Problem :-

① Calculate the force constant for HCl molecule given that stretching frequency $\bar{\nu} = 2890\ cm^{-1}$

Soln.

we know that $\bar{\nu} = \frac{1}{2\pi c}\sqrt{\frac{K}{\mu}}\ cm^{-1}$.

on squairing both side we get -

$$\bar{\nu}^2 = \frac{1}{4\pi^2 c^2} \cdot \frac{K}{\mu}$$

$$K = 4\pi^2 c^2 \mu \cdot \bar{\nu}^2 \quad \text{——— ①}$$

$$\mu_{HCl} = \frac{m_1 m_2}{m_1 + m_2} \qquad [m_1 = H \quad m_2 = Cl]$$

$$= \frac{1 \times 35.5}{1 + 35.5} = \frac{35.5}{36.5}\ amu$$

$$= 0.972\ amu$$

$$\mu_{HCl} = 0.972 \times 1.66 \times 10^{-27}\ kg.$$

$$\mu_{HCl} = 1.614 \times 10^{-27}\ kg.$$

given,

$$\bar{\nu} = 2890\ cm^{-1} = 2890 \times 10^2\ m^{-1}.$$

Thus, $K = 4 \times (3.14)^2 \times (2890 \times 10^2\ m^{-1})^2 \times (3 \times 10^8\ m/sec)^2\ 1.614 \times 10^{-27}\ kg$

$$K = 478.476\ kg\ sec^{-2}.$$

$$K = 4.78 \times 10^2\ kg\ sec^{-2}$$

$$\boxed{K = 4.78 \times 10^2\ N\ m^{-1}}$$

$[\because 1N = kg\ m\ sec^{-2}]$

(2) The spectrum of HCl shows a very intense absorption at 2886 cm^{-1}, a weak one at 5608 cm^{-1} and a very weak one at 8347 cm^{-1}. Find out the equillibrium frequency ($\bar{\omega_e}$) of the molecule and anharmonicity constant (x_e) from these data —

Sol. Since,

$$\bar{\omega_e}(1-2x_e) = 2886 \ cm^{-1} \quad \text{—(1)}$$
$$2\bar{\omega_e}(1-3x_e) = 5668 \ cm^{-1} \quad \text{—(2)}$$
$$3\bar{\omega_e}(1-4x_e) = 8347 \ cm^{-1} \quad \text{—(3)}$$

on multiplying eqn — (2) by two (2) and then eqn (3) is substracted from eqn — (2) we get —

$$2 \times [2\bar{\omega_e}(1-3x_e) = 5668 \ cm^{-1}]$$

$$\cancel{\text{or, } 4\bar{\omega_e}(2-6x_e) = 11336 \ cm^{-2}}$$

$$4\bar{\omega_e} - \cancel{12\bar{\omega_e}x_e} = 11336 \ cm^{-2}$$
$$-\ 3\bar{\omega_e} \ \underset{+}{-} \ \cancel{12\bar{\omega_e}x_e} = \underset{-}{8347} \ cm^{-1}$$

$$\boxed{\bar{\omega_e} = 2989 \ cm^{-1}}$$

$$\boxed{\text{i.e. } \bar{\omega_e} = 2990 \ cm^{-1} \ (\text{approxi..})}$$

Now putting the value of $\bar{\omega_e}$ in eqn — (2) we get —

$$2 \times \bar{\omega_e}(1-3x_e) = 5668 \ cm^{-1}$$

$$2 \times 2990 \ \cancel{cm^{-1}} (1-3x_e) = 5668 \ \cancel{cm^{-1}}$$

$$1-3x_e = \frac{\cancel{5668}^{\,2834}}{\cancel{2} \times 2990}$$

$$1-3x_e = \frac{2834}{2990}$$

$$3x_e = 1 - \frac{2834}{2990}$$

$$3x_e = \frac{2990 - 2834}{2990}$$

$$x_e = \frac{\overset{52}{\cancel{156}}}{\cancel{2990 \times 3}} = \frac{26}{1495}$$

$$\boxed{x_e = 0.0173}$$

So, the equillibrium frequency (ω_e) and anharmonicity constant (x_e) are $2990\ cm^{-1}$ and 0.0173 respectively.

force constant $K = 4\pi^2 \bar{\omega}_e^2 c^2 \mu$

$K = 516\ N\,m^{-1}$ Ans.

$(1N = kg\,m\,sec^{-2})$

Q (3). Carbon monoxide shows an absorption band at $2140\ cm^{-1}$. Calculate the force constant of the molecule.

(Ans $K = 1840\ N\,m^{-1}$)

Q (4). From the fundamental vibrational frequency of CO at $2140\ cm^{-1}$. Calculate the frequency in Hz (sec^{-1}) and the zero point energy in $KJ\ mole^{-1}$.

Q (5). The rotation-vibration spectrum of HCl gas shows a number of lines ~~...~~ centred about the fundamental vibrational band a few of which have the wave-numbers 2847, 2866, 2906 and 2927 cm^{-1}. Using this data calculate —

(a) the bond length

(b) the force constant

(c) the anharmony constant of HCl.

Soln

$$\Delta E_{J,v} = \bar{\omega}_o + 2Bm$$

$$= \bar{\omega}_o + \left(\frac{h}{4\pi^2 Ic}\right)m$$

$(m = \pm 1, \pm 2, \pm 3)$

the pair of lines $2847\ cm^{-1}$ and $2866\ cm^{-1}$ (low wave no. side belong to P-branch & pair of lines 2906 & $2927\ cm^{-1}$ belong to R-branch (i.e. m is +ve).

$$2906\ cm^{-1} = 2.906\times10^{5}\ m^{-1} = \bar{\omega}_0 + \frac{6.626\times10^{-34}(+1)}{4(3.14)^2 I(3\times10^{8})}$$

$$\& \quad 2927\ cm^{-1} = 2.927\times10^{5}\ m^{-1} = \bar{\omega}_0 + \frac{6.626\times10^{-34}(+2)}{4(3.14)^2 I(3\times10^{8})}$$

from these two data, we can calculate the value of two unknowns $\bar{\omega}_0$ & I.

$$\bar{\omega}_0 = 2.885\times10^{5}\ m^{-1}$$

$$\boxed{\bar{\omega}_0 = 2885\ cm^{-1}.}$$

$$\& \quad \boxed{I = 2.665\times10^{-47}\ kg\ m^2}$$

$$I = \mu r^2$$

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

$$= 1.292\times10^{-10}\ m.$$

$$\boxed{r. = 0.129\ nm}$$

$$K = 4\pi^2 \bar{\omega}_0^2 c^2 \mu.$$

$$K = ?$$

from.

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