(2) what are the degeneracy of the following diatomic rotational energy levels —

(a) 0 (b) h^2/I (c) $\frac{6h^2}{I}$

Sol:

degeneracy = $(2J+1)$

$$E_J = \frac{h^2}{8\pi^2 I} J(J+1)$$

or

$$e_J = \frac{h^2}{2I} J(J+1)$$

(a) $E_J = 0$

degeneracy $= 2J+1$

$= 2\times 0+1$

$= 1$ non degenerate

(b) $E_J = \frac{h^2}{I}$

$$\frac{h^2}{2I} J(J+1) = \frac{h^2}{I}$$

$$\frac{J(J+1)}{2} = 1$$

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

$$J^2+J = 2$$

$$J^2+J-2 = 0$$

$$J^2+2J-J-2 = 0$$

$$J(J+2)-1(J+2) = 0$$

$$(J-1)(J+2) = 0$$

$J = 1$ | $J = -2$

degeneracy $= 2J+1$
$= 2\times 1+1$
$= 3$

degeneracy $= 2J+1$
$= 2(-2)+1$
$= -4+1$
$= -3$

(2) $c_J = \frac{6b^2}{I}$

$\frac{b^2}{8\pi^2} J(J+1) = \frac{6b^2}{I}$

$\frac{J(J+1)}{2} = 6$

$J(J+1) = 12$

$J^2 + J - 12 = 0$

$J^2 + 4J - 3J - 12 = 0$

$J(J+4) - 3(J+4) = 0$

$(J-3)(J+4) = 0$

$J = 3$ | $J = -4$

degeneracy $= 2J+1$
$= 2 \times 3 + 1$
$= 7$

degeneracy $= 2x - 4 + 1$
$= -8 + 1$
$= -7.$

(3) The rotational constant B for CN^+ is 1.566 cm^{-1}. what is the J-value corresponding to the maximum relative population at 300K & 1000 K.

Sol:- Given

$T = 300\,K.$

we know that — Maximum population —

$J_{max} = \sqrt{\frac{KT}{2hcB}} - \frac{1}{2}$

$= \sqrt{\frac{1.38 \times 10^{-23}\ J\,K^{-1} \times 300\,K}{2 \times 6.624 \times 10^{-34}\ J\,s \times 1.566\ cm^{-1} \times 3 \times 10^{10}\ cm\,s^{-1}}} - \frac{1}{2}$

$= \sqrt{\frac{1380}{20.747}} - \frac{1}{2}$

$= \sqrt{66.575} - \frac{1}{2}$

$= \frac{8.1}{1} - \frac{1}{2}$

$\frac{16.2 - 1}{2} = \frac{15.2}{2} = 7.6 \simeq 8.$

$J_{max} = 8$

when $T = 1000K$

$$J = \sqrt{\frac{1.38 \times 10^{-23}\ J K^{-1} \times 1000\ K}{2 \times 1.586\ cm^{-1} \times 6.624 \times 10^{-34}\ J s \times 3 \times 10^{10}\ cm\ s^{-1}}} \quad -\frac{1}{2}$$

$$J = \sqrt{\frac{1.38 \times 10^{-20}}{62.239 \times 10^{-24}}}$$

$$J = \sqrt{\frac{13800}{62.239}} \quad -\frac{1}{2}$$

$$J = \sqrt{221.72} \quad -\frac{1}{2}$$

$$J = \frac{14.9}{\frac{29.8}{2} - 1} - \frac{1}{2} = \frac{28}{2} = 14.4 \simeq 14$$

$$\boxed{J_{max} = 14}$$

Q. The characteristics temperature of rotation for gaseous HI is found to 9 K. calculate its moment of inertia & equilibrium distance —

