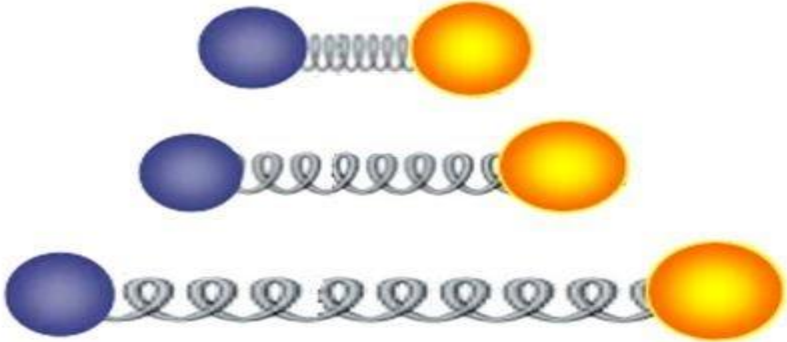
Classical Harmonic Oscillator

- A vibrating molecule behaves like 2 masses joined by a spring
- If the bond is stretch or compressed, there is a *restoring force* which is proportional to the distortion

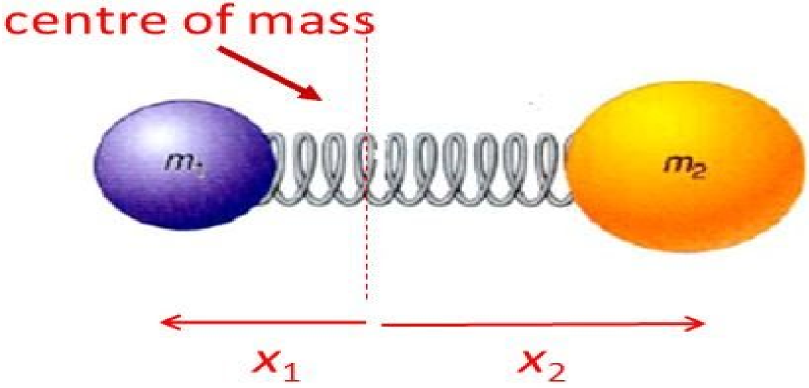


$x < 0$	$F = -kx$
$x = 0$	$F = 0$
$x > 0$	$F = -kx$

- As $dV/dx = -F$, $V = \frac{1}{2} kx^2$
- k is the *force constant*: stiff springs = strong bonds = large k

Reduced Mass

- A vibrating molecule behaves like 2 masses joined by a spring
- The motion is described in terms of the movement of the *effective* or *reduced* mass, μ , from the centre of mass

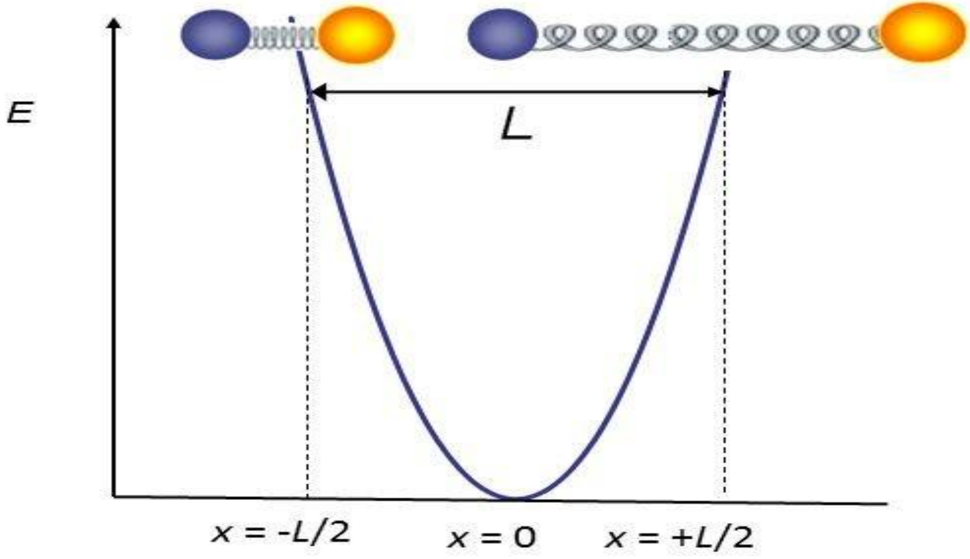


$$m_1x_1 = m_2x_2$$

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

Amplitude

- The ‘turning points’ are the maximum displacements and have $T = 0$ and $E = V$
- These occurs at $x = -L/2$ *and* $+L/2$



- $\varepsilon = V = \frac{1}{2} kx^2 = \frac{1}{2} k(L/2)^2$
- $L^2 = (8\varepsilon/k)$
- $L = (8\varepsilon/k)^{1/2}$
- Length varies with $\varepsilon^{1/2}$

