**Topics**

■    Introduction to harmonic oscillator in quantum mechanics. Energy levels and wave functions.

■    Vibrational anharmonicity in diatomic molecule (The Morse potential model).

■    Polyatomic vibrations through normal mode approximation.

■    Polyatomic vibrational spectroscopy (local modes or finger points).

■    Samples of IR spectra.

■    Problems and quizzes.

■    Solutions.

■    Harmonic oscillators - diatomic molecules.

■    Anharmonicity.


Review of important concepts from the lecture on quantum mechanics of harmonic oscillators.

**1. Harmonic Oscillator model for Diatomic molecules:**

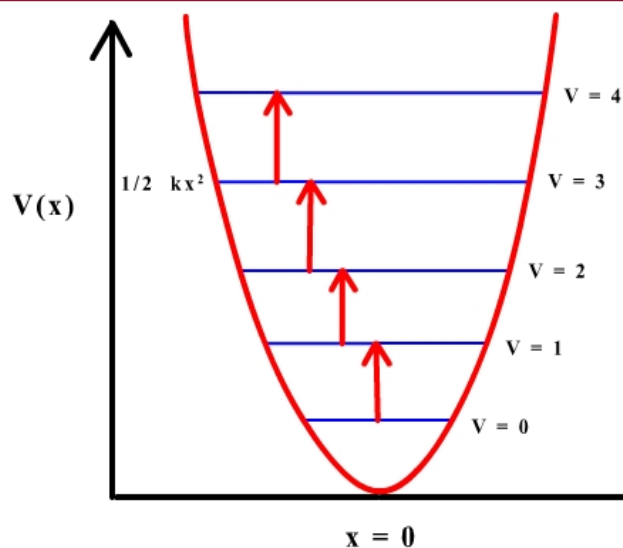■    Replace m in lecture 7 by $\mu$, the reduced mass of a diatomic: then

$$E = h\nu \left( \nu + \frac{1}{2} \right)$$

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$

where k is the force constant and is directly related to the bond strength. A high value for force constant is interpreted to be result of a stronger bond.
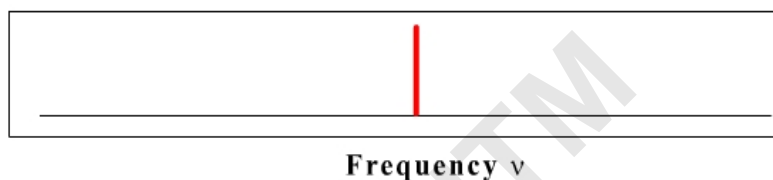

■    Pure diatomic approximated by a simple harmonic oscillator for its vibrational motion

$$E_{\nu+1} - E_{\nu} = h\nu$$

has only one spacing

**All Transitions from any V to V+1 are the same. Therefore, the resulting spectrum contains only one line and is featureless.**



**Frequency** $\nu$

Therefore a pure vibrational spectrum of a diatomic in the harmonic approximation consists of ONE LINE (and is featureless).

■   For a vibrating molecule to have an infrared spectrum, its dipole moment must undergo changes during the vibrational motion. Changing the dipole moment (oscillating dipole moment) and electromagnetic field - electric component can resonate with each other - then there is absorption of energy.

Thus:

$H_2$- microwave and IR inactive.

Hcl - microwave and IR active.

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■   Solutions.

■   Harmonic oscillators - diatomic molecules.

■   Anharmonicity.

**1. Introduction to Harmonic Oscillator.**

**Classical Mechanics**

A simple harmonic oscillator is an example of small - amplitude oscillatory motion of a mass point about an equilibrium point.

click the play button to view the animation

click the play button to view the animation

click the play button to view the animation

When the mass point is made to oscillate about the centre, a restoring force acts on the mass point. The restoring force $\vec{F}$ is proportional to the displacement from equilibrium but points in the direction opposite to the displacement vector. See the picture below.
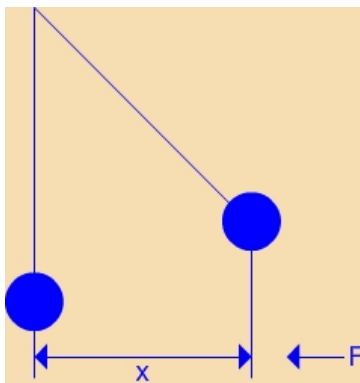


The relation: (Hooke's law).

$$\vec{F} \ \alpha \ -\vec{x}; \quad \vec{F} \ \alpha \ -k\vec{x};$$

where k is the force constant, a measure of the strength of the restoring force.

