IR Spectroscopy, Vibrational Transitions

11 September 2023 10:02

IR SPECTROSCOPY

- Study of vibrating molecules
- Homodiatomic molecules $\rightarrow H_2, N_2, O_2 \ldots$

  IR inactive

  WHY?

  Dipole moment $= \mu = 0$

- Heterodiatomic molecules $\longrightarrow HCl, HBr, CO_2 \ldots$

  IR active

  WHY?

  $\mu \neq 0$

CO_2 →

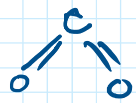
- Symmetric stretching vibration

  $O = C = O$ $\mu = 0$

- Asymmetric stretching vibration

  $O = C = O$ $\mu \neq 0$

- Bending vibration $\mu \neq 0$



H_2O

HOOKE'S LAW

$f = -k(r - r_{eq})$

f = restoring force
k = force constant
r = internuclear distance
r_{eq} = equilibrium b/w internuclear distance

The energy given is parabolic

$$E = \frac{1}{2} k (r - r_{eq})^2$$

Simple harmonic oscillations

$$\nu_{osc} = \frac{1}{2\pi} \sqrt{\frac{K}{\mu}} \text{ Hz}$$

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

$$\Longrightarrow \quad K = 4\pi^2 c^2 \bar{\nu}_{osc}^2 \mu$$

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

Quantum Mechanical Expression

Schrodinger equation (vibrational) =

$$E_v = \left(v + \frac{1}{2}\right) h \nu_{osc} \text{ Joules}$$

$$\varepsilon_v = \frac{E_v}{hc} \text{ cm}^{-1}$$

$$= \frac{\left(v + \frac{1}{2}\right) \cancel{h} \nu_{osc}}{\cancel{h} c}$$

$$\varepsilon_v = \left(v + \frac{1}{2}\right) \bar{\nu}_{osc} \text{ cm}^{-1} \quad \Bigg\} \quad \frac{\nu_{osc}}{c} = \bar{\nu}_{osc}$$

Zero Point Energy

$$E_v = \left(v + \frac{1}{2}\right) h \nu_{osc} \text{ Joules}$$

$v = 0$

$E_v = \frac{1}{2} h \nu_{osc}$ Joules

$\varepsilon_v = \left(v + \frac{1}{2}\right)\bar{\nu}_{osc}$ cm^{-1}

$v = 0$

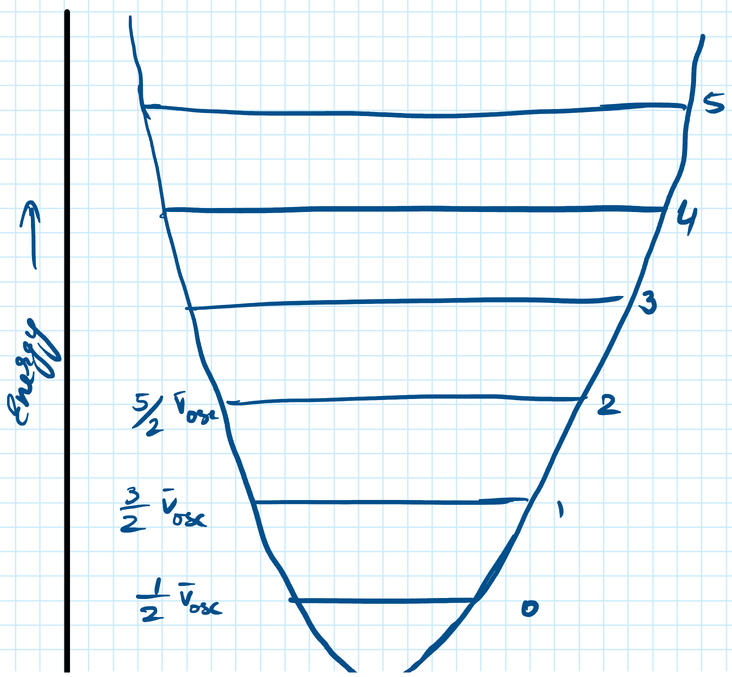
$\varepsilon_v = \frac{1}{2}\bar{\nu}_{osc}$ cm^{-1}

Selection Rule

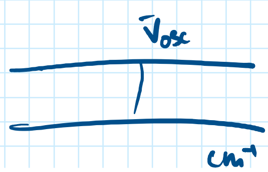
$\Delta V = \pm 1$

V	$\varepsilon_v = \left(V + \frac{1}{2}\right)\bar{\nu}_{osc}$ cm^{-1}
0	$\frac{1}{2}\bar{\nu}_{osc}$
1	$\frac{3}{2}\bar{\nu}_{osc}$
2	$\frac{5}{2}\bar{\nu}_{osc}$
3	$\frac{7}{2}\bar{\nu}_{osc}$
4	$\frac{9}{2}\bar{\nu}_{osc}$
5	$\frac{11}{2}\bar{\nu}_{osc}$

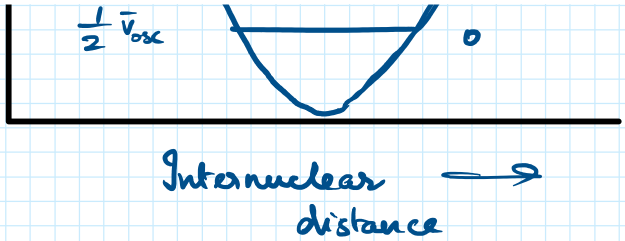
Allowed Energy Level Diagram (vibrational)

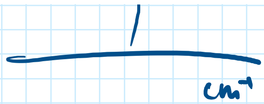


$\Delta V = \pm 1$



Why only 1 line?





1 line !

ROTATION & VIBRATION COMPARED

Rotation	Vibration
• $E_{rot} = \frac{h^2}{8\pi^2 I} J(J+1)$ Joules	• $E_{vib} = \left(v+\frac{1}{2}\right) h\nu_{osc}$
• $\varepsilon_{rot} = \frac{h}{8\pi^2 I c} J(J+1)$ cm^{-1}	• $\varepsilon_{vib} = \left(v+\frac{1}{2}\right)\bar{\nu}_{osc}$
•	