

# Atomic and Molecular Physics

Course Code: PHYS4009

Lecture Topic

## *Vibrational Spectroscopy*

By

***Prof. Sunil Kumar Srivastava***

**Department of Physics**

**Mahatma Gandhi Central University**

**Motihari, Bihar-845401**

Please see the video lecture at

[https://www.youtube.com/watch?v=FYGA5bM\\_IWA](https://www.youtube.com/watch?v=FYGA5bM_IWA)



# Introduction

## Why Vibrational Spectroscopy?

- *For the identification of characteristic vibrational motion*
- *Structural information of the molecules*
- *Detection of functional groups*
- *Information about isotopes*
- *To study molecular interactions*



# *Vibrational Spectroscopy*

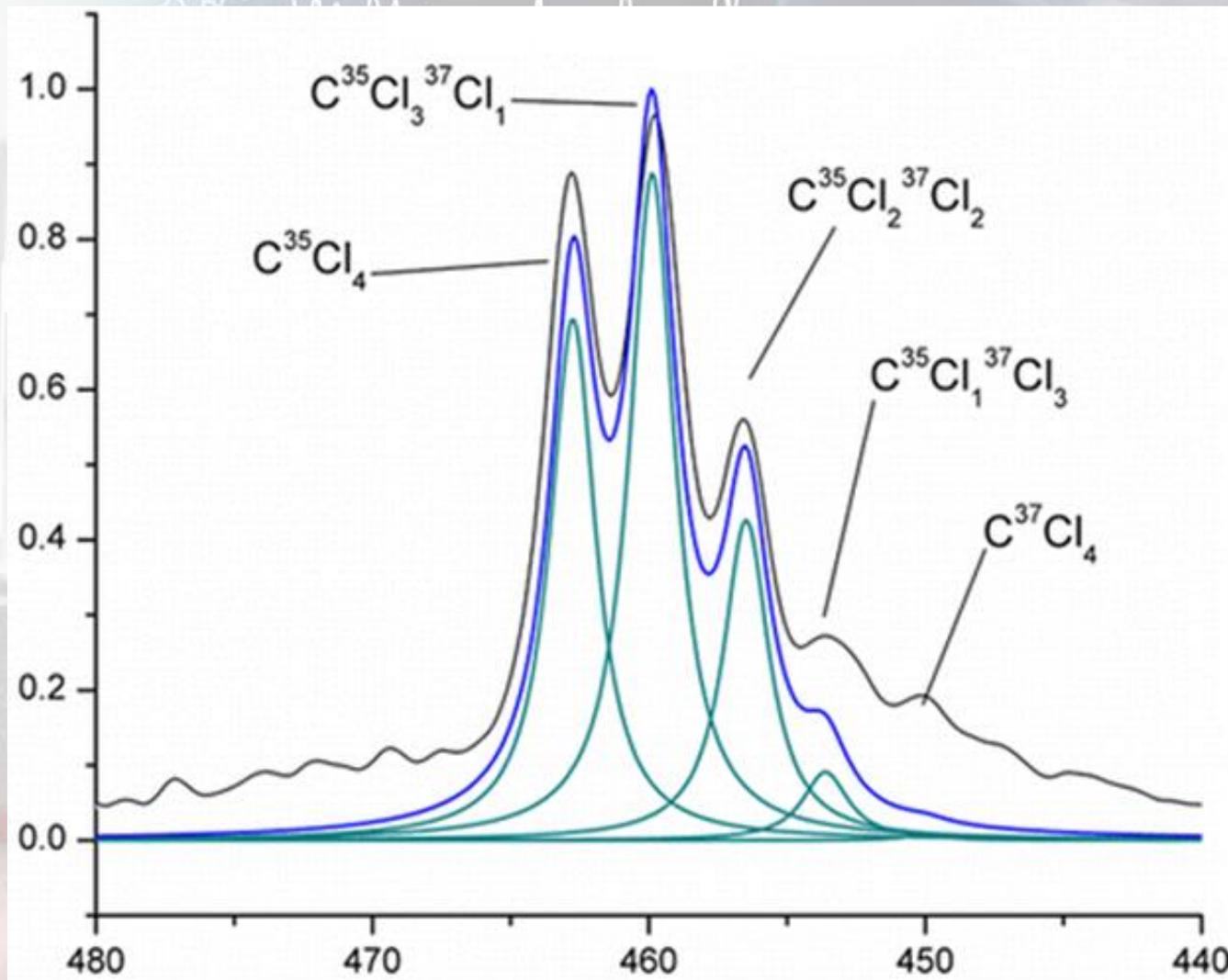
Vibrational Spectroscopy is a method of characterizing and identifying compounds that works by measuring the vibrational spectra of compounds. Each compound has a unique fingerprint or measurement of the vibrations, allowing compounds to be identified.

The vibrational spectra gives information about the composition, type of bonding, bond strength, isotopic substitution, information about functional group, complex species, etc.



# Vibrational Spectra

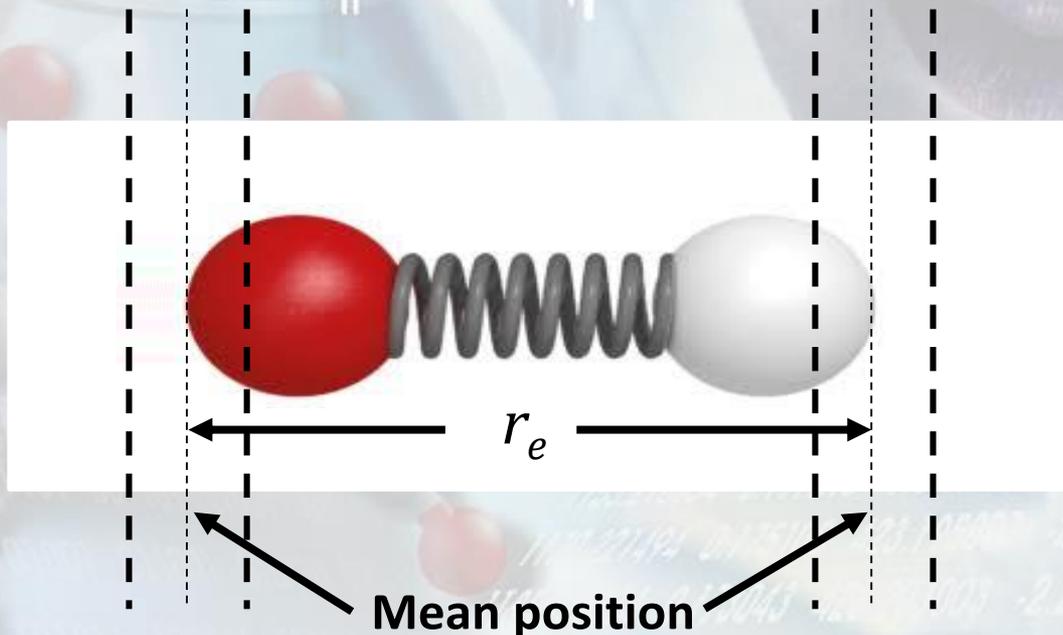
Normalized Raman Intensity



Wavenumber (cm<sup>-1</sup>)

