ENGINEERING CHEMISTRY

Department of Science and Humanities

Class content :

- ***Numericals on Molecular Spectroscopy***
    - ***Rotational Spectroscopy***
    - ***Vibrational Spectroscopy***

PES UNIVERSITY

1. Calculate the rotational constant for an NO molecule. Given atomic masses of N and O are 14.004 amu and 15.9994 amu respectively. The bond length of NO is 115 pm.
(1 amu = 1.66 x 10^{-27} kg, c = 3 x 10^{8} ms^{-1}, h=6.6x 10^{-34} Js)
Solution:

$$\mu = \frac{m_1 m_2}{m_1 + m_2} = \frac{(14.004 \times 1.66 \times 10^{-27} kg)(15.9994 \times 1.66 \times 10^{-27} kg)}{(14.004 \times 1.66 \times 10^{-27} kg) + (15.9994 \times 1.66 \times 10^{-27} kg)}$$

$$\mu = 12.3963 \times 10^{-27}\ \text{kg}$$

$$I = \mu r^2$$

$$I = 12.3963 \times 10^{-27}\ kg \times (115 \times 10^{-12}\ m)^2 = 1.63941 \times 10^{-46}\ \text{kgm}^2$$

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

$$B = \frac{6.6 \times 10^{-34}\ J.s}{8 \times (3.14)^2 \times 1.63941 \times 10^{-46}\ kgm^2 \times (3 \times 10^8\ ms^{-1})} = 170.13\ m^{-1}$$

$$B = 1.70\ \text{cm}^{-1}$$

2. The first line in the pure rotational spectrum of HCl appears at 21.18 cm^{-1} . Calculate the bond length of the molecule. Given atomic masses of H and Cl are 1.008 amu and 35.45 amu respectively.
(1 amu = 1.66 x 10^{-27} kg, c = 3 x 10^{8} ms^{-1}, h = 6.6x 10^{-34} Js)
Solution :

$$2B = 21.18\ cm^{-1},\ B = 10.59\,cm^{-1} = 10.59\ \times 10^{2} m^{-1}$$

$$\mu = \frac{m_1 m_2}{m_1 + m_2} = \frac{(1.008\times1.66\times10^{-27}kg)(35.45\times1.66\times10^{-27}kg)}{(1.008\times1.66\times10^{-27}kg)+(35.45\times1.66\times10^{-27}kg)}$$

$$\mu = 1.627\times10^{-27}\ kg$$

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

$$I = \frac{6.6\times10^{-34}J.s}{8\times(3.14)^2\times10.59\times10^{2}m^{-1}\times(3\times10^{8}ms^{-1})} = 2.634\times10^{-47}\ kgm^2$$

$$I = \mu r^2$$

$$r^2 = \frac{I}{\mu} = \frac{2.634 \times 10^{-47} \, kgm^2}{1.627 \times 10^{-27} \, kg}$$

$$r^2 = 1.619 \times 10^{-20} \, m^2$$

$$r = 127 \text{ pm}$$

3. For HBr molecule:

i) The rotational spectrum shows the first line at 17.19 cm^{-1}. Calculate the bond length of HBr molecule(Use rigid rotor model)

ii) The vibrational spectrum shows fundamental and first overtone at 2559.08 cm^{-1} and 5027.54 cm^{-1} respectively. Calculate the anharmonicity constant for the molecule. (Use anharmonic oscillator model). (1 amu = 1.66 x 10^{-27} kg, h = 6.627 x 10^{-34} Js, c = 3 x 10^{10} cms^{-1} , N = 6.023 x 10^{23} mol^{-1}, Gram molar mass of H = 1.0 and Br = 79.9)

Solution :

i) 2B = 17.19 cm^{-1} **B = 8.595 cm^{-1}**

$$\mu = \frac{m_1 m_2}{m_1 + m_2} = \frac{(0.001/6.023\times10^{23})\,(0.0799/6.023\times10^{23})}{(0.001/6.023\times10^{23}) + (0.0799/6.023\times10^{23})} = 1.6395 \times 10^{-27}\ \text{kg}$$

$$I = \frac{h}{8\pi^2 Bc} = \frac{6.627 \times 10^{-34}}{8(3.14)^2 \times 8.595 \times 3 \times 10^{10}}$$

$$I = 3.2583 \times 10^{-47}\ \text{kgm}^2$$

$$I = \mu r^2$$

$$r = \sqrt{I/\mu} = 0.141\ \text{nm}$$

ii) $$\frac{2\overline{v}(1-3x_e)}{\overline{v}(1-2x_e)} = \frac{5027.54}{2559.08} = 1.9646$$

$$x_e = 0.0171$$

4. For a KCl molecule undergoing simple harmonic motion the vibrational spectrum shows a fundamental frequency at 378 cm^{-1}.
i) Calculate the reduced mass of KCl ii) Determine force constant of KCl
iii) Determine zero point energy for KCl molecule. ($c = 3 \times 10^{10}$ cms^{-1} , $N = 6.023 \times 10^{23}$ mol^{-1}, Gram molar mass of K = 39 and Cl = 35.5)

Solution :

$$\text{i)}\ \mu = \frac{m_1 m_2}{m_1 + m_2} = \frac{(0.039/6.023\times10^{23})\,(0.0355/6.023\times10^{23})}{(0.039/6.023\times10^{23}) + (0.0355/6.023\times10^{23})}$$

$$\mu = 3.085\times10^{-26}\ \text{kg}$$

$$\text{ii)}\ \bar{v} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}$$

$$k = 4\pi^2 \bar{v}^2 c^2 \mu$$

$$k = 4\times(3.14)^2\times(378\times10^2)^2\times(3\times10^8)^2\times3.085\times10^{-26}$$

$$k = 156.313\,\text{Nm}^{-1}$$

$$\text{iii) Zero point energy} = \frac{1}{2}\bar{v} = \frac{1}{2}\times378 = 189\ \text{cm}^{-1}$$

5. The force constant of CO is 1840 Nm^{-1}. Calculate the oscillation frequency and wave number in cm^{-1}. (1 amu = 1.66 x 10^{-27} kg, c = 3 x 10^{8} ms^{-1}, Gram molar mass of C = 12.000 and O = 15.9994)

Solution :

$$\mu = \frac{m_1 m_2}{m_1 + m_2} = \frac{(12.000 \times 1.66 \times 10^{-27} kg)\ (15.9994 \times 1.66 \times 10^{-27} kg)}{(12.000 \times 1.66 \times 10^{-27} kg) + (15.9994 \times 1.66 \times 10^{-27} kg)}$$

$$\mu = 11.3827 \times 10^{-27}\ \text{kg}$$

$$v = \frac{1}{2\pi}\sqrt{k/\mu} = \frac{1}{2 \times 3.14}\sqrt{\frac{1840 \text{Nm}^{-1}}{11.3827 \times 10^{-27} kg}}$$

$$v = 6.402 \times 10^{13}\ s^{-1}$$

$$\bar{v} = \frac{v}{c} = \frac{6.402 \times 10^{13}\ s^{-1}}{3 \times 10^{8}\ ms^{-1}} = 2.134 \times 10^{5}\ m^{-1}$$

$$\bar{v} = 2134\ cm^{-1}$$

THANK YOU

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