Larger the value of k, larger the restoring force even for a small displacement.

k is a property of the harmonic oscillator system.

For a diatomic molecule, a large value of k means a strong bond. A smaller value of k means, for example, a weaker bond.

The potential energy of the oscillator is given by V(x).

When there is no displacement, V = 0. The restoring force at any point is the negative derivative of the potential energy at that point with respect to the displacement coordinate.

i.e. V(0) = 0.

$$-\frac{dV}{dx} = \vec{F} = -k\vec{x}$$

$$V(x) = \int kx \Rightarrow \frac{1}{2}kx^2 + C$$

$$C = 0 \ for \ V(0)$$

$$\therefore V(x) = \frac{1}{2}kx^2$$

The kinetic energy of the harmonic oscillator due to its motion is

$$T = \frac{1}{2}m\dot{x}^2 = \frac{p^2}{2m}$$

The total energy, or the Hamiltonian H of the harmonic oscillator is the sum of its potential and kinetic energies. Classically,

$$H = T + V = \frac{p^2}{2m} + \frac{1}{2}kx^2$$

In order to understand the relation between the harmonic oscillator Hamiltonian and molecular vibrations, consider the diatomic molecule in the picture.

Diatomic molecular vibration
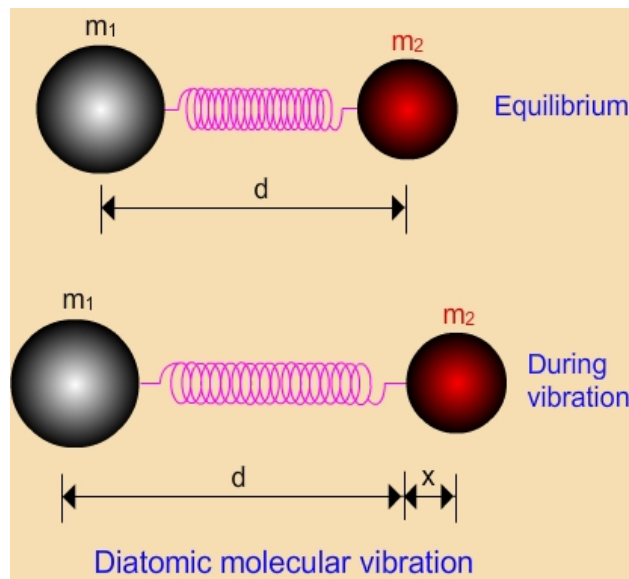
The kinetic energy of the diatomic molecule when it oscillates with a small amplitude is

$$T = \frac{1}{2}\left[ m_1\left(\frac{dx_1}{dt}\right)^2 + m_2\left(\frac{dx_2}{dt}\right)^2 \right]$$

where $x_1$ and $x_2$ are vector displacements of atoms 1 and 2 (grey and red) from their equilibrium positions.

The potential energy of a vibrating diatomic molecule is

$$V(x_1, x_2) = \frac{1}{2}k(x_1 - x_2)^2 = \frac{1}{2}kx^2$$

If we neglect the overall translational motion of the molecule (i.e. the centre-of-mass motion of the molecule), then the kinetic energy is given by

$$T = \frac{1}{2}\mu\left(\frac{dx}{dt}\right)^2 = \frac{p^2}{2\mu}$$

where $\mu = \dfrac{m_1 m_2}{m_1 + m_2}$ is the reduced mass.

Therefore the Hamiltonian for a vibrating diatomic molecule without the centre-of-mass translational motion is

$$H = \frac{p^2}{2\mu} + \frac{1}{2}kx^2$$

The Schrodinger equations for the harmonic oscillator and the eigen values and eigen functions.

The Schrodinger equations is obtained from the classical Hamiltonian by replacing both position (x) and momentum (p) by the appropriate operators. Since this is a one dimensionsional system, $p_x \to i\hbar\dfrac{d}{dx}$ and $x \to \hat{x}$.

The quantum mechanical harmonic oscillator Hamiltonian is

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}k\hat{x}^2$$

The Schrodinger equation:

$$\hat{H}\psi(x) = E\psi(x)$$
$$\Rightarrow -\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + \frac{1}{2}kx^2\psi = E\psi(x)$$

The equation is not solved here. Standard methods for solving this equation require power series expansion of the solution, slightly more advanced for this course. Hence only the solutions are given.

