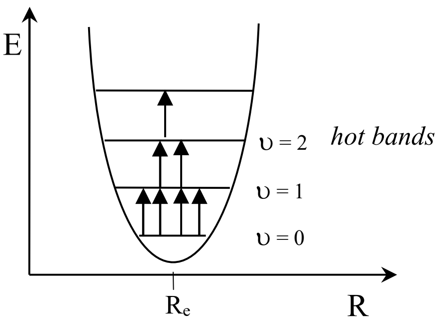
Vibrational Spectroscopy

$E_\upsilon = h\nu_e\,(\upsilon + \tfrac{1}{2}) = \hbar\omega_e\,(\upsilon + \tfrac{1}{2})$

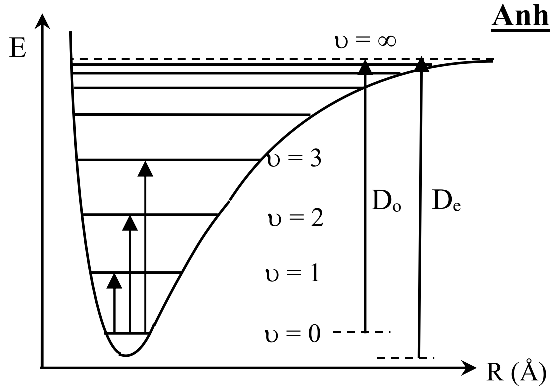
$$\nu_e = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \qquad \omega_e = 2\pi\nu_e = \sqrt{\frac{k}{\mu}}$$

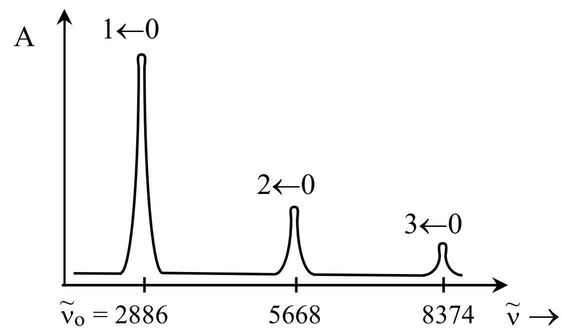
$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

$$\tilde{G}_\upsilon = \tilde{\nu}_e\,(\upsilon + \tfrac{1}{2}) \qquad \tilde{\nu}_e = \frac{\nu_e}{c} \qquad \text{in cm}^{-1}$$



Anharmonicity





$E_\upsilon = h\nu_e(\upsilon + \tfrac{1}{2}) - \chi_e\, h\nu_e(\upsilon + \tfrac{1}{2})^2 + \mathcal{Y}_e\, h\nu_e(\upsilon + \tfrac{1}{2})^3 + \ldots$ $\qquad \chi_e$ = anharmonicity

get weak $\Delta\upsilon = \pm 2$ and even weaker $\Delta\upsilon = \pm 3$ transitions called overtones

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Morse Potential

$$V = D_e\,[1 - e^{-a(R-R_e)}]^2 \qquad a = \omega_e\left(\frac{\mu}{2D_e}\right)^{1/2} \qquad \chi_e = \frac{a^2\hbar}{2\mu\omega_e} = \frac{\hbar\omega_e}{4D_e} = \frac{\tilde{\nu}_e}{4\tilde{D}_e}$$

$E_\upsilon = h\nu_e(\upsilon + \tfrac{1}{2}) - \chi_e\, h\nu_e(\upsilon + \tfrac{1}{2})^2 \qquad \tilde{G}_\upsilon = \tilde{\nu}_e(\upsilon + \tfrac{1}{2}) - \chi_e\, \tilde{\nu}_e(\upsilon + \tfrac{1}{2})^2$

$E_{\upsilon+1} - E_\upsilon = h\nu_e(\upsilon+1+\tfrac{1}{2}) - \chi_e\, h\nu_e(\upsilon + 1 + \tfrac{1}{2})^2 - h\nu_e(\upsilon+\tfrac{1}{2}) + \chi_e\, h\nu_e(\upsilon+\tfrac{1}{2})^2$

$\Delta E = h\nu_e - \chi_e h\nu_e\, 2(\upsilon+1) \qquad \Delta\tilde{G} = \tilde{\nu}_e - \chi_e\, \tilde{\nu}_e\, 2(\upsilon+1) \qquad \upsilon$ = lower level

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$D_e = D_o + \tfrac{1}{2}\, h\nu_e - \tfrac{1}{4}\, \chi_e\, h\nu_e \qquad \tilde{D}_e = \tilde{D}_o + \tfrac{1}{2}\, \tilde{\nu}_e - \tfrac{1}{4}\, \tilde{\nu}_e\, \chi_e \qquad$ in cm^{-1}

Relationship between χ_e and $\tilde{D}_e$: $\quad \Delta E = h\nu_e - \chi_e h\nu_e\, 2(\upsilon_{cl} + 1) = 0$

$1 = \chi_e\, 2(\upsilon_{cl} + 1) \qquad \upsilon_{cl} + 1 = \dfrac{1}{2\chi_e}$ upper level or $\upsilon_{cl} = \dfrac{1}{2\chi_e} - 1$ lower level

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$$\tilde{D}_e = \tilde{G}_{\upsilon cl+1} = \tilde{\nu}_e\,[(\upsilon_{cl}+1) + \tfrac{1}{2}] - \chi_e\, \tilde{\nu}_e[(\upsilon_{cl}+1) + \tfrac{1}{2}]^2$$

$$\tilde{D}_e = \frac{\tilde{\nu}_e}{2\chi_e} + \frac{\tilde{\nu}_e}{2} - \frac{\chi_e\tilde{\nu}_e}{4}\,(1/\chi_e + 1)^2 = \frac{\tilde{\nu}_e}{2\chi_e} + \frac{\tilde{\nu}_e}{2} - \frac{\chi_e\tilde{\nu}_e}{4}\left(\frac{1}{\chi_e^2} + \frac{2}{\chi_e} + 1\right)$$

$$\tilde{D}_e = \frac{\tilde{\nu}_e}{2\chi_e} + \frac{\tilde{\nu}_e}{2} - \left(\frac{\tilde{\nu}_e}{4\chi_e} + \frac{\tilde{\nu}_e}{2} + \frac{\chi_e\tilde{\nu}_e}{4}\right) = \frac{\tilde{\nu}_e}{4\chi_e} - \frac{\chi_e\tilde{\nu}_e}{4} \cong \frac{\tilde{\nu}_e}{4\chi_e} \qquad \text{or} \qquad \chi_e = \frac{\tilde{\nu}_e}{4\tilde{D}_e}$$