The Schrödinger equation

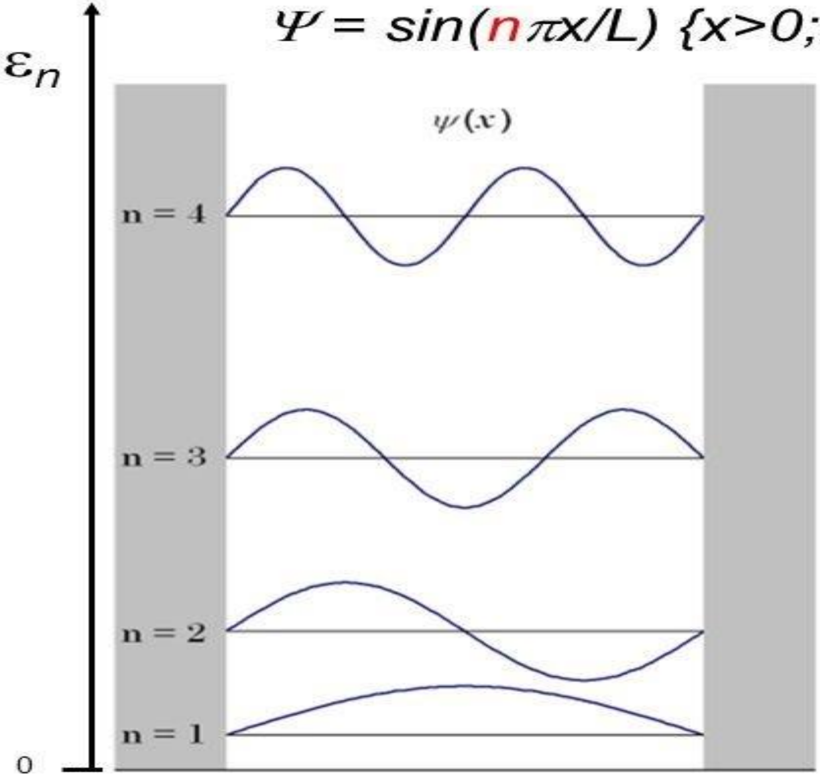
- The Hamiltonian has parts corresponding to *Kinetic Energy* and *Potential Energy*. In terms of the displacement:

$$\hat{H}\Psi(x) = \left(-\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial x^2} + V(x) \right)\Psi(x)$$

Hamiltonian operator

Recap: The particle in a box

$\Psi = \sin(n\pi x/L)$ $\{x>0; x<L; n>0$ $\varepsilon_n = \hbar^2 n^2 \pi^2 / 2mL^2$



- Wavefunction is zero at edge as potential is infinite
- Confining the particle leads to quantization of energy levels
- Energy depends on n^2
- Lowest energy possible has $n = 1$

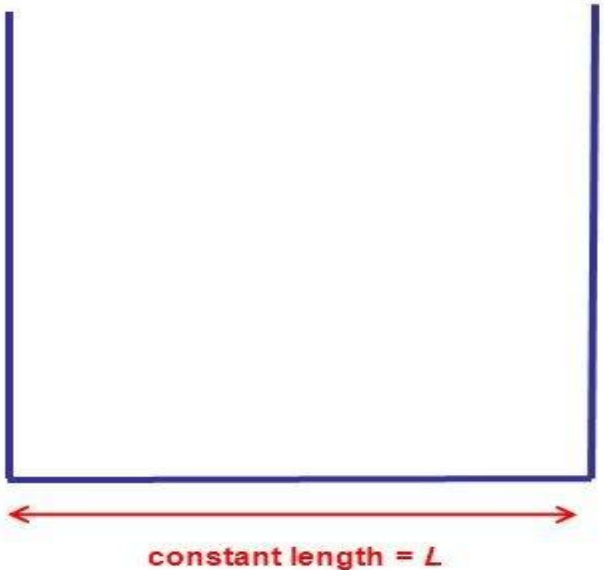
The particle in a box vs Harmonic Oscillator

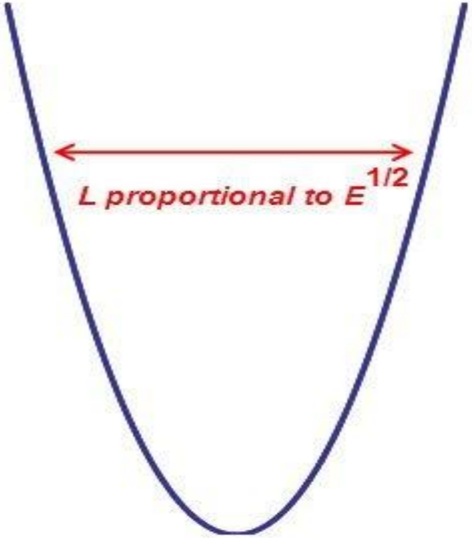
The Box:

- *The box is a 1d well, with sides of infinite potential*

The harmonic oscillator:

- $V = \frac{1}{2} kx^2$





Quantum Harmonic Oscillator

- Solving the Schrödinger equation gives the energy levels as:

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

where n is the quantum number and can be 0, 1, 2, 3....

