



ENGINEERING CHEMISTRY

Department of Science and Humanities

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Module I- Molecular Spectroscopy



Class Content:

- ***Vibrational spectroscopy-Anharmonic Oscillator***
- ***Expression for vibrational energy levels for an Anharmonic oscillator***
- ***Vibrational spectrum of an Anharmonic Oscillator***

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Vibrational spectroscopy-Anharmonic oscillator model

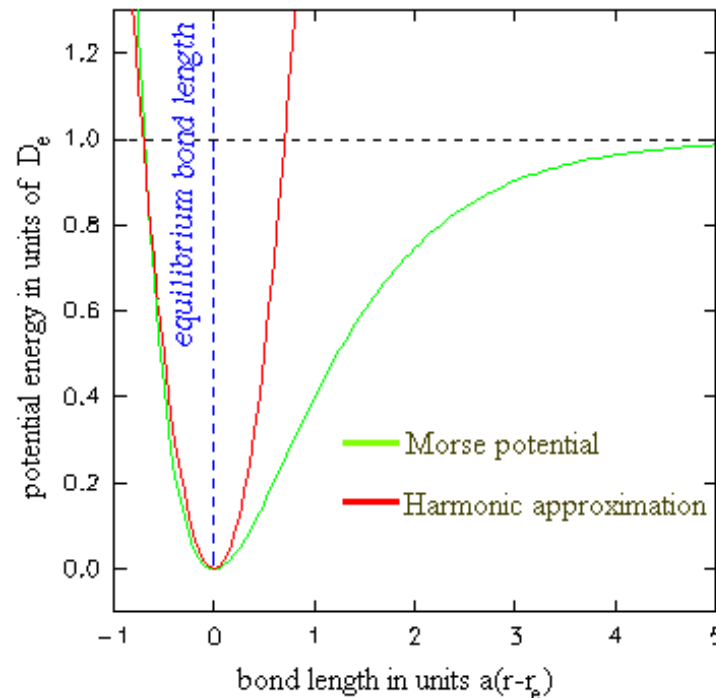
- In actual diatomics, the **potential is anharmonic** because the bond when stretched beyond a point breaks and the molecule dissociates
- A good description of an anharmonic oscillator is given by the Morse function

$$\text{P.E.} = D_{\text{eq}} [1 - \exp \{a(r_0 - r)\}]^2$$

D_{eq} is the depth of the PE curve

r_0 is the bond length

Source: <https://physics.stackexchange.com/questions/54814/why-is-there-a-global-minimum-for-the-morse-potential/55077>



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Energy levels of an anharmonic oscillator:

- Solving the **Schrodinger equation** for anharmonic oscillator the vibrational energy levels are given by the expression

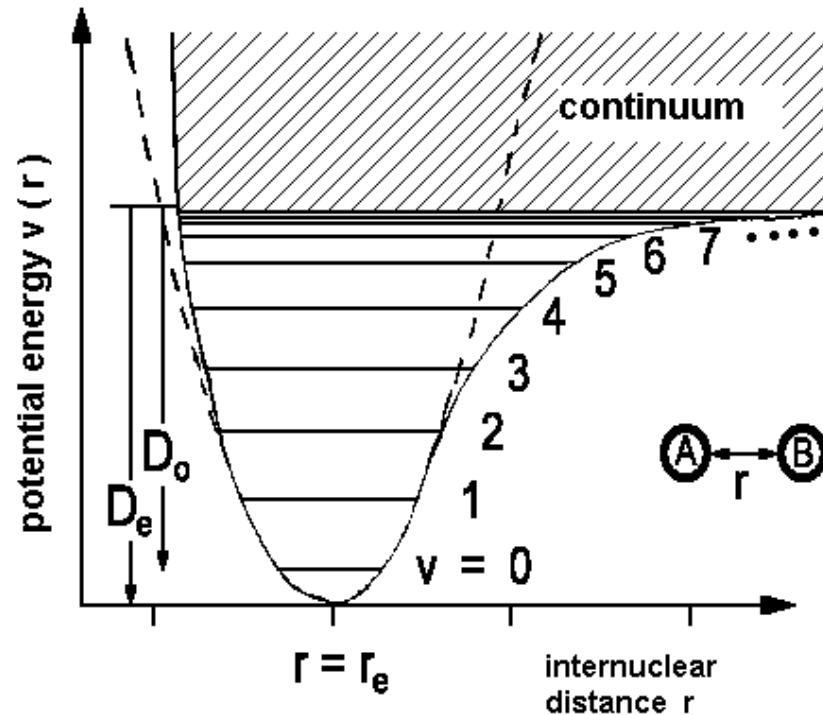
$$\varepsilon_v = \frac{E_v}{hc} = \left(v + \frac{1}{2}\right)\bar{\nu}_e - \left(v + \frac{1}{2}\right)^2 \bar{\nu}_e x_e \text{ cm}^{-1}$$

- x_e , is called the **anharmonicity constant** whose value for bond stretching vibrations is always small and positive
- $\bar{\nu}_e$ is the **oscillation frequency** expressed in wavenumbers
- v is the **vibrational quantum number** which can take up values 0,1,2,3....
- Substituting values for v we get the energy levels for an anharmonic oscillator

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Energy level diagram for a diatomic molecule showing anharmonicity



$$\epsilon_v = \frac{E_v}{hc} = \left(v + \frac{1}{2}\right) \bar{\nu}_e - \left(v + \frac{1}{2}\right)^2 \bar{\nu}_e x_e \text{ cm}^{-1}$$