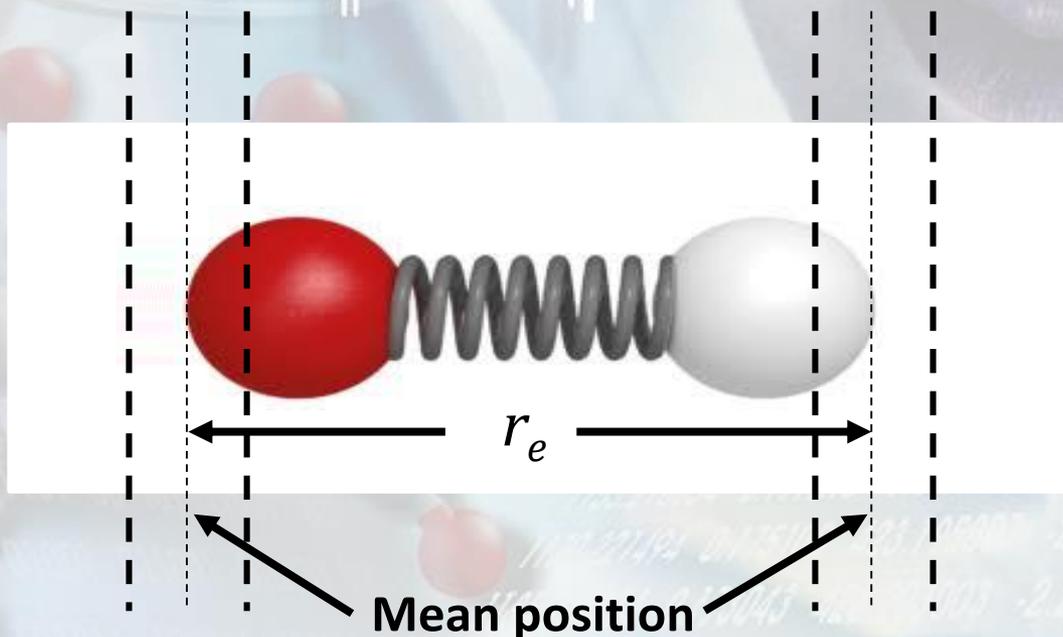
# Origin of Vibrational Spectra

- *Non-rigid nature of bonds*
- *Bond get stretched while rotation*
- *The elastic nature of bond causes vibration of atoms of the molecule about the mean position.*



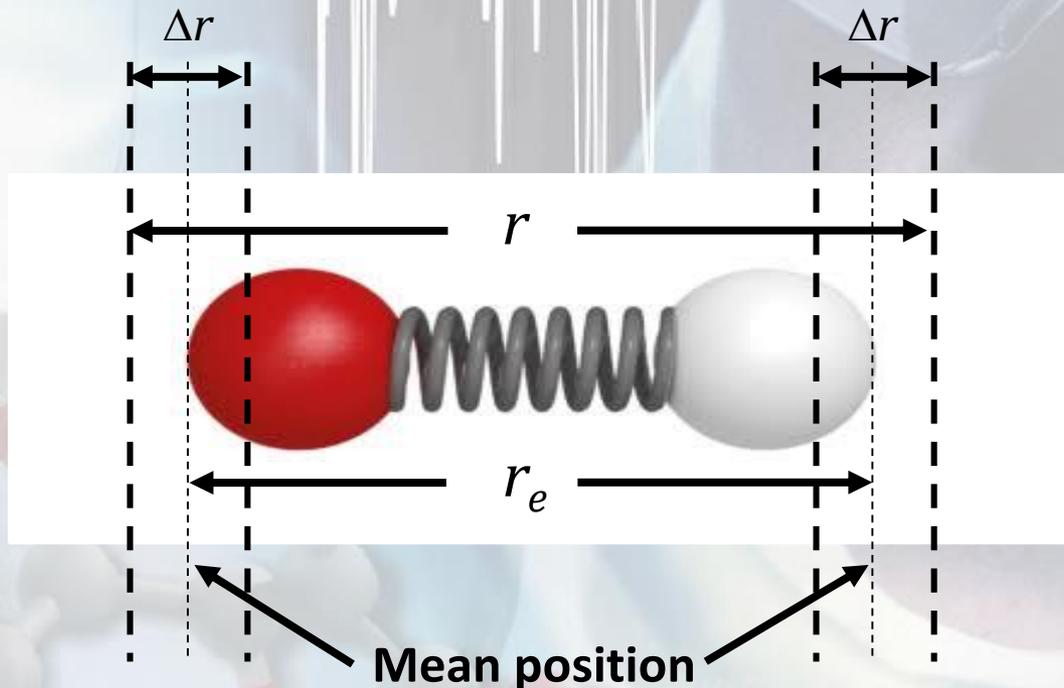
# Origin of Vibrational Spectra

- *Non-rigid nature of bonds*
- *Bond get stretched while rotation*
- *The elastic nature of bond causes vibration of atoms of the molecule about the mean position.*



# Classical Harmonic Oscillator

Consider simple case of a vibrating diatomic molecule, For small displacements the stretching and compression of the bond, represented by the spring, obeys Hooke's law.