$$\varepsilon_n = \left(n + \frac{1}{2}\right)h\,\nu$$

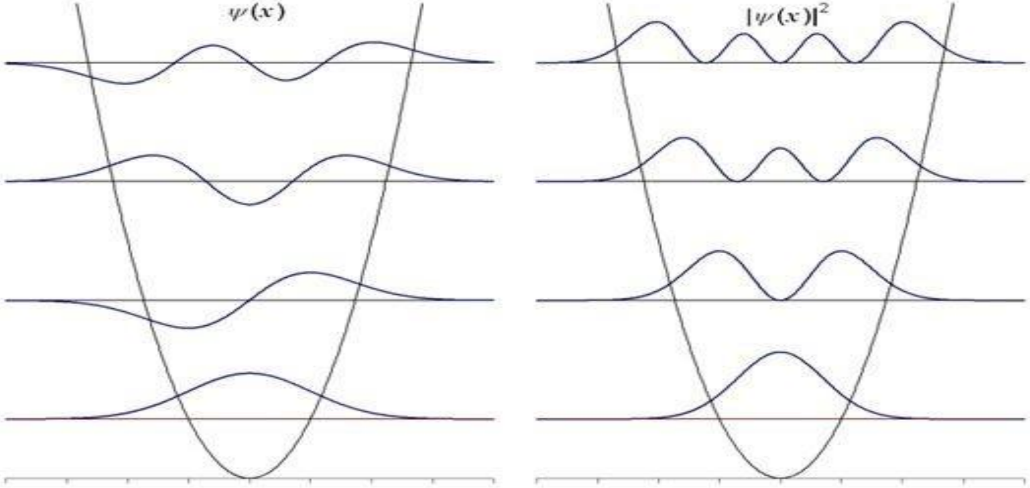
where $\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$

quantum number

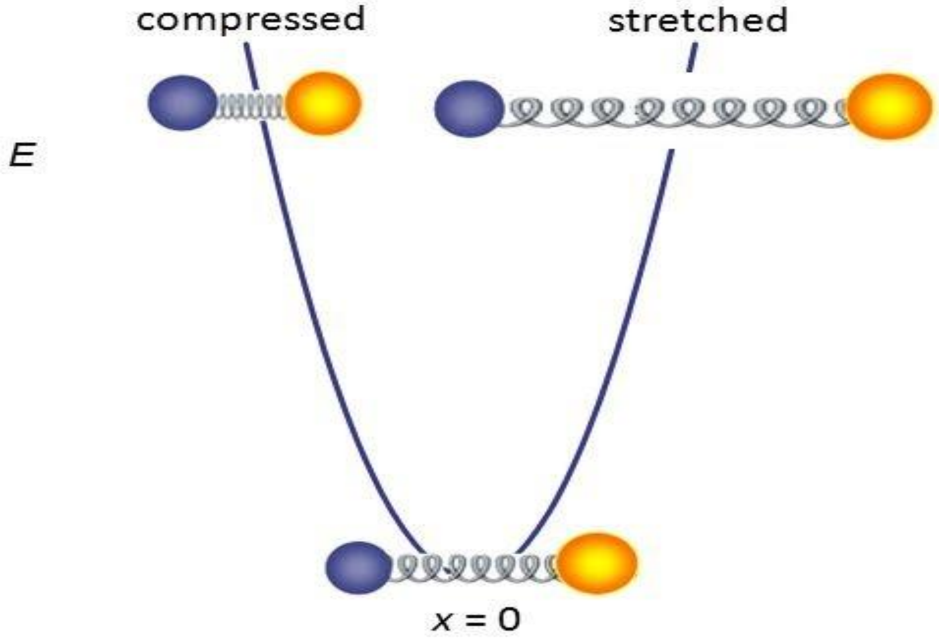
Classical vibrational frequency:
ν (“nu”)

Harmonic Oscillator Wavefunctions

- wavefunctions are not simple sine waves (but resemble them)
- at low energies, ψ^2 is largest in the centre (as for particle in the box) akin to classical non-vibrating ground state
- at high energies, ψ^2 has increasing value at classical turning points
- wavefunction "leaks" outside classically allowed potential region. Here *V* > *E* and as *E* = *T* + *V*, the kinetic energy is negative!



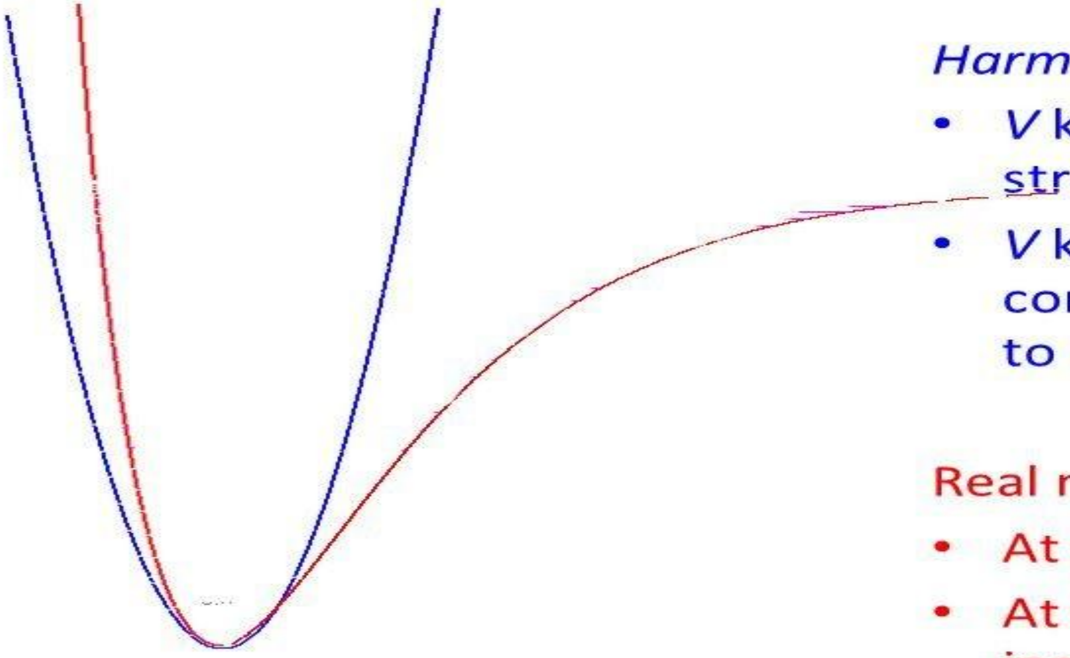
Problems with the Harmonic Oscillator



Harmonic oscillator:

- *V* keeps increasing as bond is stretched but it *never* breaks!
- *V* keeps increasing as bond compressed but allows nuclei to run into one another

Improvements to Harmonic Oscillator



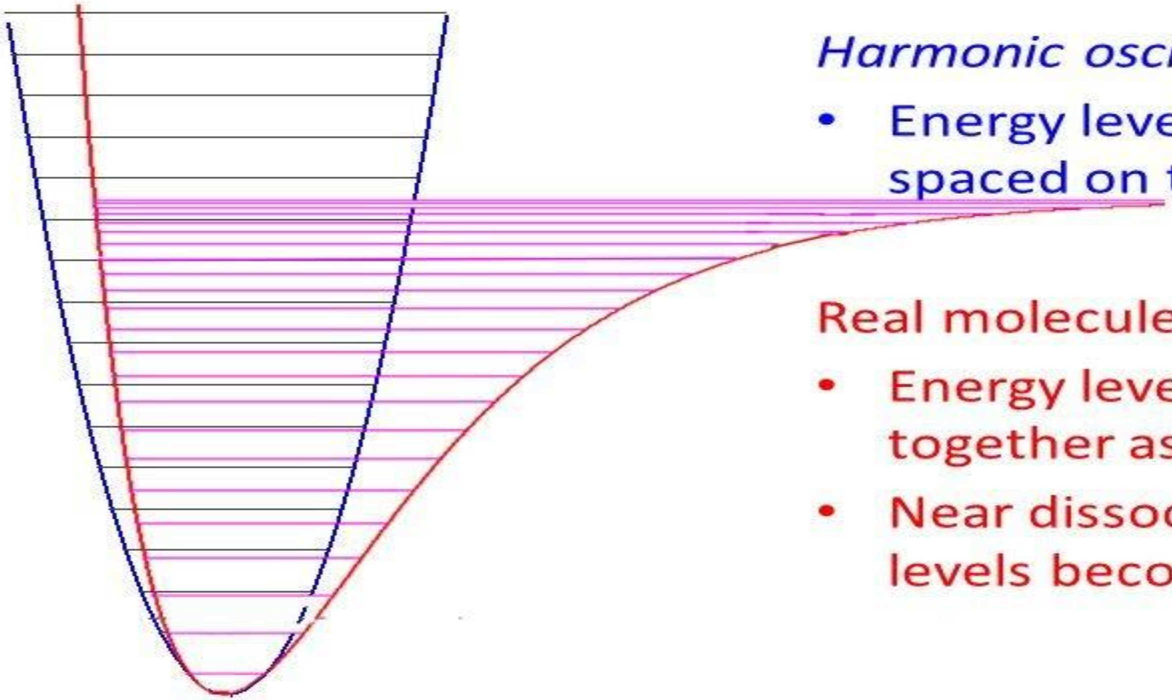
Harmonic oscillator:

- *V* keeps increasing as bond is stretched but it *never* breaks!
- *V* keeps increasing as bond compressed but allows nuclei to run into one another

Real molecule

- At large *x*, bond will break
- At small *x*, energy must increase more sharply

Improvements to Harmonic Oscilla



Harmonic oscillator:

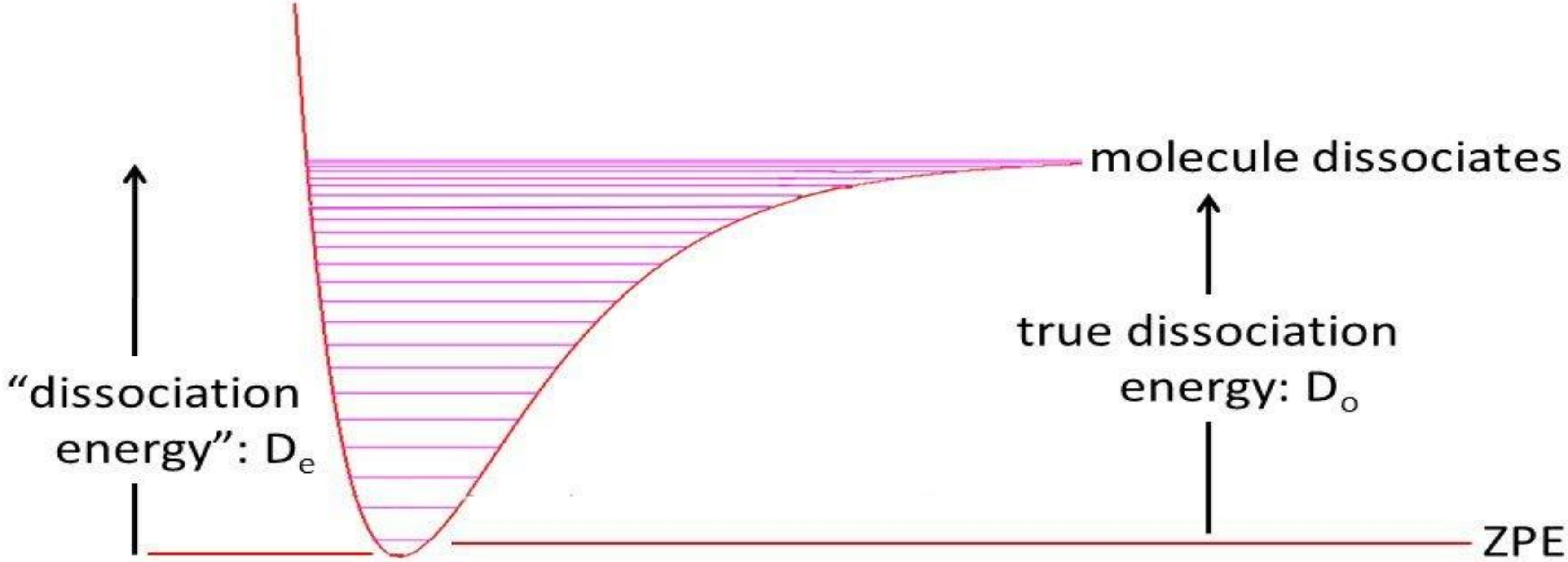
- Energy levels are equally spaced on the ladder

Real molecule

- Energy levels get closer together as energy increases
- Near dissociation, energy levels become continuous

Anharmonic Oscillator (AHO)

- The lowest possible energy is the ZPE = ½ hv
- $D_e = D_o + ½ hv$



molecule dissociates

“dissociation energy”: D_e

true dissociation energy: D_o

ZPE

Summary

- The wavefunctions for the harmonic oscillator resemble those of the particle in a box but spill outside the classically allowed region
- The energy levels for the harmonic oscillator increase linearly with the quantum number v: they are equally spaced on the energy ladder
- There is a minimum energy, called the zero point energy, associated with the vibrations of a molecule
- The potential energy curve for a real molecule rises more steeply for compressed bonds than for the harmonic oscillator and leads to dissociation for large separations
- The vibrational energy levels of a real molecule get closer

Vibrational Spectroscopy

- A key experimental technique use to probe the vibrational modes (normal modes) of a material.
- Raman spectroscopy is commonly used in chemistry to provide a fingerprint by which molecules can be identified.
- Can be used to explore relative composition of a material (i.e. relative concentration of a known compound in solution).
- Widely used in industry and quality assurance.
- Key technique in **condensed matter research**.

Simple harmonic motion

Atoms connected via chemical bonds are equivalent to masses connected by springs. We can describe these using Hooke's law (Q is a displacement of an atom away from eqn position)

$$F = \quad kQ$$

From Newton's second law

$$F = \quad \frac{d^2Q}{dt^2}$$

Where μ is the reduced mass

Thus

$$\frac{d^2Q}{dt^2} + kQ = 0$$

Find a general solution

where

$$Q(t) = A\cos(\quad {}_{vib}t)$$

$${}_{vib} = \sqrt{\frac{k}{}}$$

From classical to quantum

If two nuclei are slightly displaced from equilibrium positions ($x = R - R_e$), can express their potential energy in a Taylor series:

$$V(x) = V(0) + x\ \frac{dV}{dx} \div + \frac{1}{2} x^2\ \frac{d^2V}{dx^2} \div + \frac{1}{3!} x^3\ \frac{d^3V}{dx^3} \div + \ldots$$

Not interested in absolute potential, so set V(0) = 0.
At equilibrium, dV/dx = 0 (a potential minimum). Providing displacement is small, third order term can be neglected. We can therefore write:

$$V(x) = \frac{1}{2} kx^2 \qquad k = \ \frac{d^2V}{dx^2} \div$$

Insert potential into time independent Schrodinger equation:

$$E\ \ (x) = \left[\ \frac{\ ^2}{2} \nabla^2 + V(x) \right]\ \ (x)$$

To find quantized solutions

$$E_n = \square\ \ _{vib}(n + \frac{1}{2})$$

This creates a ladder of vibrational modes

This is well-known case of a harmonic oscillator.

