increases and speed of rotations increases without breaking the bond.

But in actual, above room temp. with increase in ene. centrifugal force dominates over bond strength. & at certain energy bond breaks.

Rotational spectra - Due to excitations



ΔE Calculation -

Energy difference between two successive rotational energy levels.

Consider a transition,

$$J \rightarrow J+1.$$

$$\Rightarrow E_J = B J (J+1)$$

$$\Rightarrow E_{J+1} = B (J+1) (J+1+1)$$

$$\therefore \Delta E = E_{J+1} - E_J$$

$$= B (J+1) (J+2) - B J (J+1)$$

$$= B (J+1) (\cancel{J} + 2 - \cancel{J})$$

$$\boxed{\Delta E = 2B (J+1)}$$

→ lower ene. level.

$$\Delta E = 2B(J+1)$$

Ques. transition - $J=10 \rightarrow J=11$

$$\Delta E = 2207 \text{ cm}^{-1}$$

$$B = ?$$

Ans.

$$\Delta E = 2B(J+1)$$

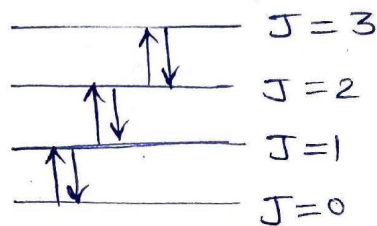
$$2207 = 2B(10+1)$$

$$B = \frac{2207}{22} \text{ cm}^{-1}$$

Intensity of spectral lines -

⇒ Selection rule for possible transitions -

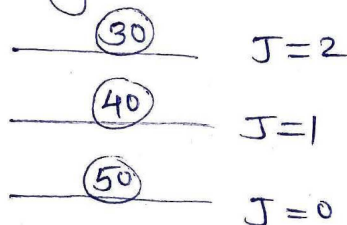
$$\Delta J = \pm 1$$



Probability of transition from $J=0 \rightarrow J=1$ is equal to that of from $J=1 \rightarrow J=2$ and so on. Hence, Intensity cannot be determined by selection rule.

⇒ Intensity depends on population difference.

According to Boltzmann distribution law, Lower energy level has higher no. of molecules / population density.



degeneracy

$$\frac{N_J}{N_0} = \frac{g_J}{g_0} e^{-\Delta E / k_B T}$$

Population in higher ene. level

lower ene. population

energy population difference

Boltzmann constant.

$$(1.38 \times 10^{-23} \text{ J K}^{-1})$$

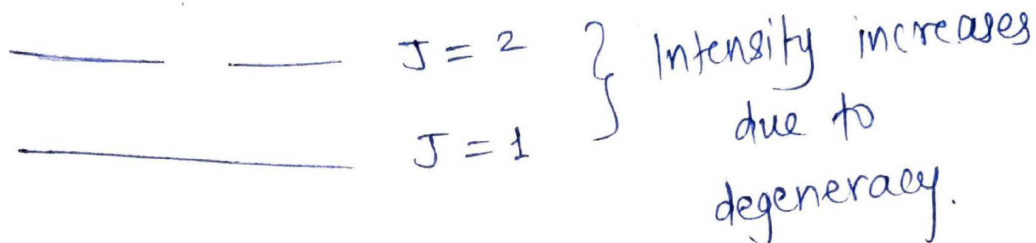
$$k_B = \frac{R}{N_A}$$

$$= \frac{8.314}{6.022 \times 10^{23}}$$

⇒ Intensity also depends on degeneracy

$$(2J+1)$$

$P \propto$ degeneracy:



J_{\max} Calculations-

$$P \propto \left[e^{-\Delta E / k_B T \times (2J+1)} \right]$$

$$\frac{dP}{dJ} = \frac{d}{dJ} \left[e^{-\Delta E / k_B T \times (2J+1)} \right]$$

For J_{\max} , we put $\frac{dP}{dJ} = 0$.

$$\Rightarrow J_{\max} = \sqrt{\frac{kT}{2Bhc}} - \frac{1}{2}$$

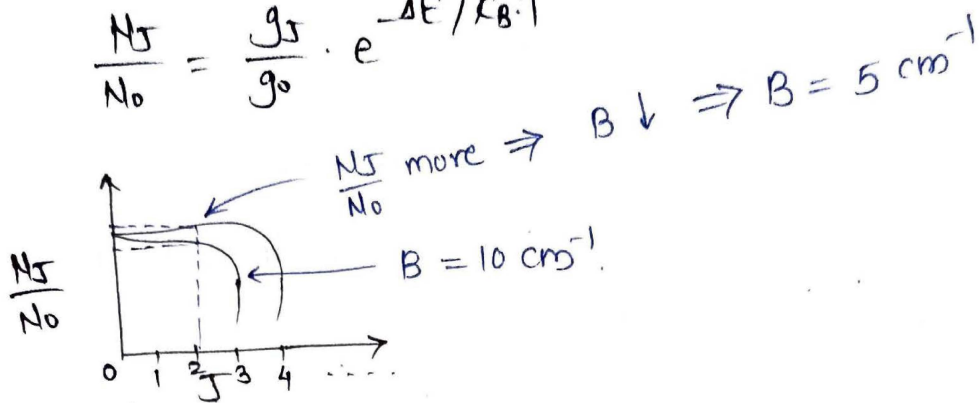
$T \Rightarrow$ Temperature of flame
(temp. given to molecule for excitation)

$$\Rightarrow J_{\max} = 11$$

Means that - At energy level $J=11$
Intensity of transition is maximum
($J_{11} \rightarrow J_{12}$)