$$\text{Restoring Force} = -\frac{dV(r)}{dr} = -k\Delta r$$

where,

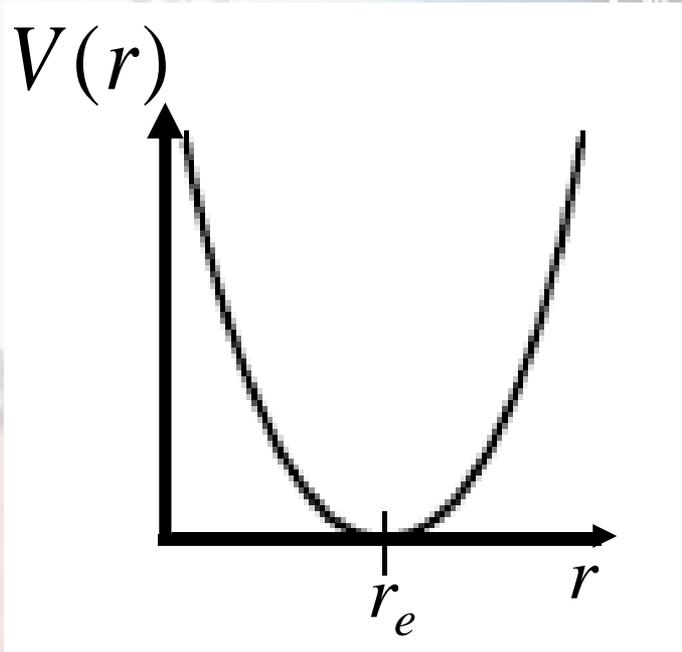
$$\Delta r = r - r_e$$

$k$  is spring constant or force constant



# Potential Energy of Harmonic Oscillator

$$V(r) = -\int F dr = \frac{1}{2} k (r - r_e)^2$$



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

$$\omega = 2\pi\nu = \sqrt{\frac{k}{\mu}}$$



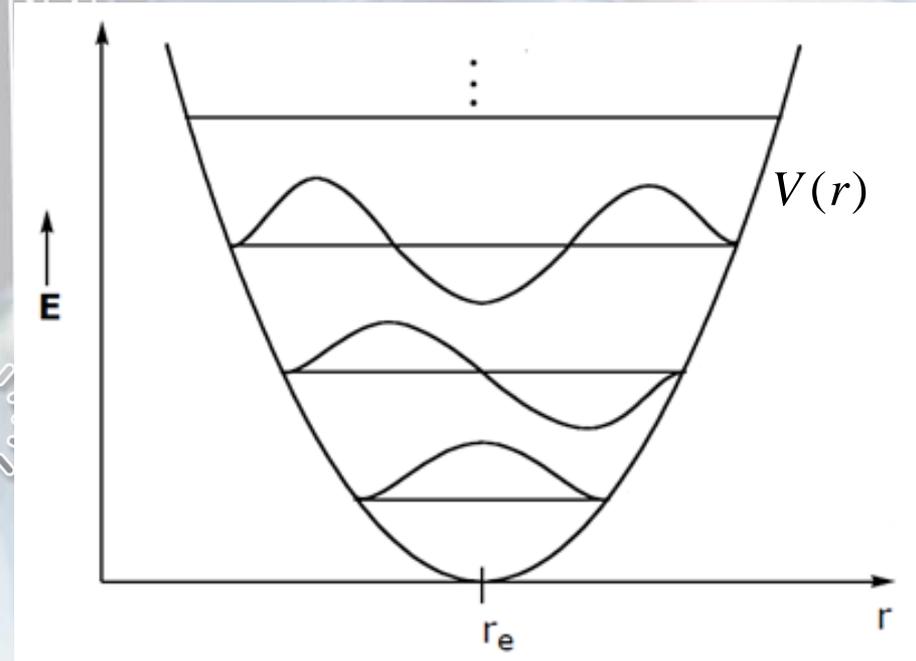
# Quantum Mechanical Harmonic Oscillator

$$H\psi_{vib} = E_{vib}\psi_{vib}$$

$$\left[ -\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial r^2} + V(r) \right] \psi_{vib} = E_{vib} \psi_{vib}$$

$$V(r) = \frac{1}{2} k (r - r_e)^2$$

$$\frac{\partial^2 \psi_{vib}}{\partial r^2} + \frac{2\mu}{\hbar^2} \left[ E_{vib} - \frac{1}{2} k (r - r_e)^2 \right] \psi_{vib} = 0$$



# Normalized Vibrational Wavefunction

$$\psi_{\text{vib}}(y) = \frac{(\alpha / \pi)^{\frac{1}{4}}}{\sqrt{2^n n!}} e^{\alpha r^2 / 2} H_n(y) \quad \text{where } y = \sqrt{\alpha} r \text{ and } \alpha = \frac{\mu \omega}{\hbar}$$

$H_n(y)$  is Hermite polynomial

$$H_n(y) = (-1)^n e^{y^2} \frac{d^n}{dy^n} e^{-y^2}$$

$$n = 0: H_0(y) = 1$$

$$n = 1: H_1(y) = 2y$$

$$n = 2: H_2(y) = 4y^2 - 2$$

$$n = 3: H_3(y) = 8y^3 - 12y$$

$$n = 4: H_4(y) = 16y^4 - 48y^2 + 12$$

$$n = 5: H_5(y) = 32y^5 - 160y^3 + 120y$$

# Normalized Vibrational Wavefunction

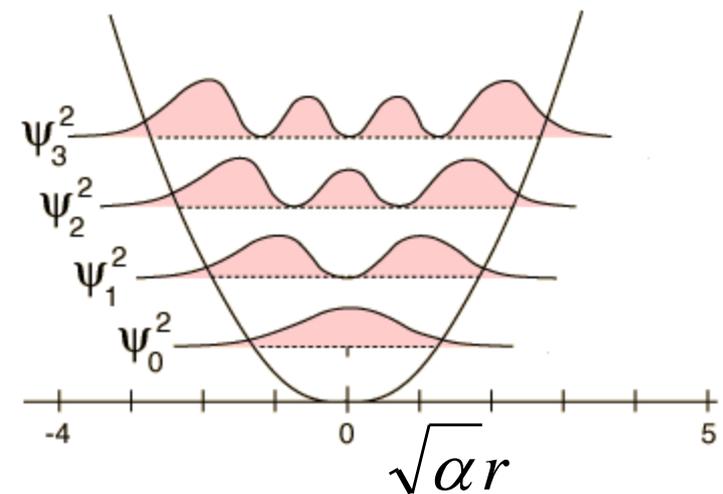
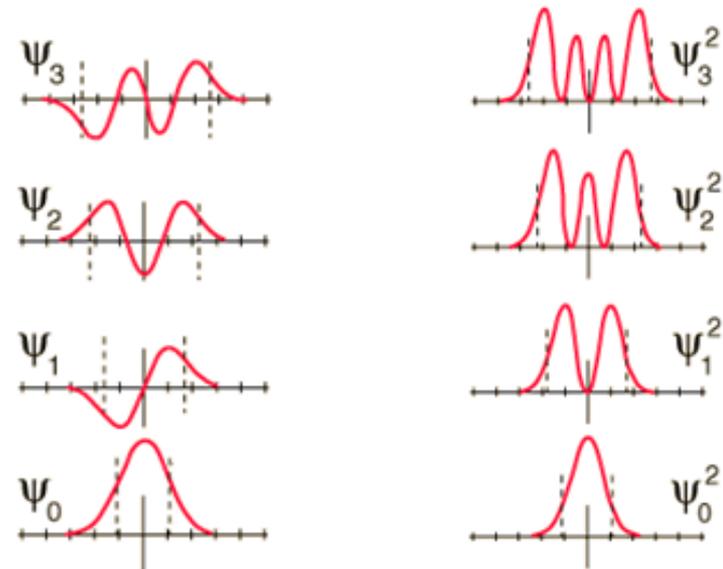
$$\psi_0 = \left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}} e^{-y^2/2}$$