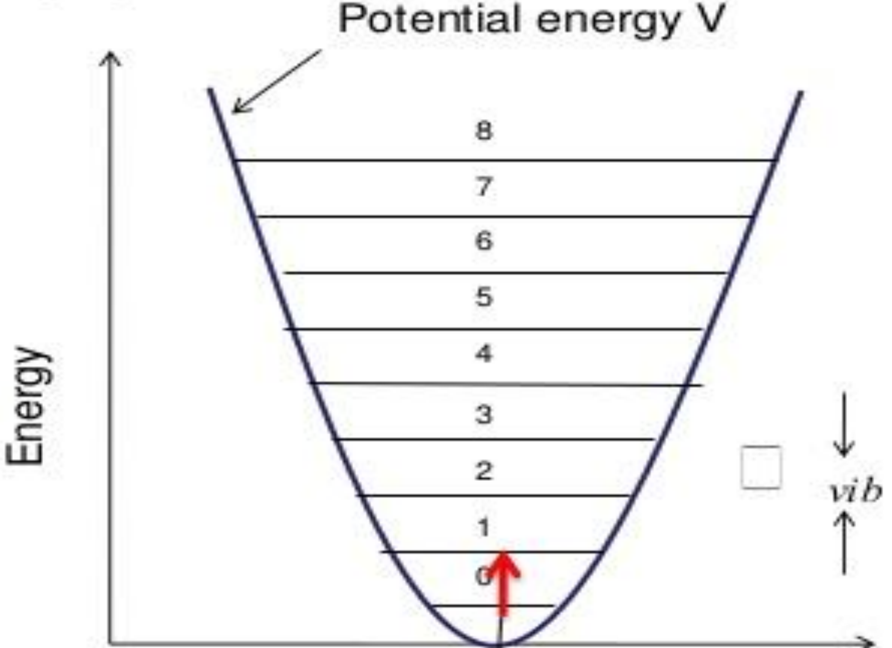
$$V(x) = \frac{1}{2}kx^2$$

The energy of a quantum-mechanical harmonic oscillator is quantized and limited to the values.

$$E = (n+\frac{1}{2})\square_{vib}$$

Selection rules dictate that harmonic Oscillator transitions are only allowed for

$$\Delta n = \pm 1$$



Vibrational Spectra

Molecules are not Static

Vibration of bonds occurs in the liquid, solid and gaseous phase

Vibrating* ⇔ *Energy* ⇔ *Frequency (and the appropriate frequencies for molecular vibrations are in the ***Infrared*** region of the electromagnetic spectrum

Vibrations form therefore, a fundamental basis for spectroscopy in chemistry--*the bonds are what makes the chemistry work in structure and function*

For Organic Chemistry the most important uses of these vibrations is for analysis of:

- functional groups
- structural identity, "fingerprinting"