The solutions are constructed using Hermite polynomials. In the process of solving the differential equation above, one can transform the Schrodinger equation in to the Hermite's differential equation whose solutions are known as Hermite polynomials. The polynomials are infinite in number and form the class of orthogonal polynomials. They are denoted by the symbol $H_V(x)$ where V = 0,1,2,3,....., is the order of the polynomial and x is the variable.

The first few Hermite polynomials are given as

| $H_0(x)$ | $1$ |
|----------|-----|
| $H_1(x)$ | $2x$ |
| $H_2(x)$ | $4x^2 - 2$ |
| $H_3(x)$ | $8x^3 - 12x$ |
| $H_4(x)$ | $16x^4 - 48x^2 + 12$ |
| $H_5(x)$ | $32x^5 - 160x^3 + 120x$ |
| $H_6(x)$ | $64x^6 - 480x^4 + 720x^2 - 120$ |
| $H_7(x)$ | $128x^7 - 1344x^5 + 3360x^3 - 1680x$ |
| $H_8(x)$ | $256x^8 - 3594x^6 + 13,440x^4 - 13,440x_2 + 1680$ |

There is a recursion relation between these polynomials which can be used to generate any Hermite polynomial from two preceding ones,

$$H_{V+1}(x) = 2x \, H_V(x) - 2\upsilon \, H_{V-1}(x)$$

The harmonic oscillator eigen values and eigen functions are obtained in tems of the Hermite polynomials as

$$E_V = \hbar\sqrt{\frac{k}{m}}\left(V + \frac{1}{2}\right), \quad V = 0,1,2,3\ldots,(eigen\ values)$$

$$\psi_V(x) = N_V H_V\left(\sqrt{\alpha}x\right)e^{-\alpha x^2/2}, \quad \alpha = \sqrt{\frac{km}{\hbar^2}}$$

$$where\ N_V = \frac{1}{\sqrt{2^V V!}}\left(\frac{\alpha}{\pi}\right)^{1/4}$$

Here $\psi_V(x)$ is the eigen function of the Hamiltonian $\hat{H}$ with an eigenvalue $E_V$. The constant $N_V$ is called the normalization constant, so that

$$\int_{-\infty}^{\infty} \psi_V^*(x)\, \psi_V(x)\, dx = 1$$

(the conservation of total probability)

Read

$$H_1\left(\sqrt{\alpha}x\right) = 2\sqrt{\alpha}x$$

$$H_2\left(\sqrt{\alpha}x\right) = 4\alpha x^2 - 2\ etc$$

Recall: x has the dimensions of length in the oscillator problem, so that the wave function when expressed in x, must have the overall dimensions $L^{-\frac{1}{2}}$.

$$\int_{-\infty}^{\infty} \psi(x)\psi(x)\, dx = 1 \Rightarrow \int\left(L^{-\frac{1}{2}}L^{-\frac{1}{2}}L\right) = 1\ (diemensionless)$$

The function $e^{-\alpha x^2}$ must be dimensionless.

i.e., $\alpha$ must have the dimension of $L^{-2}$.

$\therefore \sqrt{\alpha}x$ is dimensionless, and $H_V\left(\sqrt{\alpha}x\right)$ are expressed in terms of dimensionless quantities.

The harmonic oscillator energies are quantized and are equidistant. What is meant by this statement is the following: the difference between any two adjacent levels is the same for all energy levels. The energy levels are equally spaced.

