Lecl2

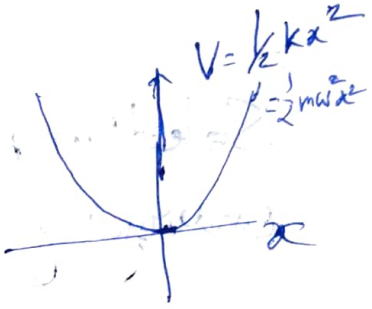
INFRA-RED SPECTROSCOPY

$1\,\mu m \lesssim \lambda \lesssim 100\,\mu m$

Deals with vibration of molecule

Simplest example :

Vibrating diatomic molecule



Model : Simple harmonic Oscillator

If the oscillation frequency ω_{osc}

Quantum Mechanics calculation

Energy of simple harmonic oscillator

$$E_v = \left(v + \frac{1}{2}\right)\hbar\omega_{osc} \qquad v = 0, 1, 2, \ldots$$

lowest vibrational energy $E_0 = \frac{1}{2}\hbar\omega_{osc}$.

3 ——
2 ——
1 ——
0 ——

Equally separated

purely Quantum result

No classical analogue of this.

$$E_{v+1} - E_v = \left(v+1+\tfrac{1}{2}\right)\hbar\omega_{osc} - \left(v+\tfrac{1}{2}\right)\hbar\omega_{osc}$$

$$= \hbar\omega_{osc}.$$

Separation is independent of vibrational quantum number v

Selection rule for harmonic oscillator undergoing vibrational changes:

