Quadrant II – Transcript and Related Materials

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Paper Title: Physical Chemistry

Unit: MOLECULAR SPECTROSCOPY-2

Module Name: COMPUTATION OF FORCE CONSTANT

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A DIATOMIC MOLECULE with atomic masses m_1 and m_2 joined by a chemical bond vibrates as a one-dimensional simple harmonic oscillator.

Classically, the vibrational frequency ν of a mass point m connected by a spring of force constant *k* is given by

$$\nu = \frac{1}{2\pi}\left(\frac{k}{m}\right)^{1/2} \qquad (1)$$

In the case of a diatomic molecule, the masses m_1 and m_2 vibrate back and forth relative to their centre of mass in opposite directions.

Two masses reach the extreme of their respective motions at the same time. The vibrational frequency of the molecule is given by a relation analogous to that of equation (1) with mass m replaced by reduced mass μ

$$\nu = \frac{1}{2\pi}\left(\frac{k}{\mu}\right)^{1/2} \quad s^{-1} \qquad (2)$$

To convert the frequency ν from s^{-1} (hertz) to cm^{-1}, we divide by *c*, the velocity of light. Thus, $\bar{\nu} = \frac{1}{2\pi c}\left(\frac{k}{\mu}\right)^{1/2}$ cm^{-1} (3)

1. The fundamental vibrational frequency of HCl is 2890 cm^{-1}. Calculate the force constant of this molecule. The atomic masses are $^{1}H = 1.673 \times 10^{(-27)}$ kg ; $^{35}Cl = 58.06 \times 10^{(-27)}$ kg.

Solution: $\bar{\nu} = \frac{1}{2\pi c}\left(\frac{k}{\mu}\right)^{1/2}$ cm^{-1}

$\bar{\nu}$ = 2890 cm^{-1}; c = $3 \times 10^{(10)}$ cm; μ = ?

$$\mu = \frac{m_1 m_2}{m_1 + m_2} = \frac{1.673\times10^{(-27)}\ \ 58.06\times10^{(-27)}}{1.673\times10^{(-27)} + 58.06\times10^{(-27)}} = 1.626 \times 10^{(-27)}\ \text{kg}$$

As $\bar{\nu} = \frac{1}{2\pi c}\left(\frac{k}{\mu}\right)^{1/2}$

Therefore, $k = 4\pi^2 c^2 (\bar{\nu})^2 \mu$

$= 4\pi^2 (3 \times 10^{(10)}\ \text{cm})^2 (2890\ \text{cm}^{-1})^2 (1.626 \times 10^{(-27)}\ \text{kg})$

$= 4.83 \times 10^{(2)}\ \text{kg s}^{-2}$

$= 4.83 \times 10^{(2)}\ \text{kg m s}^{-2}\ \text{m}^{-1}$

$= 4.83\ \text{N m}^{-1}$

2. The force constant of CO is 1840 N m^{-1}. Calculate the vibrational frequency in cm^{-1} and spacing between the vibrational energy levels in eV. Compare this spacing with the thermal energy at room temperature and comment on your result. The atomic masses are $^{12}C = 19.9 \times 10^{(-27)}$ kg ; $^{16}O = 26.6 \times 10^{(-27)}$ kg. (1 eV = 8066 cm^{-1})

Solution:

$$\bar{\nu} = \frac{1}{2\pi c}\left(\frac{k}{\mu}\right)^{1/2} \quad cm^{-1}$$

$m_1 = 19.9 \times 10^{(-27)}$ kg ; $m_2 = 26.6 \times 10^{(-27)}$ kg

$$\mu = \frac{m_1 m_2}{m_1 + m_2} = \frac{19.9 \times 10^{(-27)}\ 26.6 \times 10^{(-27)}}{19.9 \times 10^{(-27)} + 26.6 \times 10^{(-27)}} = 11.4 \times 10^{(-27)}\ kg$$

$$\bar{\nu} = \frac{1}{2\pi c}\left(\frac{k}{\mu}\right)^{1/2}$$

$$= \frac{1}{2\ (3.1416)\ (3 \times 10^{10}\ cm\ s^{-1})}\left(\frac{1840\ kg\ s^{-2}}{11.4 \times 10^{-27}\ kg}\right)$$

$$= 2140\ cm^{-1}$$

The spacing between energy levels

$\Delta E = E_{v+1} - E_v = h\nu$ joules $= h\nu/hc = \nu/c$

$\bar{\nu}$ = 2140 cm^{-1}

1 eV = 8066 cm^{-1}

$$\Delta E = \frac{2140\ cm^{-1}}{8066\ cm^{-1}\ /eV} = 0.265 \text{ eV}$$

$$\text{Thermal energy} = k\,T = \frac{1.38 \times 10^{(-23)}\ J\,K^{-1} \times\ 300\ K}{1.602 \times 10^{-19}\ J/eV}$$

$$= 2.6\ \times 10^{-2} \text{ eV}$$

$$= 0.026 \text{ eV}$$

kT < ΔE, hence we conclude that most of the molecules are in the ground vibrational state at room temperature.

This situation is in contrast with the rotational states where kT > ΔE and consequently most of the molecules are in the excited rotational states at room temperature.