Sol:- Given $\theta_{rot} = 9K$

we know that —

$$\theta_{rot} = \frac{\hbar^2}{2kI}$$

where, $\hbar = \frac{h}{2\pi}$

or $\hbar^2 = \frac{h^2}{4\pi^2}$

$$\therefore 9K = \frac{h^2}{8\pi^2 kI}$$

$1J = 10^{-7}$ erg

or $I = \frac{h^2}{8\pi^2 K I \times 9K}$

$= \frac{6.624 \times 10^{-27} \text{ erg sec} \times 6.624 \times 10^{-27} \text{ erg sec}}{8 \times (3.14)^2 \times 1.38 \times 10^{-19} \text{ erg K}^{-1} \times 9K}$

$= \frac{43.88 \times 10^{-54} \text{ erg sec}^2}{722.31 \times 10^{-19}}$

$= \frac{43.88 \times 10^{-35}}{722.31} \text{ erg sec}^2$

$= \frac{4388 \times 10^{-33}}{722.31} \text{ erg sec}^2$

$I = 6.07 \times 10^{-33} \text{ erg sec}^2$

$\because$ [1erg = gm cm^2 sec^{-2}] [1J = kg m^2 sec^{-2}]

$\therefore I = 6.07 \times 10^{-33}$ erg gm cm^2 sec^{-2} sec^2

$\boxed{I = 6.07 \times 10^{-33} \text{ gm cm}^2}$

$H_{H_2} = \frac{1 \times 127}{1+127}$ amu

$= 127/128$ amu

$= 0.9921$ amu

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

$\because$ [1amu = 1.67×10^{-24} gm] = [1.67×10^{-27} kg]

$M_{H_2} = 1.67 \times 10^{-24} \times 0.9921$ gm

$\boxed{M_{H_2} = 1.65 \times 10^{-24} \text{ gm}}$

$$r = \sqrt{I/\mu}$$

$$= \sqrt{\frac{6.07 \times 10^{-33} \text{ gm cm}^2}{1.65 \times 10^{-24} \text{ gm}}}$$

$$= \sqrt{\frac{6.07 \times 10^{-9} \text{ cm}^2}{1.65}}$$

$$= \sqrt{\frac{60.7 \times 10^{-8} \text{ cm}^2}{1.65}}$$

$$= \sqrt{36.78 \times 10^{-8} \text{ cm}^2}$$

$$r = 6.03 \times 10^{-4} \text{ cm} \quad \checkmark \left[\because 10^{-4} \text{ cm} = 1 \mu\text{m}\right]$$

$$\therefore \boxed{r = 6.03 \ \mu\text{m}}$$

*. Effects of Isotopic Substitution :-

$C^{12} - C^{13}$

They are chemically equivalent No change in internuclear distance but there is a change in mass.

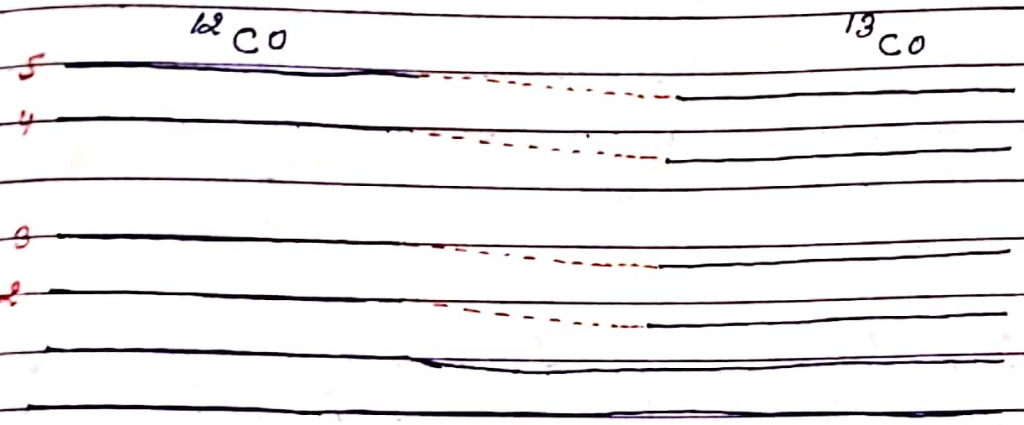
- Since,

$$I = \mu r^2$$

moment of inertia will changes and hence B. Its separation between rotational levels will decrease due to higher mass. as -