$$\psi_1 = \left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}} \sqrt{2} y e^{-y^2/2}$$

$$\psi_2 = \left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}} \frac{1}{\sqrt{2}} (2y^2 - 1) e^{-y^2/2}$$

$$\psi_3 = \left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}} \frac{1}{\sqrt{3}} (2y^3 - 3y) e^{-y^2/2}$$

$$P(r) = |\psi_n(r)|^2$$



# Energy of Vibrational States

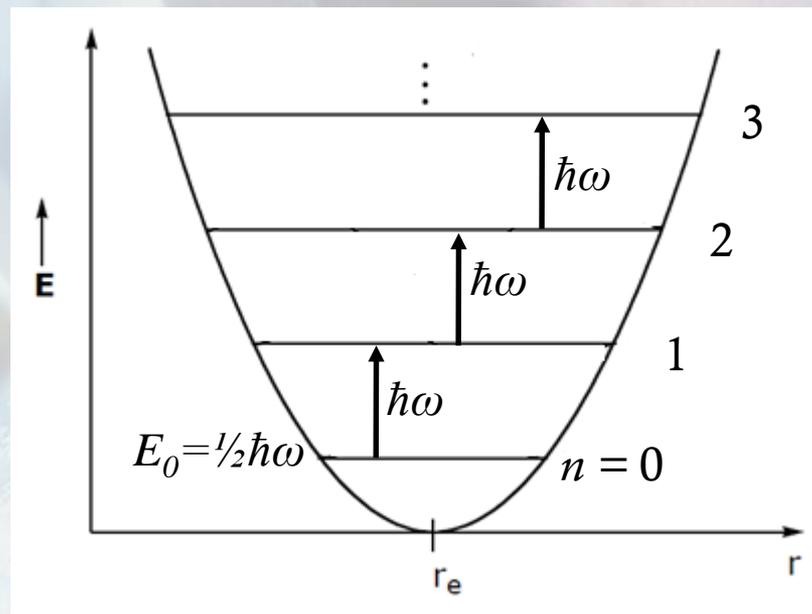
$$E_n = \left( n + \frac{1}{2} \right) \frac{h}{2\pi} \sqrt{\frac{k}{\mu}} = \hbar\omega \left( n + \frac{1}{2} \right)$$

Energy of each state:  $E_n = (n + 1/2)\hbar\omega$

Energy level separation:  $E(n + 1) - E(n) = \hbar\omega$

## Selection Rule

Harmonic Oscillator:  $\Delta n = \pm 1$

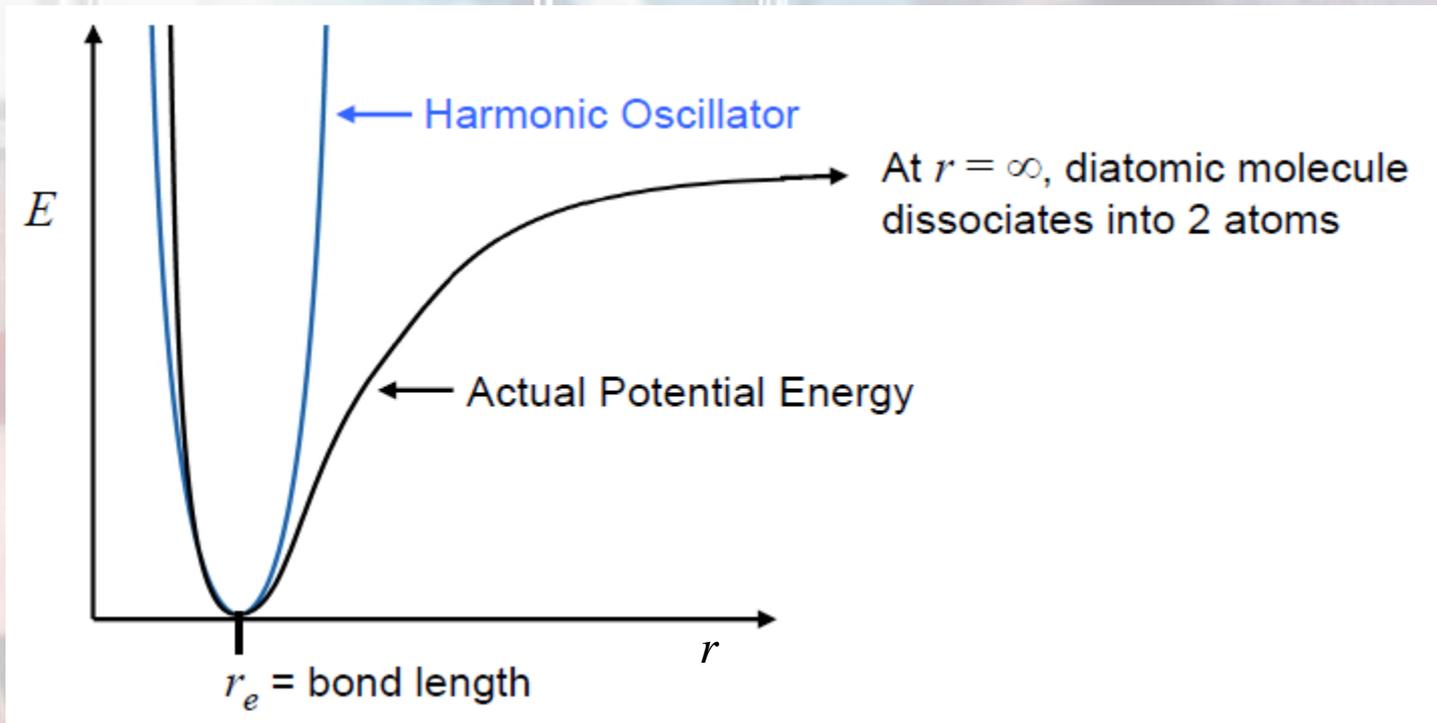


# Limitations of Simple Harmonic Oscillator

Simple harmonic oscillator does not predict bond dissociation.

Simple harmonic oscillator fits well at low excitation but fits poorly at high excitation.

Simple harmonic oscillator explains only fundamental vibrations but not the overtones.



