4. Anharmonic Oscillations

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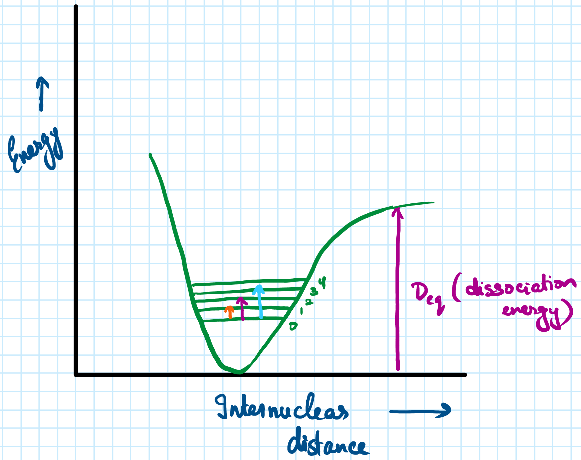
ANHARMONIC OSCILLATION (P.M. MORSE)



Selection Rule

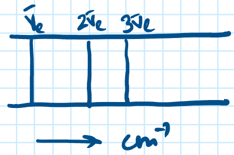
$\Delta V = \pm 1, \pm 2, \pm 3$

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

potential energy

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

Spectrum



SCHRODINGER'S EQUATION (ANHARMONIC)

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

$$\boxed{\varepsilon_v = \left(V + \frac{1}{2}\right)\bar{\nu}_e - \left(V + \frac{1}{2}\right)^2 \bar{\nu}_e \cdot x_e \quad cm^{-1}}$$

anharmonicity constant

oscillation frequency

ZERO POINT ENERGY

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

$$\varepsilon_v = \frac{1}{2}\bar{\nu}_e - \frac{1}{4}\bar{\nu}_e \cdot x_e$$

$$\boxed{\varepsilon_v = \frac{1}{2}\bar{\nu}_e\left[1 - \frac{1}{2} \cdot x_e\right]}$$

FUNDAMENTAL ABSORPTION ($V=0 \rightarrow V=1$)

$$V=0 \longrightarrow V=1$$

$$\Delta E = E_1 - E_0$$

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

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

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

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

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

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

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

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

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

At high temperatures,

$v=1 \longrightarrow v=2$

$\mathcal{E}_2 - \mathcal{E}_1$

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

Anharmonic Oscillations: A Summary

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

LKG Problems

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

Soln: Fundamental

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

Second

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

Zero Point

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

Soln: Fundamental

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

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

First

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

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

Second

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

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

Hot Band

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

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

Zero Point

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

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

Space b/w 2 lines = 2B

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

$$I = \mu r_0^2$$

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

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

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

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

(3) $k = 970$

$\mu = ?$ $\quad\quad$ $\nu = ?$

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

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

$$=$$