$$E_1 - E_0 = E_2 - E_1 = E_3 - E_2 = \ldots\ldots = \hbar\sqrt{\frac{k}{m}}$$

Harmonic oscillator energy levels
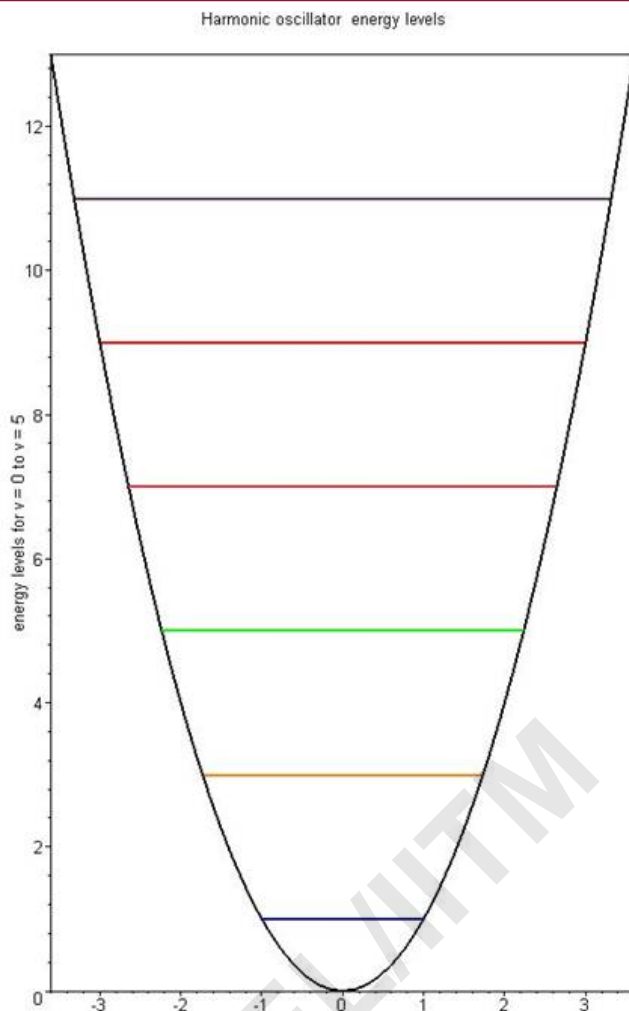


The quantities $\sqrt{\dfrac{k}{m}}$ and $\dfrac{1}{2\pi}\sqrt{\dfrac{k}{m}}$ are known as angular frequency and frequency respectively.

Note: $h\upsilon = \hbar\omega = \left(\dfrac{h}{2\pi}\right)(2\pi\upsilon)$

thus $\omega = 2\pi\upsilon = \sqrt{\dfrac{k}{m}}$ or $\upsilon = \dfrac{1}{2\pi}\sqrt{\dfrac{k}{m}}$, has the dimension $T^{-1}$.

The lowest quantum number is V=0, unlike the particle-in-a box. The plot of the wave functions and the squares of the wave functions are given below and indicate the number of nodes for each quantum number V. The number of noded of a wavefunction for quantum number V is V itself. The functions also display the odd-even characteristics, namely wavefunctions corresponding to odd quantum numbers are all odd function and the wave functions corresponding to even quantum numbers are all even functions.

**Significance of the solutions. (Why is harmonic oscillator important?)**

1. The quantum mechanical harmonic oscillator has some energy even when the quantum number is zero. (i.e. it cannot have zero energy of vibration). Classically an oscillator having zero energy does not oscillate!!

2. Zero point energy (referring to the above) is a purely quantum mechanical concept and is fundamentally important for molecules and solids.

3.. Plot of the wave functions:

Harmonic oscillator wavefunctions
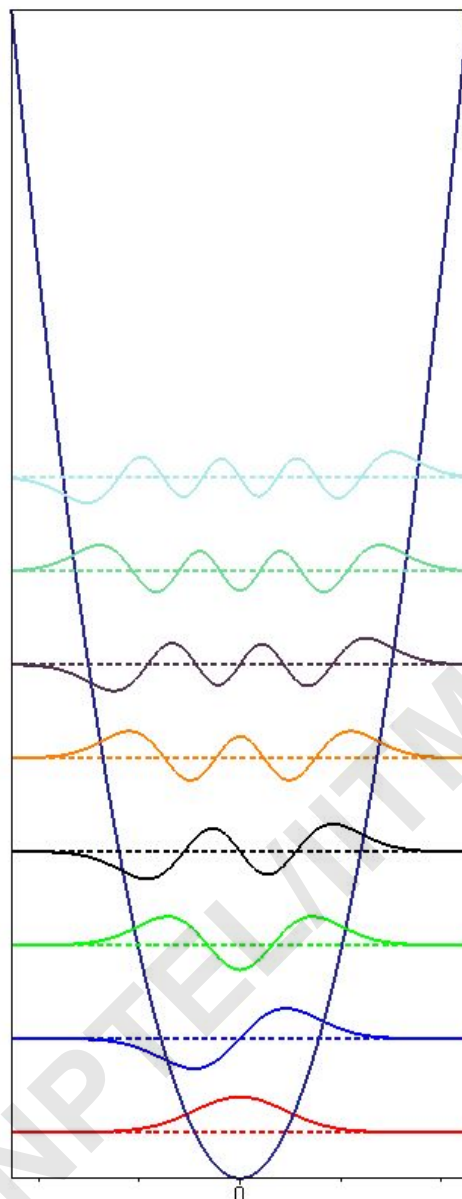


The squares of the wave functions for low vibrational quantum numbers are given below in the figure:

Squares of Harmonic oscillator wavefunctions
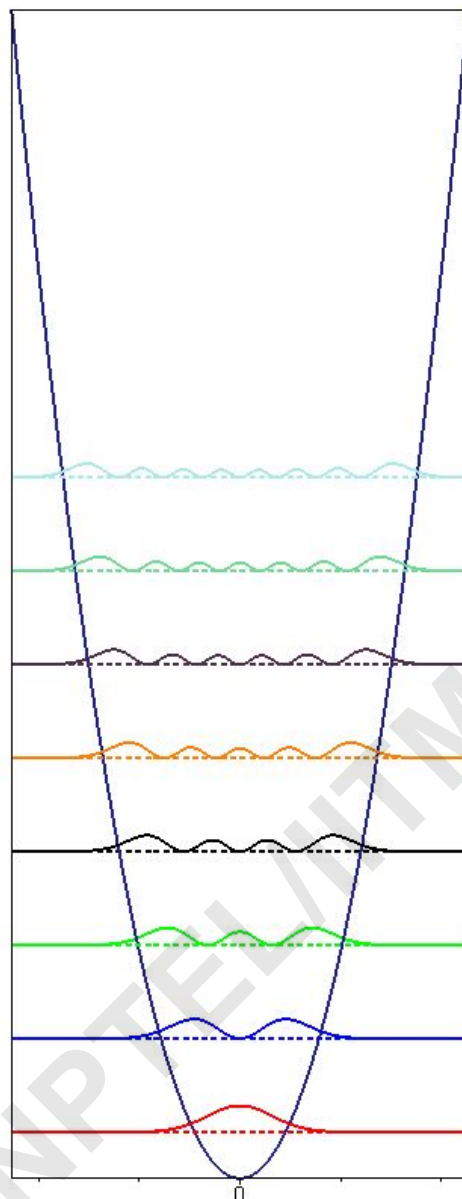


4. The boundary for an oscillator is endless. What does the potential look like? It is a parabola and the classical oscillator can ONLY oscillate between the two ends of the parabola. The total energy of the oscillator is all potential energy at the turning points and all kinetic energy midway between the two points. However, in quantum mechanics the the wave function outside of this classical parabola is nonzero for all values of x, though very small. Thus, the square of the wave function which represents probability density is nonzero everywhere, except for a finite number of points. It goes to zero as x tends towards infinity. This leads to a very interesting phenomenon called quantum mechanical tunneling. This means that the quantum mechanical oscillator can be found to oscillate into regions which are forbidden by classical mechanics. Experimentally tunneling phenomena have been amply demonstrated. This can be seen from the plots of the squares of wavefunctions which extend outside of the classically forbidden region, namely, outside the parabola for the potential energy. The scanning tunneling microscope used by metallurgists and nanotechnologists worldwide is based on tunneling phenomenon. Harmonic oscillator provides a beautiful example for tunneling.

5. For small values of energy you notice that the oscillator is more likely to be found in the middle of the potential well. (The wave functions associated with lower energies have peaks in the centre of the parabolic curve. This is against classical intuition as it is in these regions that the oscillator has the maximum kinetic energy, classically speaking, and is least likely to be spotted!!

6. The diatomic molecular vibrational energy is quantized and the simplest model above explains the basic features of the vibrational spectra of most stable molecules. Replace the mass of the oscillator by the reduced mass of the diatomic molecule and the connection between the two systems is established immediately as you have seen in the previous page.

### 2. Anharmonicity:

- Harmonic approximation, and all of the above valid for small amplitude vibrations.


■ For large amplitudes , or excitation by radiation to very high energy levels - the potential energy of vibrational motion is

$$\frac{1}{2}kx^2 \quad but \quad \frac{1}{2}kx^2 + \frac{k'}{6}x^3 + \frac{k''}{24}x^4 \quad etc$$

The vibrational motion which is the result of motion due to such potential energies is called anharmonic motion.