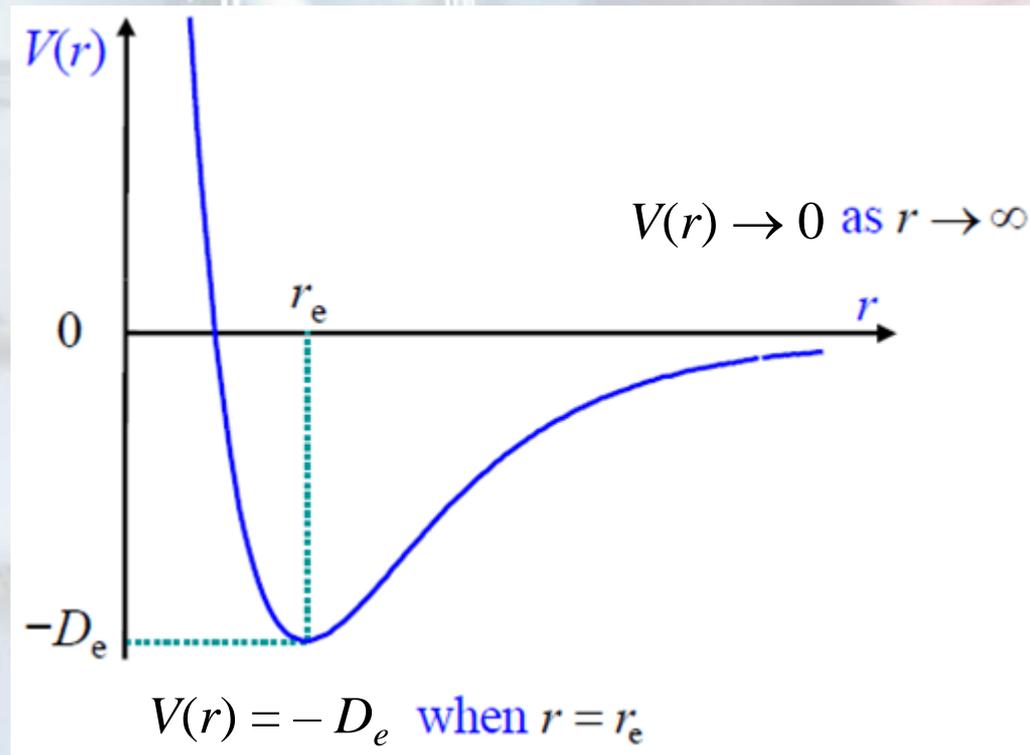
# The Morse Potential

Morse potential give the better approximation to potential energy of vibrating diatomic molecules

$$V(r) = D_e \left[ 1 - e^{-a(r-r_e)} \right]^2 - D_e$$

$D_e$  is depth of potential well

$$a = \sqrt{\frac{\mu\omega^2}{2D_e}}$$



# Anharmonic Oscillator

Schrödinger wave equation for the diatomic molecule with Morse potential is given by

$$\hat{H}\psi = E\psi \quad \equiv \quad \left[ \underbrace{-\frac{\hbar^2}{2\mu} \frac{d^2}{dx^2}}_{\text{Kinetic energy}} + \underbrace{D_e \left[ 1 - e^{-a(r-r_e)} \right]^2}_{\text{Potential energy given by Morse Potential}} \right] \psi(x) = E\psi(x)$$

$$E_n = (n + 1/2)\hbar\omega_e - (n + 1/2)^2 x_e \hbar\omega_e \dots \text{(Joules)}$$

Where:  $n = 0, 1, 2, 3,$

Anharmonicity Constant:  $x_e = \frac{a^2 \hbar}{2\mu\omega_e}$

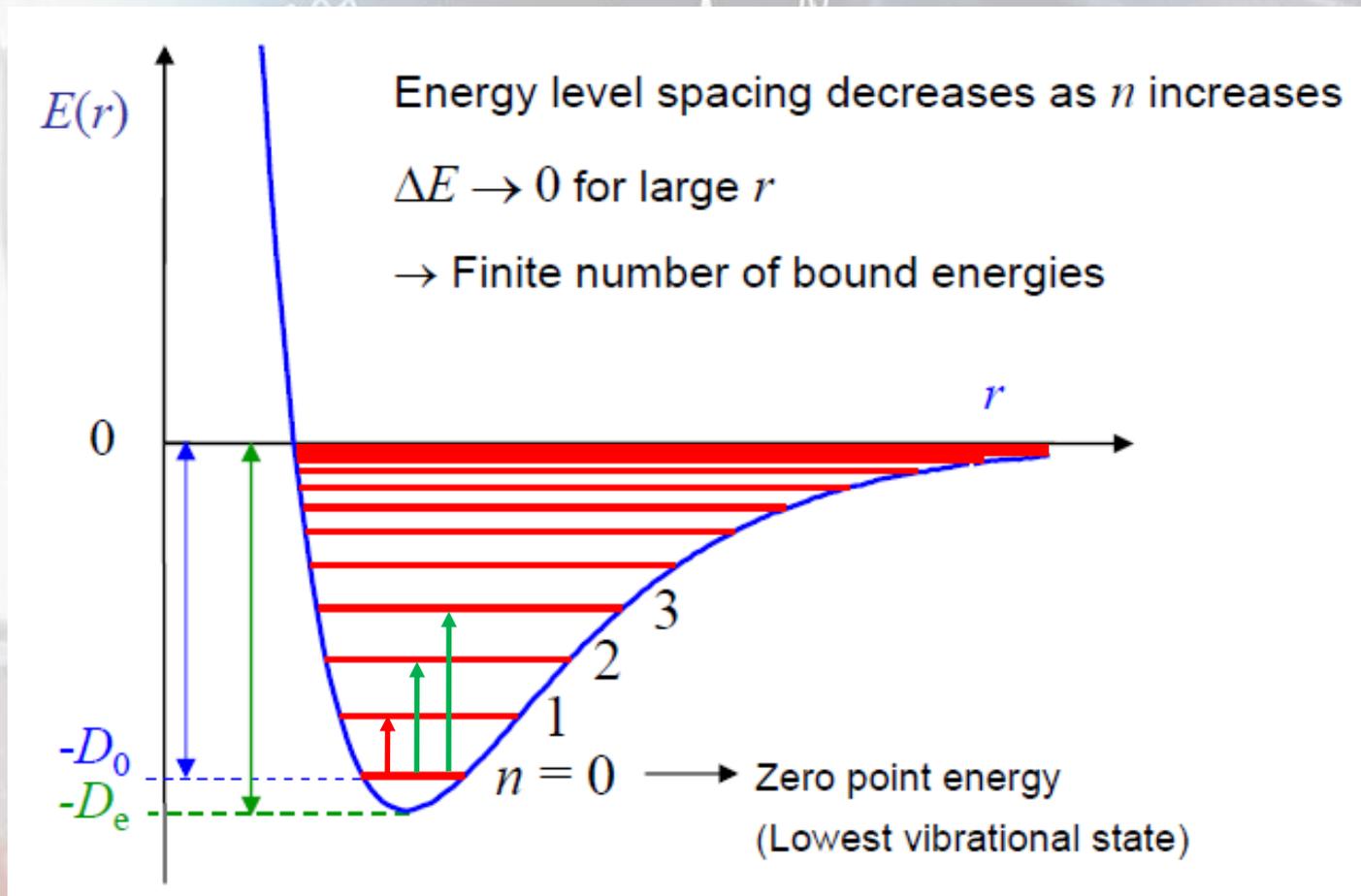
Recall: **Energies of Harmonic Oscillator**