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

Hence, the spectrum of heavier species will show a smaller separation between rotational levels.



$$B = \frac{h}{8\pi^2 I c} \quad \& \quad B' = \frac{h}{8\pi^2 I' c}$$

[with higher mass]

$$\therefore \quad \boxed{\frac{B'}{B} = \frac{I}{I'} = \frac{\mu}{\mu'}}$$

* Non-rigid Rotator or Rotor :-

It is observed that the seperation between successive lines decreases with increasing value of J. So, the bond length increases with J. Hence, assumption of rigid body is not proved to be an approximation. Increase in bond length with J reflects the fact that quickly a diatomic molecule rotates, greater is the centrifugal force leading to move the atom aparts. So, when the bond is elastic, a molecule must have vibrational energy i.e the bond will stretches and compresed periodically with a

certain fundamental vibrational frequency depending on the masses of atom and the elasticity of bond (force constant).

$$K = 4\pi^2 \omega^2 c^2 \mu$$ (If the motion is periodic).

owing to the elasticity of the bond r and B varies during a vibration. when r and B are calculated by microwave techenique, many hundreds of vibrations occurs during a rotation. Hence, the measured value is an average.

*. Spectrum of a non-rigid Rotator :—

The schrödinger equation set up for a non-rigid molecule for which the rotational energy value is —

$$\epsilon_J = \frac{h^2}{8\pi^2 I} J(J+1) - \frac{h^4}{32\pi^4 I^2 r^2 k} J^2(J+1)^2 \text{ Joules} \quad \text{——— (1)}$$

where k = force constant.

when eqn — (1) is divided by hc then wave no. is produced. i.e.

$$\epsilon_J(\bar{\nu}) = \frac{h}{8\pi^2 Ic} J(J+1) - \frac{h^3}{32\pi^4 I^2 r^2 kc} J^2(J+1)^2 \text{ cm}^{-1}.$$

on solving this we get —

$$\epsilon_J(\bar{\nu}) = BJ(J+1) - DJ^2(J+1)^2 \text{ cm}^{-1}. \quad \text{——— (2)}$$

where, $B = \frac{h}{8\pi^2 Ic}$ cm^{-1}.

& $D = \frac{h^3}{32\pi^4 I^2 r^2 kc}$ cm^{-1}.

D = centrifugal distortion constant (a positive quantity)

This Eq^n - (2) applied only for periodic motion. If the motion is not periodic. Then Eq^n - (2) becomes.

$$E_J = BJ(J+1) - DJ^2(J+1)^2 + HJ^3(J+1)^3 + KJ^4(J+1)^4 \text{ cm}^{-1}.$$

where, H, K are small constant which depend upon the geometry of the molecule. So, It is neglected.

$$\therefore \quad \boxed{E_J = BJ(J+1) - DJ^2(J+1)^2 \text{ cm}^{-1}.}$$

* Calculation of D :-

Centrifugal distortion constant :-

we know that -

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

on multiply & divide $16\pi^2 I c^2$ then we get -

$$D = \frac{16 h^3 \pi^2 I c^2}{512 \pi^6 I^3 r^2 k c^3} \text{ cm}^{-1}$$

since $B = \frac{h}{8\pi^2 I c}$ or $B^3 = \frac{h^3}{512\pi^6 I^3 c^3}$

$r^2 = I/\mu$

$$\therefore D = \frac{16 B^3 \pi^2 I c^2}{k I/\mu} = \frac{16 B^3 \pi^2 c^2 \mu}{k} \text{ cm}^{-1}.$$

since $k = 4\pi^2 c^2 \mu \omega^2$

$$\therefore D = \frac{4 k B^3 \pi^2 c^2 \mu}{4\pi^2 c^2 \mu \omega^2} = 4B^3/\omega^2 \quad \therefore \boxed{D = \frac{4B^3}{\omega^2}}$$