■ A very useful model for describing anharmonic vibrations is given by the Morse oscillator.

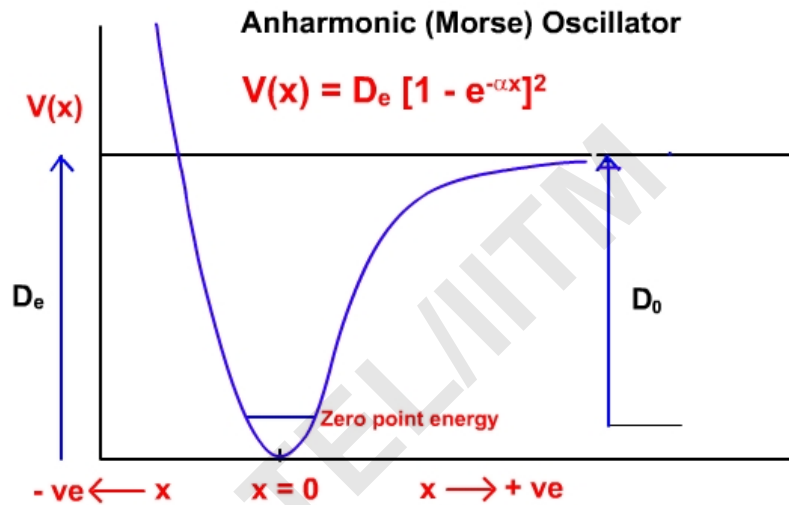The potential energy for a diatomic in the Morse oscillator model is given blow by the expression for V(x).

$$v(x) = D_e \left[1 - e^{-\alpha x}\right]^2$$
$$D_e\text{'s and } \alpha\text{'s are cons tan ts}$$
$$\alpha \text{ has the dimensions of } L^{-1}$$

De has - dimension of energy.

■ The Morse curve is represented graphically as follows:



It takes into account the possibility (eventuality) of the diatomic molecule dissociating eventually if its vibrational amplitude becomes quite large compared to the bond length.

■ The quantum mechanical results for the Morse oscillator model can be obtained by solving the Schrodinger equation for a Morse oscillator :

$$-\frac{\hbar^2}{2\mu}\frac{d^2}{dx^2}\psi + D_e\left(1 - e^{-\alpha x}\right)^2 \psi = E\psi$$
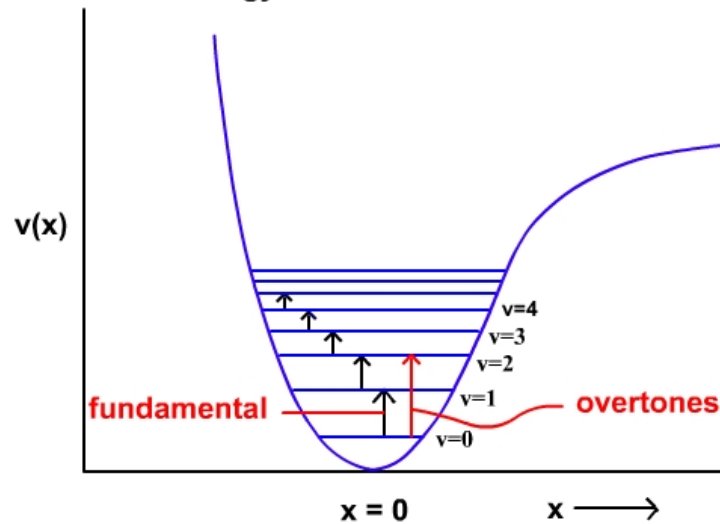
The solutions - eigenvalues are given as follows :

$$E_v = \left(v + \frac{1}{2}\right)h\nu_e - \left(v + \frac{1}{2}\right)^2 h\nu_e x_e$$

$$x_e = \frac{h\nu_e}{4D_e}, \nu_e \text{ is the fundamental frequency.}$$

(Eigenvectors of Morse oscillator will not be given here.)

■ The successive energy levels of a Morse oscillator are not equidistant.