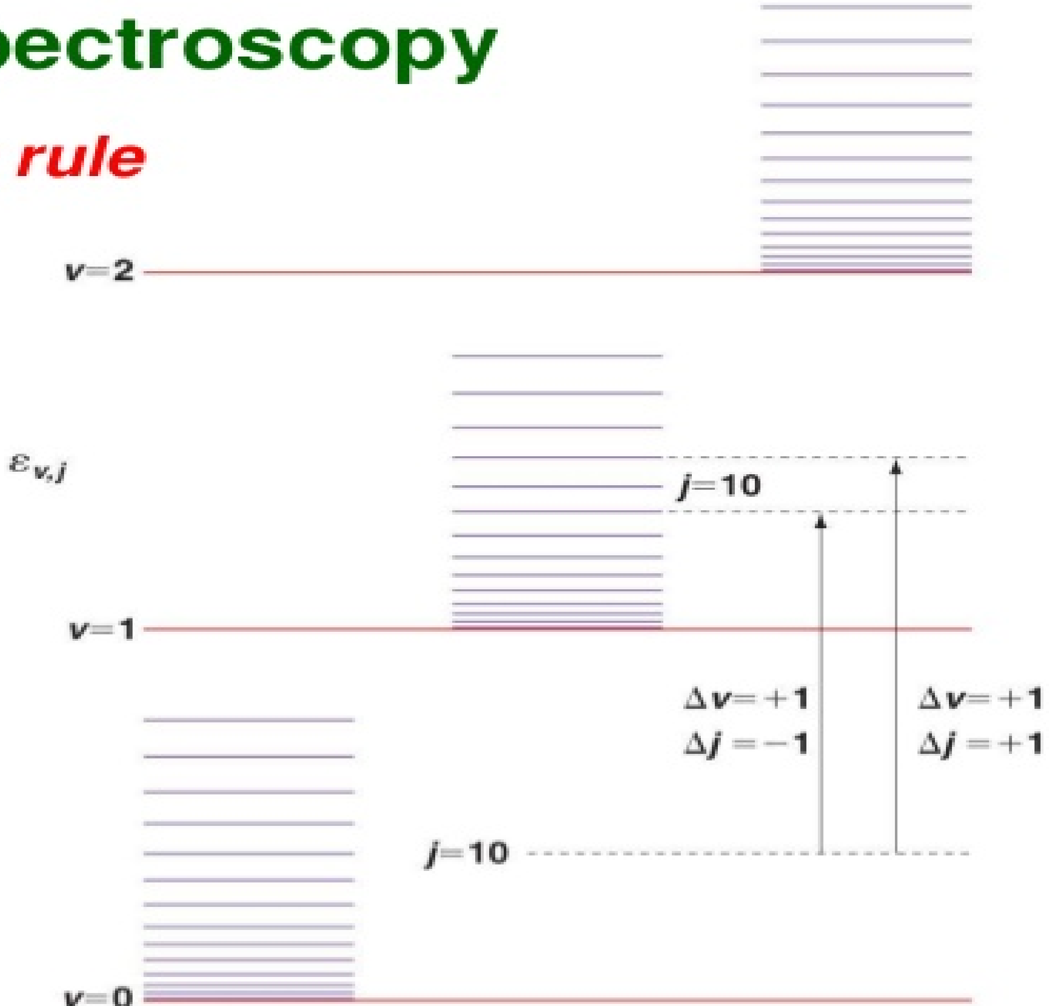
Vibrational Spectroscopy

Vibrational selection rule

$$\Delta \upsilon = \pm 1$$

$$\Delta \upsilon = +1 \ (absorption)$$

$$\Delta \upsilon = -1 \ (emission)$$



INTRODUCTION OF IR SPECTROSCOPY

- Infrared spectroscopy is an important analytical technique for determining the structure of both inorganic & organic compounds. It is also known as vibrational spectroscopy
- IR radiations lies in the wavelength range of 0.7 - 400 μm.
- IR spectroscopy is based upon selective absorption of IR radiations by the molecule which induces vibration of the molecules of the compound.
- IR instruments are of 2 types namely, dispersive instruments (spectrophotometers) and Fourier transform IR instrument.
- The radiation sources used are incandescent lamp, Nernst glower etc., and the detectors used are thermal and photon detectors.

APPLICATIONS OF IR SPECTROSCOPY

- Identification of functional groups & structure elucidation of organic compounds.
- Quantitative analysis of a number of organic compounds.
- Study of covalent bonds in molecules.
- Studying the progress of reactions.
- Detection of impurities in a compound.
- Ratio of cis-trans isomers in a mixture of compounds.
- Shape of symmetry of an inorganic molecule.
- Study the presence of water in a sample.
- Measurement of paints and varnishes.

LIMITATIONS OF IR SPECTROSCOPY

- Cannot determine the molecular weight of the compound.
- Does not give information about the relative position of different functional groups in a molecule.
- From the single IR spectrum of an unknown substance, it is not possible to know whether it is pure compound or a mixture of compound.
- Sample cells are made of halaogen salts which are susceptible to moisture.
- Gas samples cannot be analyzed as they lack sensitivity.

NATURE OF IR SPECTRA

- IR spectrum is a graph of band intensities on ordinate versus position of band on abscissa.
- Band intensities can be given in terms of transmittance(T) or absorbance(A).
- Position of band can be expressed in terms of wave number (n) or wavelength(λ).
- In IR spectra, wave numbers (n) are used instead of wavelength (λ) for mentioning the characteristic peak as this unit has advantage of being linear with energy of radiation (E) .

$E = h\,c/\lambda$ or, $E = h\,c\,n$

[$n = 1/\lambda$, c= velocity of light, h= Planck's constant]

TRANSMISSION vs. ABSORPTION

- When a chemical sample is exposed to the action of IR LIGHT, it can absorb (retain) specific frequencies and allow the rest to pass through it (transmitted light).
- Some of the light can also be reflected back to the source.

IR source

Chemical sample

Transmitted light

Detector

- Transmittance (T) is defined as the ratio of radiant power transmitted by a sample to the radiant power incident on the

CHARACTER OF VIBRATION

Fundamental modes of molecular vibrations can be classified into two types: Stretching and Bending vibrations.

1. STRETCHING VIBRATIONS

- They involve movement of atom within the same bond axis such that the bond length changes without any change in bond angle in regular interval.
- Symmetrical molecules like O=C=O are not IR active because no change in dipole moment is observed upon stretching vibrations.
- Non- cyclic systems show (n-1) stretching vibrations because these vibrations describes one directional motion.

Types of stretching vibrations-

a. Symmetrical stretching: The atoms of a molecule either move away or towards the central atom, but in the same direction.

b. Asymmetric Stretching: One atom approach towards the central atom while other departs from it.

Stretching

2. BENDING OR DEFORMING VIBRATIONS

- They involve movement of atoms which are attached to a common central atom, such that there is change in bond axis and bond angle of each individual atom without change in their bond lengths.
- Bending vibrations generally requires less energy and occur at longer wavelengths (lower cm-1) than stretching vibrations.
- Types of bending vibrations

I) In-plane vibrations

a. Scissoring b. Rocking

II) Out-plane vibrations

a. Wagging b. Twisting

I) In plane vibration

a) **Rocking:** In-plane bending of atoms occurs wherein they swing back and forth with respect to the central atom.

a) **Scissoring:** In-plane bending of atoms occur wherein they move back and forth. i.e., they approach to each other.

In-plane deformations

II) Out plane vibration:

a) **Wagging:-** Two atoms oscillate up and below the plane with respect to the central atom.

b) **Twisting:-** One of atom moved up the plane while other down the plane with respect to central atom.