Source: http://www.pci.tu-bs.de/aggericke/PC4e/Kap_III/Vibration.htm

The spacing between energy levels decreases as v , the vibrational quantum number, increases

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- **Selection rules** for vibrational transition of anharmonic oscillator :
 - **Gross selection rule** : When a molecule vibrates there should be change in dipole moment
 - **$\Delta v = \pm 1, \pm 2, \pm 3, \dots$**
- Most of the transitions start from **$v=0$ level** because this state is most populated
- The transitions observed are :
 - $v=0 \rightarrow v=1$ Fundamental absorption**
 - $v=0 \rightarrow v=2$ First overtone**
 - $v=0 \rightarrow v=3$ Second overtone**

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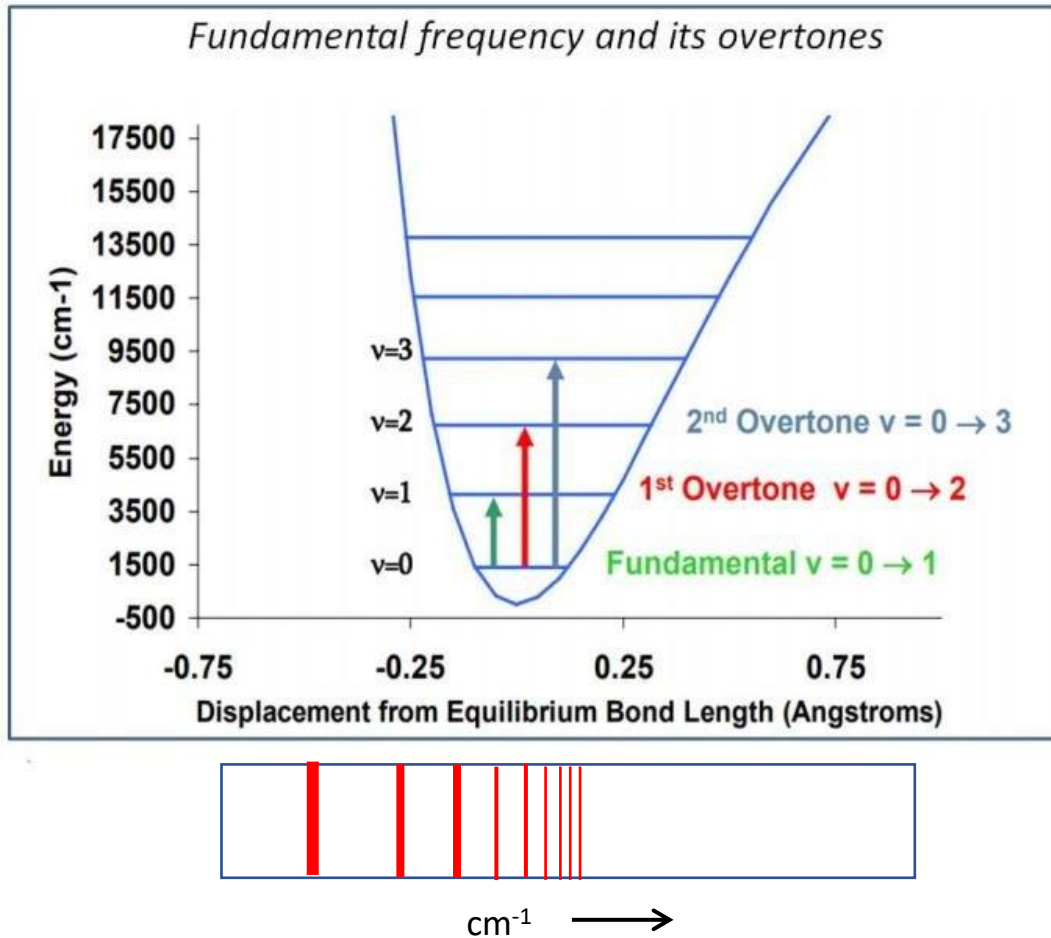
Substituting for values of v , we get the **energy gap** $\Delta\epsilon_{v+1 \leftarrow v}$

| Transition | Energy gap | |
|----------------|--|------------------------|
| $v=0$ to $v=1$ | $\Delta\epsilon_{1 \leftarrow 0} = \overline{\nu}_e(1 - 2x_e)cm^{-1}$ | Fundamental absorption |
| $v=0$ to $v=2$ | $\Delta\epsilon_{2 \leftarrow 0} = 2\overline{\nu}_e(1 - 3x_e)cm^{-1}$ | First overtone |
| $v=0$ to $v=3$ | $\Delta\epsilon_{3 \leftarrow 0} = 3\overline{\nu}_e(1 - 4x_e)cm^{-1}$ | Second overtone |

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Vibrational transitions for diatomic molecule undergoing anharmonic oscillations



Source: https://www.researchgate.net/figure/Fundamental-frequency-and-overtones-see-lecture-N-Antaris_fig2_331976119

The spacing between the lines in the spectrum decreases as we go to higher values of v

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At **higher temperatures** additional lines are visible in the spectrum as higher vibrational levels may also get populated and these lines originating from the higher vibrational levels are called **hot bands**
e.g., Energy absorbed for the transition from **v=1 to v=2** is given by,

$$\Delta \epsilon_{2 \leftarrow 1} = \overline{\nu}_e (1 - 4x_e) cm^{-1}$$

The expression shows that this line will appear to the left of the fundamental absorption in the spectrum



THANK YOU

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