## Energy levels of a Morse Oscillator

The gap between a given vibrational level v and the next vibrational level (V+1) decreases as v increases. Therefore,

$$\Delta E_{0\to1} = E_1 - E_0 = hv_e(1 - 2x_e)$$
$$\Delta E_{1\to2} = E_2 - E_1 = hv_e(1 - 4x_e)$$
$$\Delta E_{2\to3} = E_3 - E_2 = hv_e(1 - 6x_e)$$

Anharmonicity also implies vibrational transitions are no longer for $\Delta v = \pm 1$ only,transitions between any level and any other level is indeed nonzero. Thus the Morse oscillator model takes into account the dissociative possibility also. Because the energy differences are different even for nearby levels, the spectrum now contains more than a single line and has some characteristic features of the given molecule

- De - dissociation energy from equilibrium geometry.

  Zero point energy of the molecule :

  $$\frac{1}{2}hv - \frac{1}{4}x_e hv$$

  Therefore, actual measurable dissociation energy :

  $$|D_0| = (E_\alpha - E_0) < |D_e|$$

### 3. Polyatomic molecules : Normal modes of vibration.

- Triatomic : three vibrational modes for a nonlinear polyatomic. Four modes for a linear triatomic
  - classification of vibrational modes - as normal modes or local ( bond vibrational ) modes

- Normal modes :

  Visualize vibrational motion in a polyatomic molecules. How many vibrational modes are there in a polyatomic molecule containing N atoms?

  Answer:For N - atoms there are 3N independent coordinates.

  There are 3 translational degrees of freedom, namely one each about the three mutually orthogonal directions in a three dimensional world.

  There are 3 rotational degrees of freedom for a nonlinear molecule.

  Therefore, there are 3N-6 vibrational degrees of freedom

- For a linear molecule there are 3 translational degrees of freedom., but only 2 rotational degrees of freedom and therefore, the remaining 3N-5 degrees are vibrational degrees of freedom.

  Example :
  $H_2O$ , $O_3$ etc. ( non -linear)
  3 degrees of freedom vibrational

- Normal modes : Motion in which all atoms vibrate with the same frequency but different amplitudes of vibration.

■   For a bent triatomic molecule, three such, different frequencies can be detected.


■   The vibrational modes are such that the center of mass of the molecule remains stationary. ( otherwise the molecule is said to undergo translational motion ). Also the different vibrations are orthogonal to each other.


■   Two examples of normal modes of vibration of a bent triatomic molecule are given here. Study the figures carefully.

Normal modes of vibration of Ozone molecule

1.Symmetric stretch

Click the play button to view the animation

2.Asymmetric stretch

Click the play button to view the animation

3.Bending modes

click the play button to view the animation

Normal modes of vibration of water molecule

1.Symmetric stretch

Click the play button to view the animation

2.Asymmetric stretch

Click the play button to view the animation

3.Bending

Click the play button to view the animation

$$\nu_1 \approx \nu_3 > \nu_2$$

- All the three modes are experimentally observed since dipole moments change during vibration.

$CO_2$- is a linear molecule. Its normal modes of vibration are given in the figure below.

Normal modes of vibration of $co_2$ molecule

1.Symmetric stretch

Click the play button to view the animation

2.Asymmetric stretch

Click the play button to view the animation

3.Bending modes ( first of the two degenerate modes)

Click the play button to view the animation

4.Bending modes( second of the two degenerate modes)

click the play button to view the animation

■  Normal modes are very useful in understanding vibrational spectra of poly atomic molecules

### 4. Local modes of molecules

- Detection of molecular structure using IR Spectra.

■  Often a group of atoms in a molecule exhibit vibrational modes.

■  The group vibrational frequencies are characteristic of the members of the group as well as the surroundings in which the group is placed.

■  Thus the same group such as a -COOH or a -OH or a CHO group has frequencies which are similar between different compounds.

■  This enables the experimental spectroscopits and analytical chemists to identify typical functional groups present in a molecule and eventually the molecule itself.

■  The analysis of molecular structure can be greatly helped by the IR spectrum of the molecule.

■  The IR spectra of a few polyatomic molecules - explain the appearance of particular functional groups in certain frequency range.However we use them to assign structures to unknown compounds.

