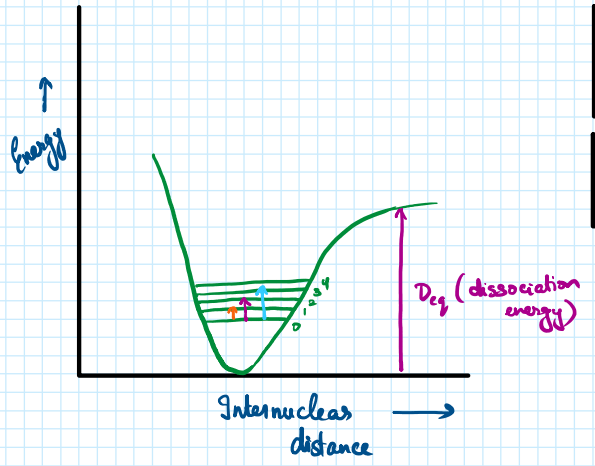
Anharmonic Oscillations

14 September 2023 09:56

Anharmonic Oscillation (P.M. Morse)



Selection Rule

$\Delta V = \pm 1, \pm 2, \pm 3$

$$P.E. = D_{eq}\left[1 - \exp\left(a\left(r_{eq} - r\right)\right)\right]^2$$

D_{eq} → potential energy

- Fundamental absorption: $V = 0 \rightarrow V = 1$
- First Overtone: $V = 0 \rightarrow V = 2$
- Second Overtone: $V = 0 \rightarrow V = 3$

Schrodinger's Equation (Anharmonic)

$$\mathcal{E}_v = \frac{E}{hc} \quad cm^{-1}$$

$$\mathcal{E}_v = \left(v + \frac{1}{2}\right)\bar{\nu}_e - \left(v + \frac{1}{2}\right)^2 \bar{\nu}_e \cdot x_e \quad cm^{-1}$$

x_e → anharmonicity constant

$\bar{\nu}_e$ → oscillation frequency

Zero Point Energy

$$\mathcal{E}_v = \left(0 + \frac{1}{2}\right)\bar{\nu}_e - \left(0 + \frac{1}{2}\right)^2 \bar{\nu}_e \cdot x_e$$

$$\mathcal{E}_v = \frac{1}{2}\bar{\nu}_e - \frac{1}{4}\bar{\nu}_e \cdot x_e$$

$$\mathcal{E}_v = \frac{1}{2}\bar{\nu}_e\left[1 - \frac{1}{2} \cdot x_e\right]$$

Fundamental Absorption ($V = 0 \rightarrow V = 1$)

$V = 0 \longrightarrow V = 1$

$\Delta E = E_1 - E_0$

$$\Delta E = \left(v + \frac{1}{2}\right)\bar{\nu}_e - \left(v + \frac{1}{2}\right)^2 \bar{\nu}_e \cdot x_e - \left[\left(v + \frac{1}{2}\right)\bar{\nu}_e - \left(v + \frac{1}{2}\right)^2 \bar{\nu}_e \cdot x_e\right]$$

$$\Delta E = \left(v+\tfrac{1}{2}\right)\bar{\nu}_e - \left(v+\tfrac{1}{2}\right)^2 \bar{\nu}_e x_e - \left[\left(v+\tfrac{1}{2}\right)\bar{\nu}_e - \left(v+\tfrac{1}{2}\right)^2 \bar{\nu}_e x_e\right]$$

$$= v\bar{\nu}_e + \tfrac{1}{2}\bar{\nu}_e - \left[v^2 + \tfrac{1}{4} + v\right]\bar{\nu}_e x_e - \left[\tfrac{1}{2}\bar{\nu}_e\left(1 - \tfrac{1}{2}x_e\right)\right]$$

$$\boxed{\Delta E = \bar{\nu}_e\left[1 - 2x_e\right] \text{ cm}^{-1}}$$

First Overtone ($v=0 \rightarrow v=2$)

$$\boxed{\Delta E = 2\bar{\nu}_e\left[1 - 3x_e\right] \text{ cm}^{-1}}$$

Second Overtone ($v=0 \rightarrow v=3$)

$$\boxed{\Delta E = 3\bar{\nu}_e\left[1 - 4x_e\right] \text{ cm}^{-1}}$$

Hot Band ($v=1 \rightarrow v=2$)

At high temperatures,

$v=1 \longrightarrow v=2$

$E_2 - E_1$

$$\boxed{\Delta E = \bar{\nu}_e\left[1 - 4x_e\right] \text{ cm}^{-1}}$$

Anharmonic Oscillations: A Summary

Fundamental Absorption	$v=0 \rightarrow v=1$	$E_1 - E_0$	$\Delta E = \bar{\nu}_e\left[1 - 2x_e\right]$ cm^{-1}
First Overtone	$v=0 \rightarrow v=2$	$E_2 - E_0$	$\Delta E = 2\bar{\nu}_e\left[1 - 3x_e\right]$ cm^{-1}
Second Overtone	$v=0 \rightarrow v=3$	$E_3 - E_0$	$\Delta E = 3\bar{\nu}_e\left[1 - 4x_e\right]$ cm^{-1}
Hot Band	$v=1 \rightarrow v=2$ (high temp)	$E_2 - E_1$	$\Delta E = \bar{\nu}_e\left[1 - 4x_e\right]$ cm^{-1}
Zero Point Energy	$v=0$	—	$\Delta E = \frac{1}{2}\bar{\nu}_e\left[1 - \frac{1}{2}x_e\right]$ cm^{-1}

LKG Problems

① Calculate E in cm^{-1}, Fundamental Absorption, First Overtone, second Overtone, Hot Band, Zero Point Energy; $\bar{\nu}_e = 2134$ cm^{-1} and $x_e = 0.017$

Soln: Fundamental

$\Delta E = \bar{\nu}_e\left[1 - 2x_e\right]$

Second

$\Delta E = 3\bar{\nu}_e\left[1 - 4x_e\right]$

Zero Point

$\Delta E = \frac{1}{2}\bar{\nu}_e\left[1 - \frac{1}{2}x_e\right]$ cm^{-1}

Soln: **fundamental**

$$\Delta E = \bar{\nu}_e \left[1 - 2x_e\right]$$

$$= 2061.444 \text{ cm}^{-1}$$

First

$$\Delta E = 2\bar{\nu}_e \left[1 - 3x_e\right]$$

$$= 4050.332 \text{ cm}^{-1}$$

Second

$$\Delta E = 3\bar{\nu}_e \left[1 - 4x_e\right]$$

$$= 5966.664 \text{ cm}^{-1}$$

Hot Band

$$\Delta E = \bar{\nu}_e \left[1 - 4x_e\right]$$

$$= 1988.888 \text{ cm}^{-1}$$

Zero line

$$\Delta E = \frac{1}{2}\bar{\nu}_e \left[1 - \frac{1}{2}x_e\right] \text{ cm}^{-1}$$

$$= 1057.9305 \text{ cm}^{-1}$$

Space b/w 2 lines $= 2B$

(2) $\bar{\nu} = 12.604 \text{ cm}^{-1}$

$I = \mu r_0^2$

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

$\mu = 1.613 \times 10^{-23}$ kg

$$12.604 = \frac{h}{8\pi^2 Ic}(J)(J+1)$$

$$I = \frac{h}{8\pi^2 c(12.604)}(J)(J+1)$$

(3) $K = 970$

$\mu = ?$ $\quad V = ?$

$\mu = 1.588 \times 10^{-27}$

$$\bar{\nu}_{osc} = \frac{1}{2\pi c}\sqrt{\frac{K}{\mu}}$$

$=$