$$E_n = (n + 1/2)\hbar\omega$$

$$E_n = (n + 1/2)\tilde{\nu}_e - (n + 1/2)^2 x_e \tilde{\nu}_e \quad (\text{cm}^{-1})$$



# Vibrational Energy States



## Selection Rule

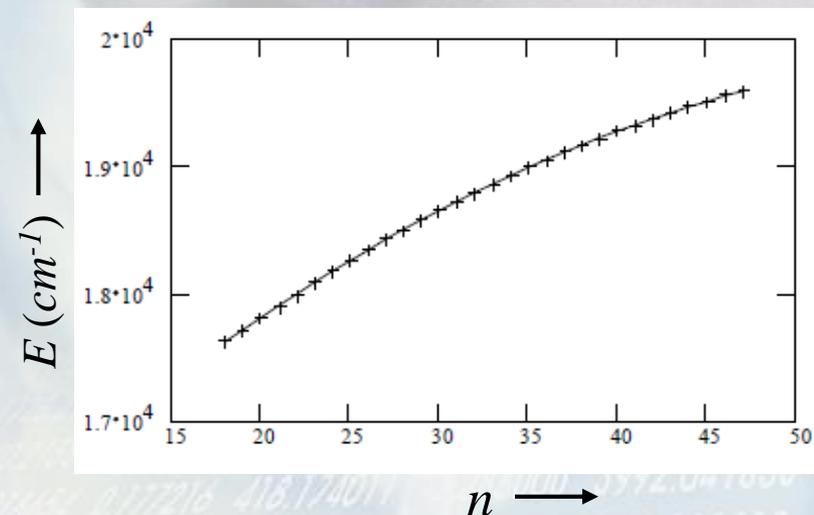
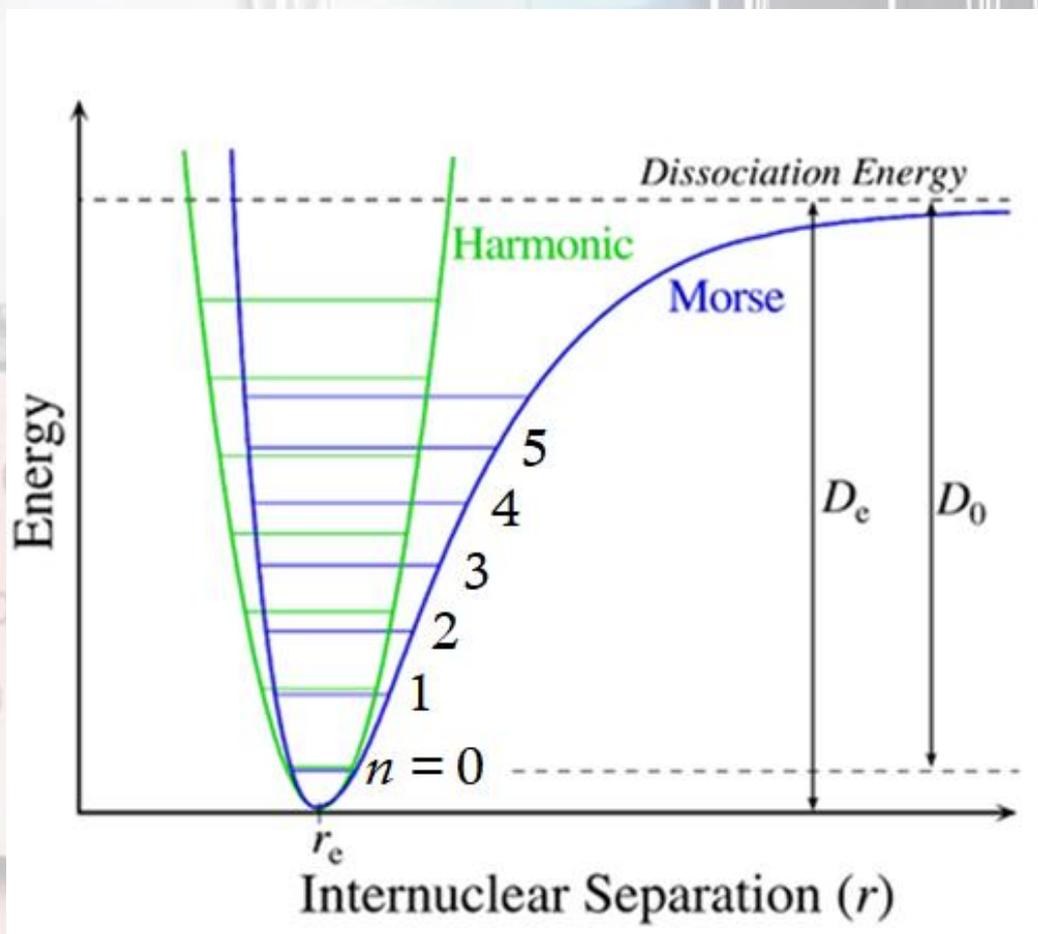
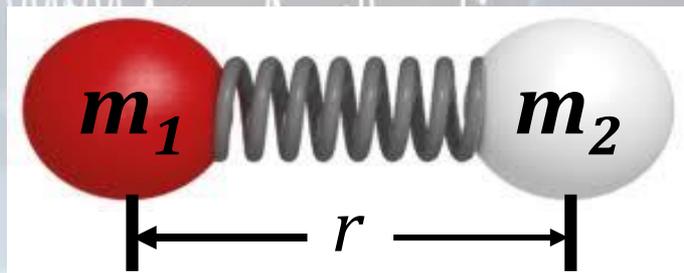
Anharmonic Oscillator:  $\Delta n = \pm 1, \pm 2, \pm 3, \dots$