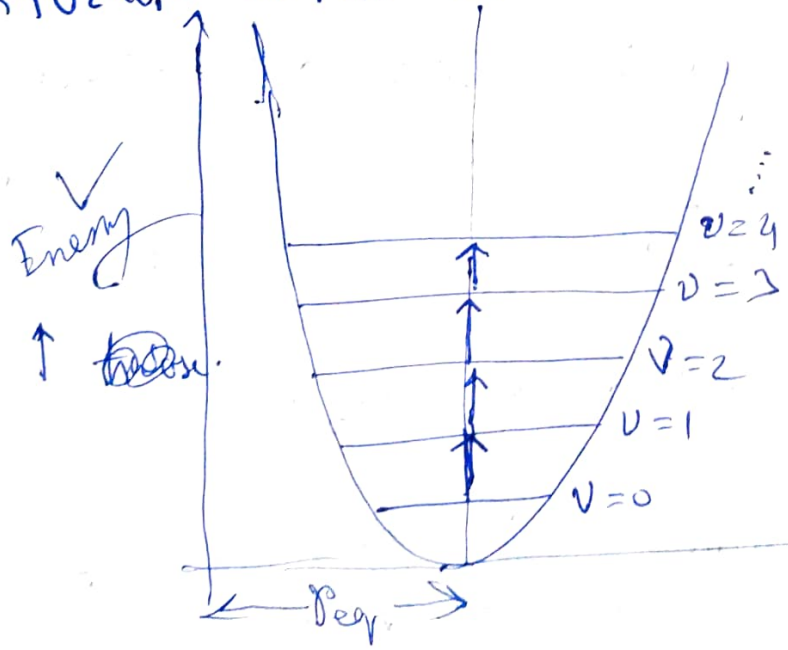
$$\Delta v = \pm 1$$

So only one wavenumber $\frac{\omega_{osc}}{hc}$

One line is spectrum

Additionally the diatomic molecule must be heteronuclear

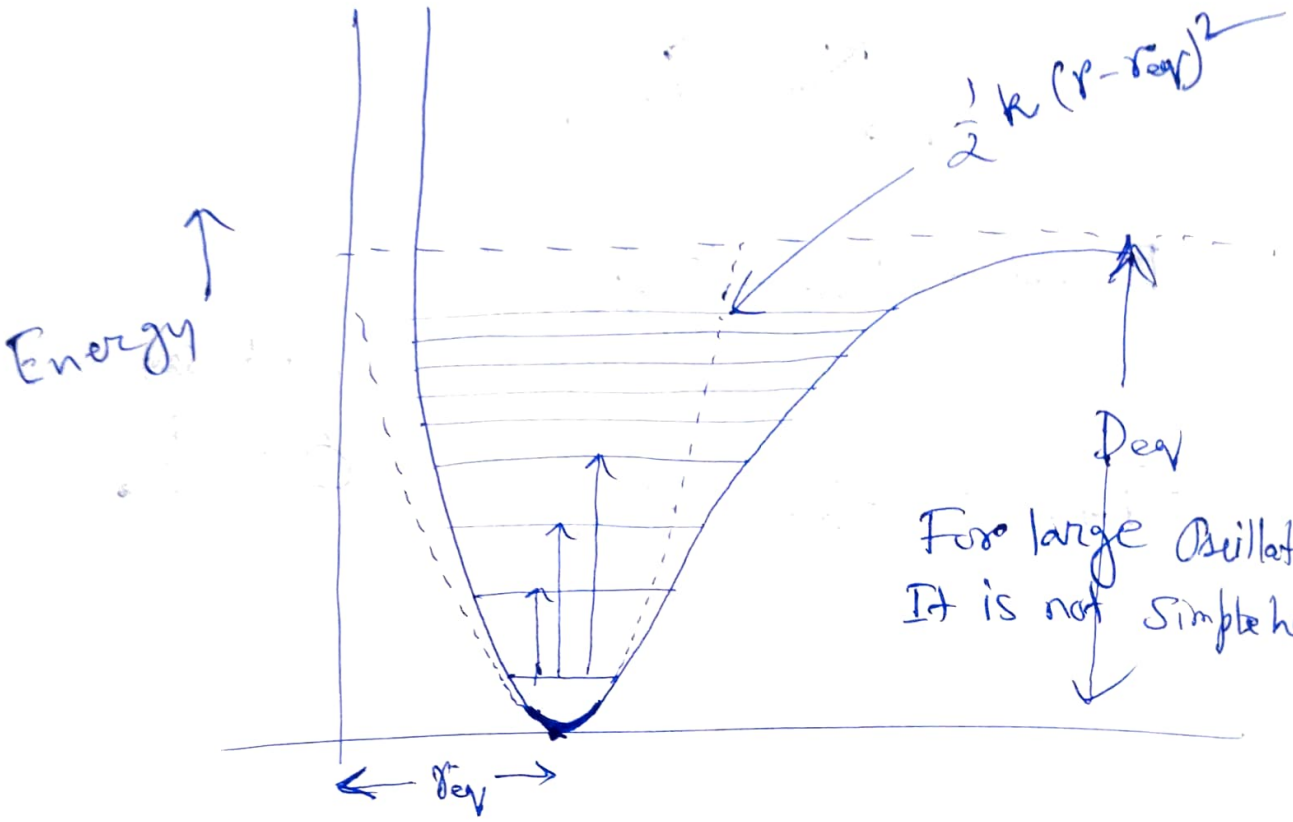
Because homonuclear molecule don't have dipole moment and can't interact with radiation.



$$V = \frac{1}{2}k_0\left(r_0 - r_{eq}\right)^2$$

The Anharmonic Oscillator

Reality



Empirical expression

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

D_{eq} dissociation energy.

From Calculation of Schrödinger equation.

The levels $E_v \simeq \left(v + \frac{1}{2}\right) \hbar \omega_{osc} - \left(v + \frac{1}{2}\right)^2 \hbar \omega_{osc} x_e$

x_e anharmonicity constant $\quad v = 0, 1, 2, \ldots$

In wave number

$$\varepsilon_v \simeq \frac{E_v}{hc} = \left(v+\tfrac{1}{2}\right)\frac{\omega_e}{2\pi c} - \left(v+\tfrac{1}{2}\right)^2 \frac{\omega_e}{2\pi c} x_e$$

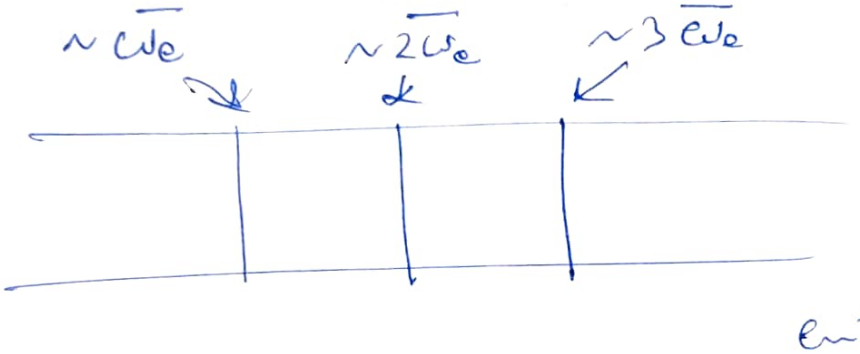
$$\simeq \left(v+\tfrac{1}{2}\right)\bar{\omega}_e - \left(v+\tfrac{1}{2}\right)^2 \bar{\omega}_e x_e$$

wave number

$$\frac{1}{\lambda} = \bar{\omega}_e = \frac{\omega_e}{2\pi c}$$

This approx. is good for initial few energy levels

Emission wave numbers



Selection rule $\Delta v = \pm 1, \pm 2, \pm 3, \ldots$

The diatomic vibrating rotator

Born - Oppenheimer approx.