■  **The spectra of benzene, toluene and m-xylene are given here to show how the structural similarities and differences between them are present in their correponding IR spectra.**

Benzene, 99+%



m-Xylene, 99%
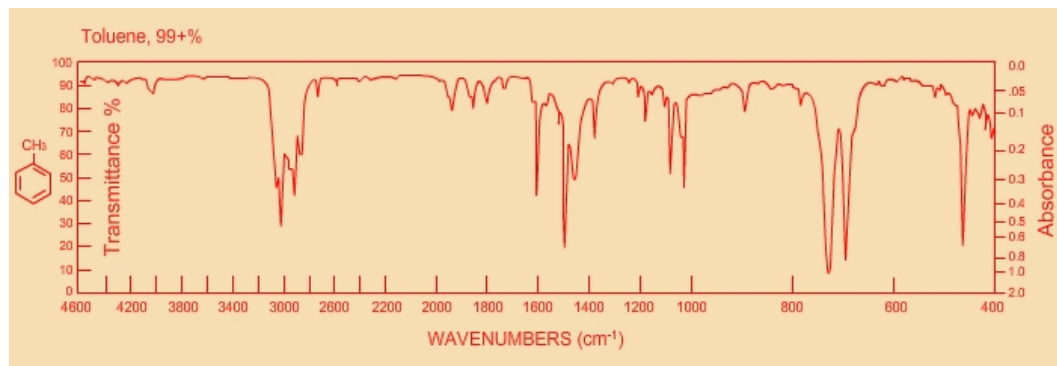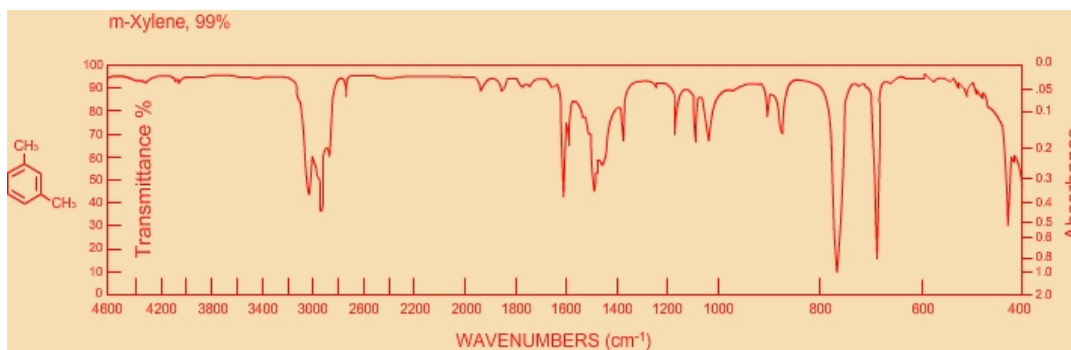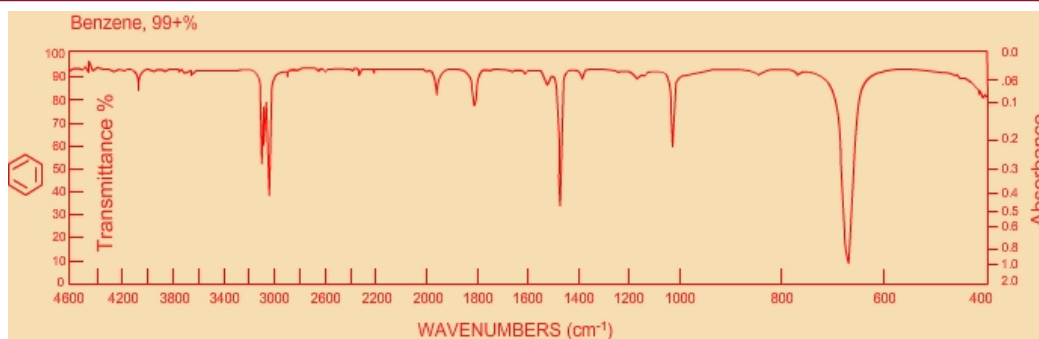
--------------------------End of lecture-3 --------------------------

Note: Several very good text books exist for infrared spectroscopy. The monumental work by Gerhard Herzberg between 1939-1965 is available in the library as three volumes and is the source and inspiration for many researchers in this field. Herzberg, a physicist, won the Nobel prize in chemistry in 1971 for his contribution to molecular spectroscopy. A collection of IR spectra of many polyatomic molecules such as the above can be found in a beautiful book by R. M. Silverstein, G. C. Bassler and T. C. Morrill, Spectrometric identification of organic compounds, John Wiley and Sons, 1991, New York. The three IR spectra have been given from Silverstein et al.'s book.

We have not included Raman spectroscopy in this lecture and will hopefully cover some of it in the future years.