Fundamental

Overtones



# Harmonic vs Anharmonic Oscillator



$$\Delta \tilde{\nu} (cm^{-1}) = E_{n+1} - E_n$$

*If higher order anharmonicity is negligible*

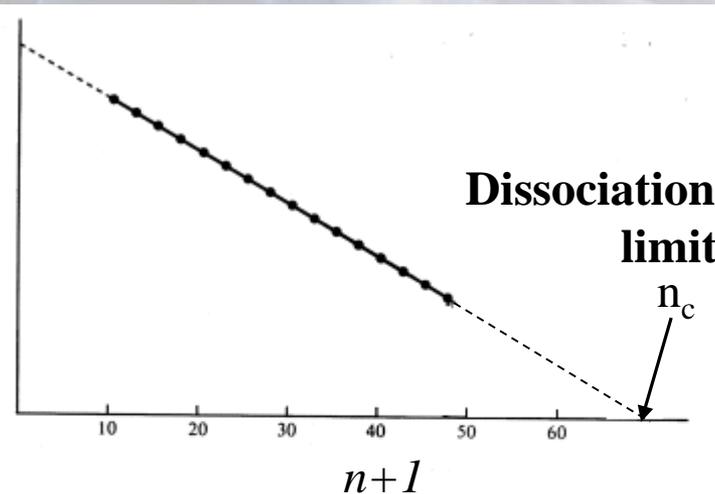
$$\Delta \tilde{\nu} (cm^{-1}) = \tilde{\nu}_e - 2(n+1)x_e \tilde{\nu}_e$$

$$D_0 = \sum_{n=0}^{n=n_c} \Delta \tilde{\nu} = \int_0^{n_c} \Delta \tilde{\nu} dn$$

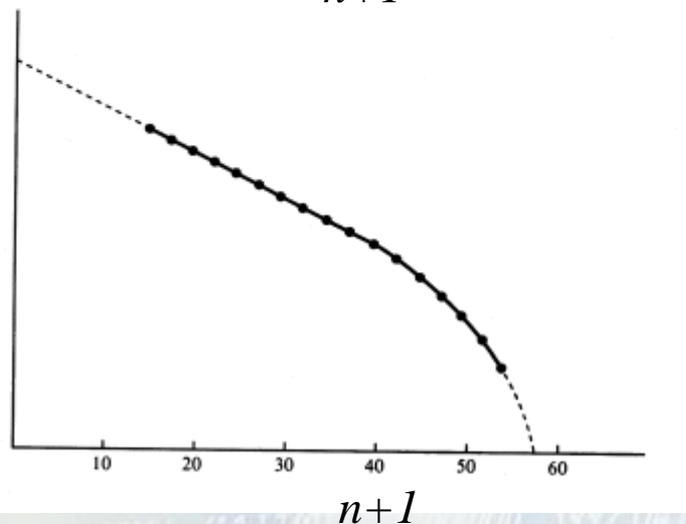
*If higher order anharmonicity is not negligible*

$$\Delta \tilde{\nu} (cm^{-1}) = \tilde{\nu}_e - 2(n+1)x_e \tilde{\nu}_e + (3n^2 + 6n + 13/4)y_e \tilde{\nu}_e + \dots$$