Graphical Interpretation -

$$\frac{N_J}{N_0} = \frac{g_J}{g_0} \cdot e^{-\Delta E / k_B T}$$



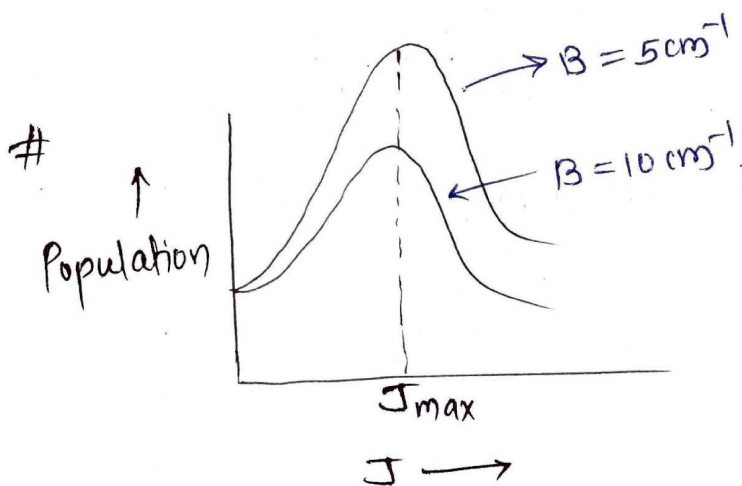
$B = 10 \text{ cm}^{-1}$
 $B = 5 \text{ cm}^{-1}$ } find the curves from graph.

Ans.

$$\frac{N_J}{N_0} = e^{-\frac{B J (J+1)}{kT}}$$

$$= \frac{1}{e^{+\Delta E / kT}}$$

Hence, If $B \uparrow$, $\Delta E \uparrow$, $\frac{N_J}{N_0} \downarrow$



$P \propto \frac{N_J}{N_0} \& \text{ degeneracy}$

$$(2J+1) \cdot e^{-\Delta E / kT}$$

IMP

Isotopic Substitution -

ex. ^{12}CO replaced by ^{13}CO .

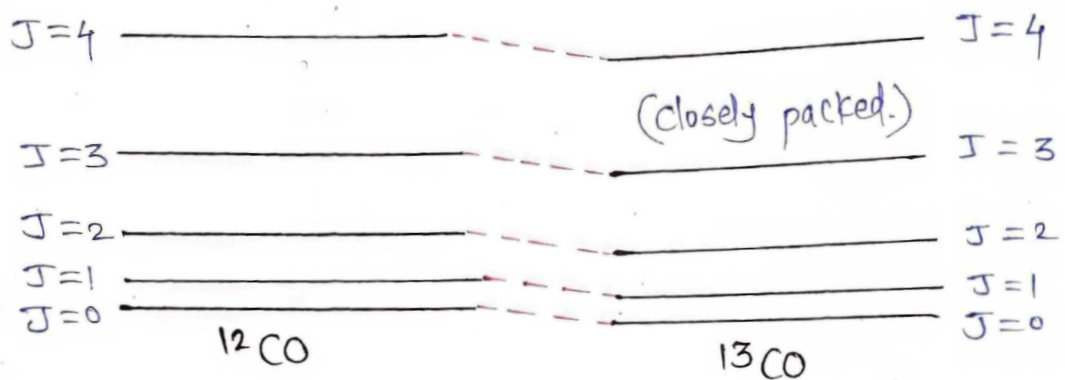
Conditions - ① electronic distribution does not change.
② Internuclear distance doesn't change.

⇒ Change in mass no. only.

⇒ As $m \uparrow$, $I \uparrow$, $B \downarrow$

$$I = \frac{m_1 m_2}{m_1 + m_2} \cdot r_0^2 \quad \Rightarrow \quad I \propto m$$

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



(energy level diagram)

Consider,

$$^{12}\text{CO} \quad \downarrow \downarrow \quad h \\ B = \frac{h}{8\pi^2 I_1 c}$$

$$^{13}\text{CO} \quad \downarrow \downarrow \quad h \\ B' = \frac{h}{8\pi^2 I_2 c}$$

$$\text{Now, } \frac{B}{B'} = \frac{h}{8\pi^2 I_1 c} \times \frac{8\pi^2 I_2 c}{h} = \frac{I_2}{I_1}$$

$$\boxed{\frac{B}{B'} = \frac{I_2}{I_1}}$$

Now, $I = \mu r_0^2$ → internuclear dist. doesn't change.
Here, we assumed that r_0 doesn't change.

Hence, $I \propto \mu$

$$\boxed{\frac{B}{B'} = \frac{\mu_2}{\mu_1}}$$

Que. Now if B is given to be 15 cm^{-1} for ^{12}CO .
And we have to find B' of ^{13}CO .

Ans. -

$$\mu_2 = \frac{13 \times 16}{13 + 16} = 7.17$$

$$\mu_1 = \frac{12 \times 16}{12 + 16} = 6.86$$

By using formula -

$$B' = B \times \frac{\mu_1}{\mu_2} = 15 \times \frac{6.86}{7.17} = 14.35 \text{ cm}^{-1}$$

$$\boxed{\Rightarrow B' = 14.35 \text{ cm}^{-1}}$$

#



\Rightarrow dipole moment = 0 \Rightarrow Microwave inactive.



\Rightarrow Microwave inactive.

Ans.

In isotopic substitution, electronic distribution and internuclear distance doesn't change.

\therefore No change in dipole moment.

\Rightarrow Microwave inactive.

Non-rigid Rotor -

Here, value of B is not constant.
Value of B is different for each ene. level.

$$\Delta E = BJ(J+1) - D J^2(J+1)^2$$

↓
Distortion constant
or centrifugal constant.

$$D = \frac{4B^3}{\omega^2}$$

$$\omega = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}$$

→ vibrational frequency.

re inactive.

distribution and