$$E_{tot} = E_{rot} + E_{vib}$$

in wave number

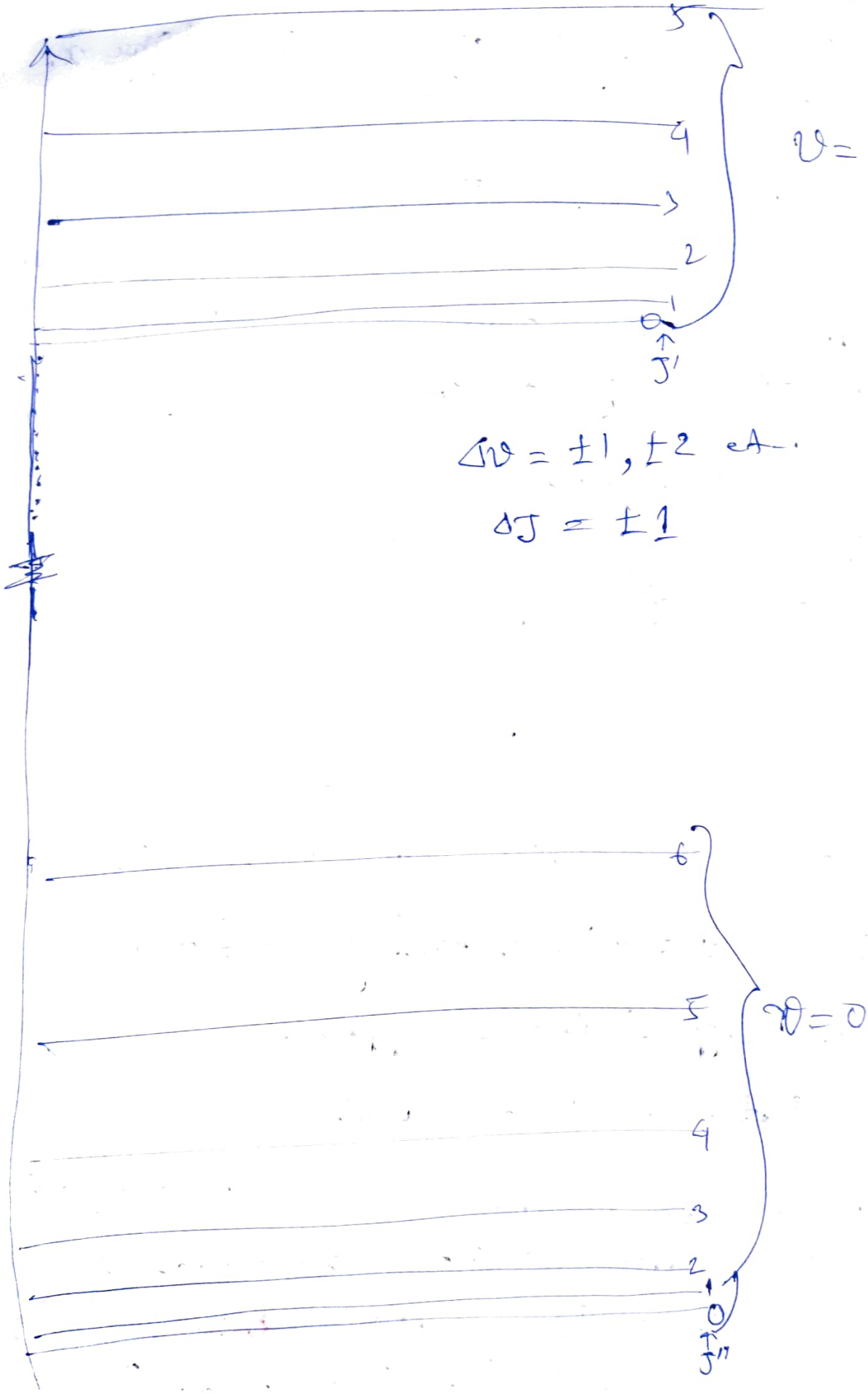
$$\varepsilon_{tot} = \varepsilon_{rot} + \varepsilon_{vib}$$

in wave number unit e.g. cm^{-1}

However this approx. doesn't always hold.

$$\varepsilon_{J,v} = \varepsilon_J + \varepsilon_v \quad \text{(More realistic)}$$

$$= B\,J(J+1) - D\,J^2(J+1)^2 + H\,J^3(J+1)^3 + \ldots$$
$$+ \left(v+\tfrac{1}{2}\right)\bar{\omega}_e - x_e\left(v+\tfrac{1}{2}\right)^2 \bar{\omega}_e$$



$\Delta v = \pm 1, \pm 2$ etc.

$\Delta J = \pm 1$