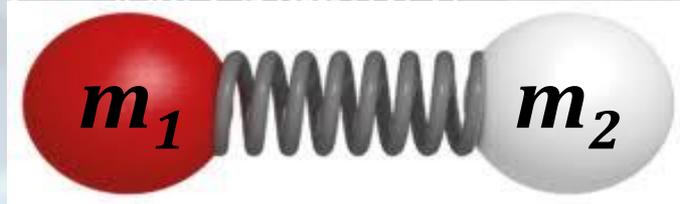
$\Delta \tilde{\nu} (cm^{-1})$



$\Delta \tilde{\nu} (cm^{-1})$



# Summary

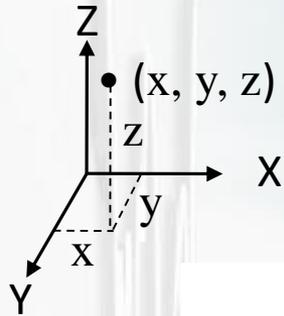


$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

$$\omega = 2\pi\nu = \sqrt{\frac{k}{\mu}}$$

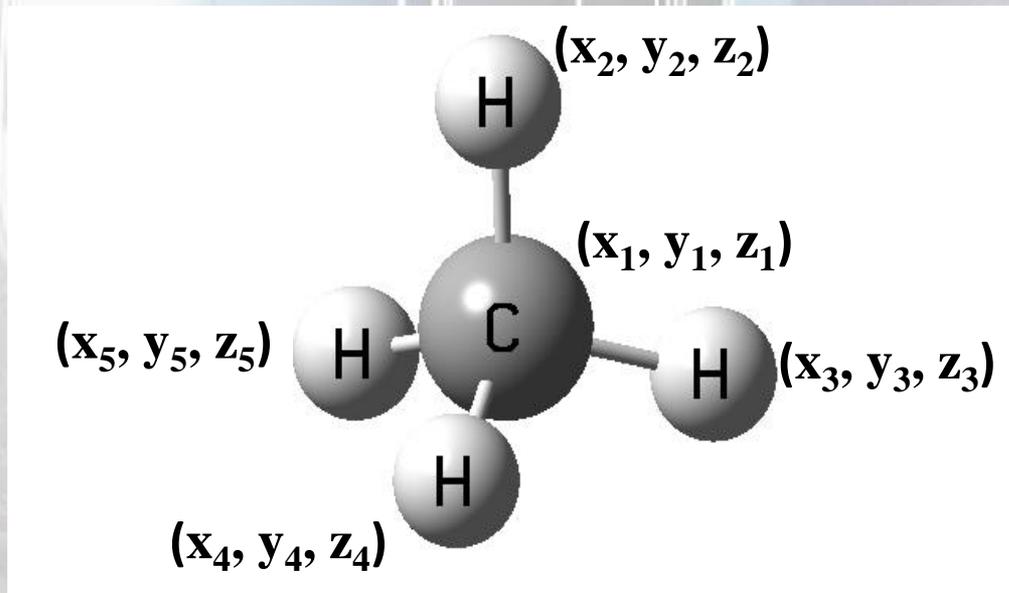


# Vibrations in Polyatomic Molecule



## *Cartesian coordinates*

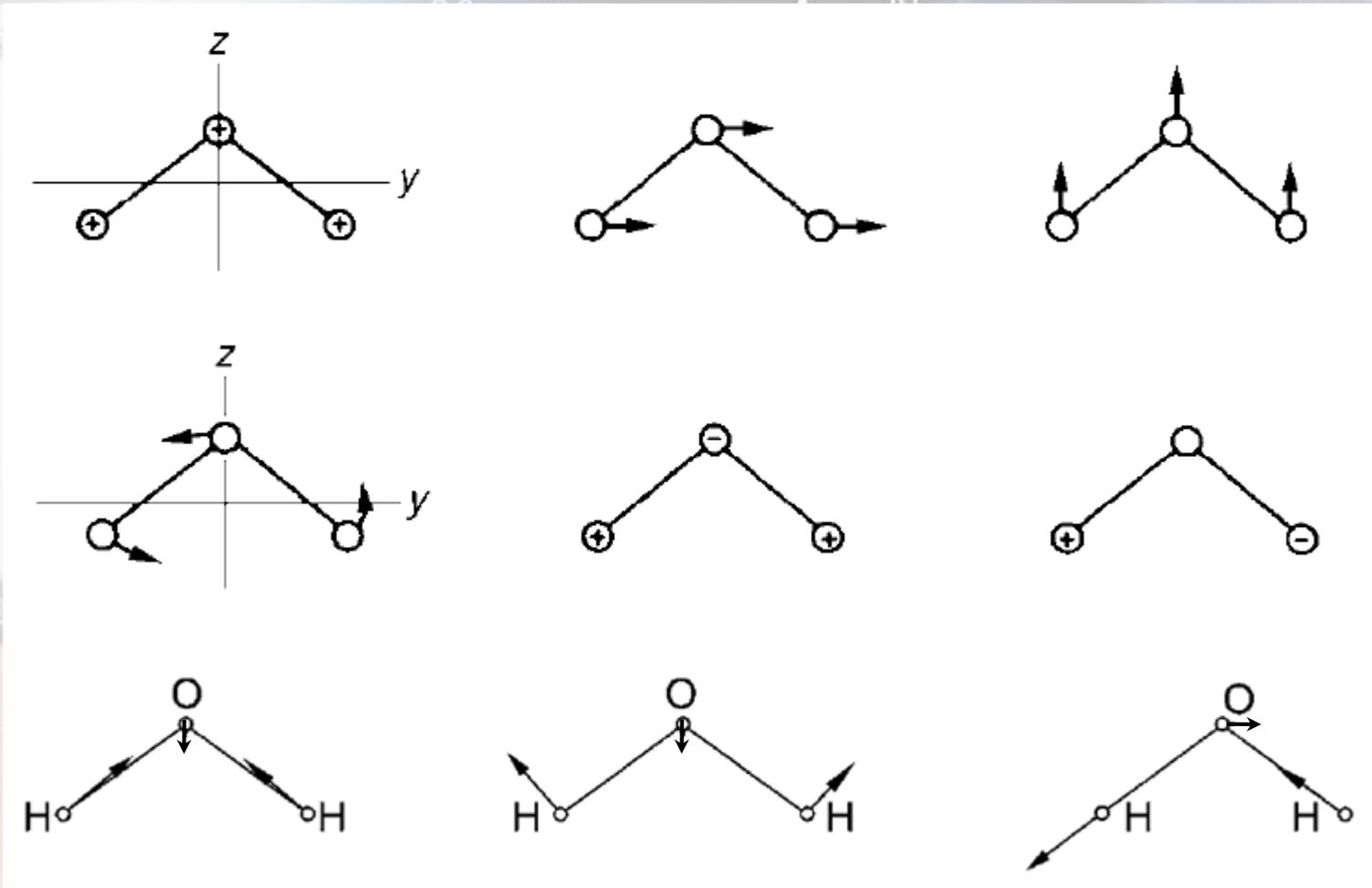
C	$x_1$	$y_1$	$z_1$
H	$x_2$	$y_2$	$z_2$
H	$x_3$	$y_3$	$z_3$
H	$x_4$	$y_4$	$z_4$
H	$x_5$	$y_5$	$z_5$



For molecule having N atoms:  $3N$  Cartesian coordinates

For molecule having N atoms:  $3N$  Degree of Freedom

# Distribution of 3N Degree of Freedom



Translation

Rotation

Vibration

*The vibrational degree of freedom in molecule having N atom*

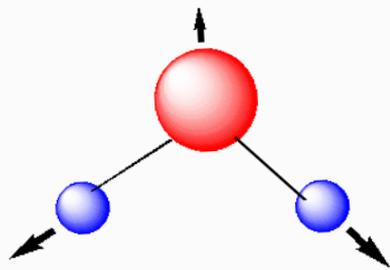
*For non-linear molecule :  $3N - 6$*

*For linear molecule :  $3N - 5$*

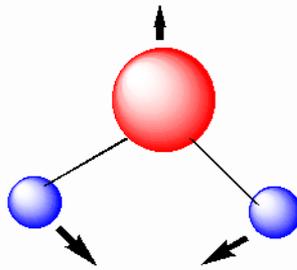


# Normal Mode of Vibration

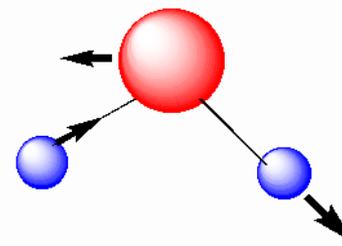
A mode of vibration is called normal mode of vibration in which all atoms of a molecule oscillate with same frequency and in phase such that the center of mass must not change.



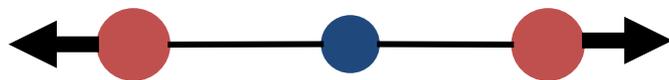
Symmetric stretching



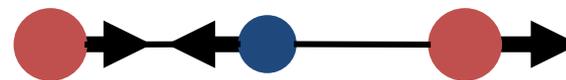
Bending



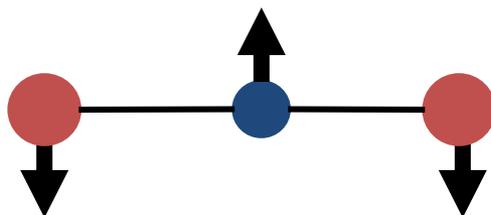
Anti-symmetric stretching



Symmetric stretching



Anti-symmetric stretching



Bending



# Books for Further Reading

1. Fundamentals of Molecular Spectroscopy by C. N. Banwell (McGraw Hill)
2. Basic Atomic & Molecular Spectroscopy by J. M. Hollas (Royal Society of Chemistry)

## References:

<http://hyperphysics.phy-astr.gsu.edu/hbase/index.html>





Thank you

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