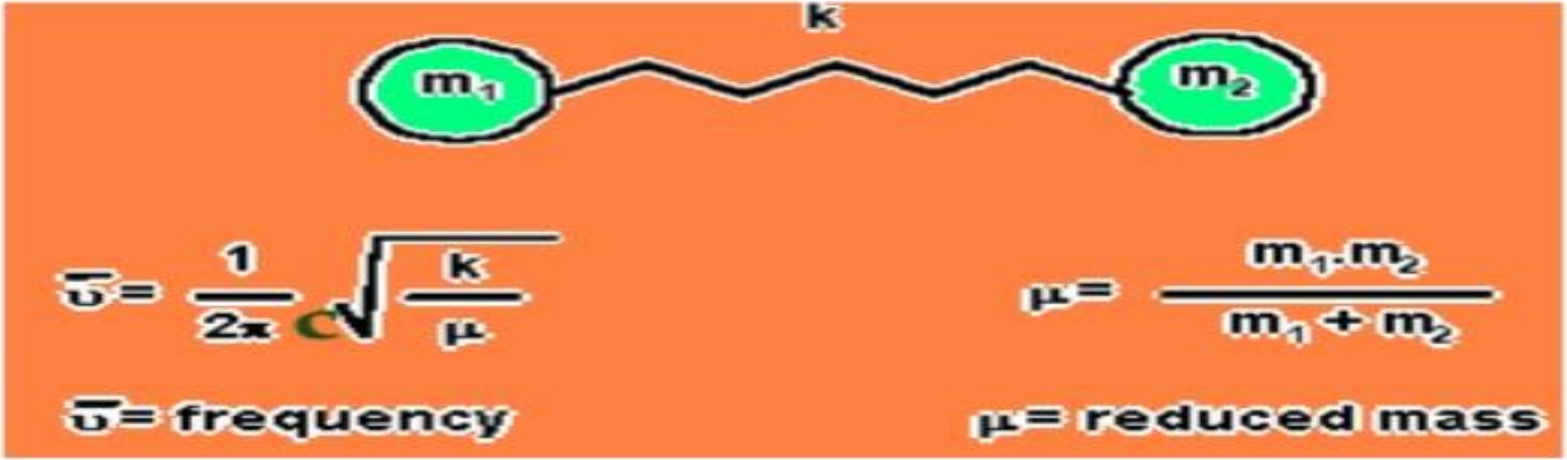
Wagging

Twisting

Out-of-plane deformations

Vibrational Frequency

- The value of stretching vibrational frequency of bond can be calculated by using Hooke's law.
- Hooke's law states that the vibrational frequency of a bond is directly proportional to the bond strength and inversely proportional to the masses at the ends of the bond.



$$\bar{\upsilon} = \frac{1}{2\pi C}\sqrt{\frac{k}{\mu}} \qquad \mu = \frac{m_1 . m_2}{m_1 + m_2}$$

$\bar{\upsilon}$ = frequency

μ = reduced mass

Vibrational frequency or wave number depend upon following:

1. BOND STRENGTH

The frequency of vibration will be directly proportional to strength of bond (K).

E.g.- Stretching vibration of triple bond will appear at high frequency than that of either a double or single bond

	$C\equiv C$	$C=C$	C-C
Frequency=	2150 cm^{-1}	1650 cm^{-1}	1200 cm^{-1}

2. MASS : Vibrational frequency is inversely proportional to the masses at the ends of the bond.

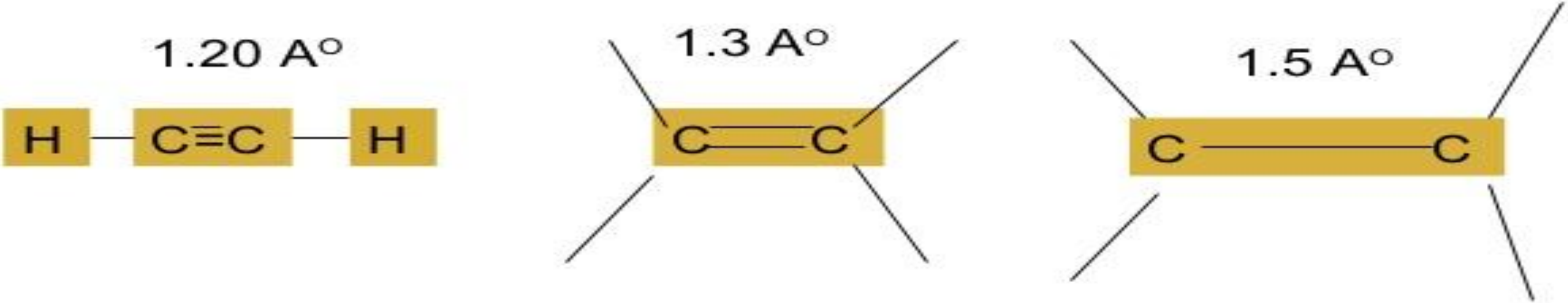
C-H	C-C	C-O	C-Cl	C-Br	C-I
3000	1200	1100	750	600	500 Cm^{-1}

3. Hybridization:

- Hybridization affects the bond strength or force constant(K).
- Bonds are stronger in order :

SP > SP^2 > sp^3

3300 CM^{-1} 3100 CM^{-1} 2900 CM^{-1}



Factor affecting vibrational frequency

1. Coupling interaction.
2. Fermi resonance.
3. Hydrogen bonding.
4. Electronic displacement effects.

2. Fingerprint region

- This region accounts for many absorption bands characteristic of functional group. Since numbers of sharp bands of varying intensities are encountered, close examination is needed.
- This region is useful for the identification of compounds since no two compounds can have identical IR spectra under identical conditions.
- Regions present below 1500 cm-1 shows absorption bands due to bending vibrations and stretching vibrations of C-C, C-O and C-N bonds.
- Regions less than 1250 cm-1 consists of complex vibrational and rotational spectra of the complete molecule.

Fingerprint region is further divided into three regions.

i. Region 1500- 1350 cm-1

- The presence of double peaks near 1380 cm-1 and 1365 cm-1 indicates presence of tertiary butyl group in the compound.

ii. Regions 1350-1000 cm-1

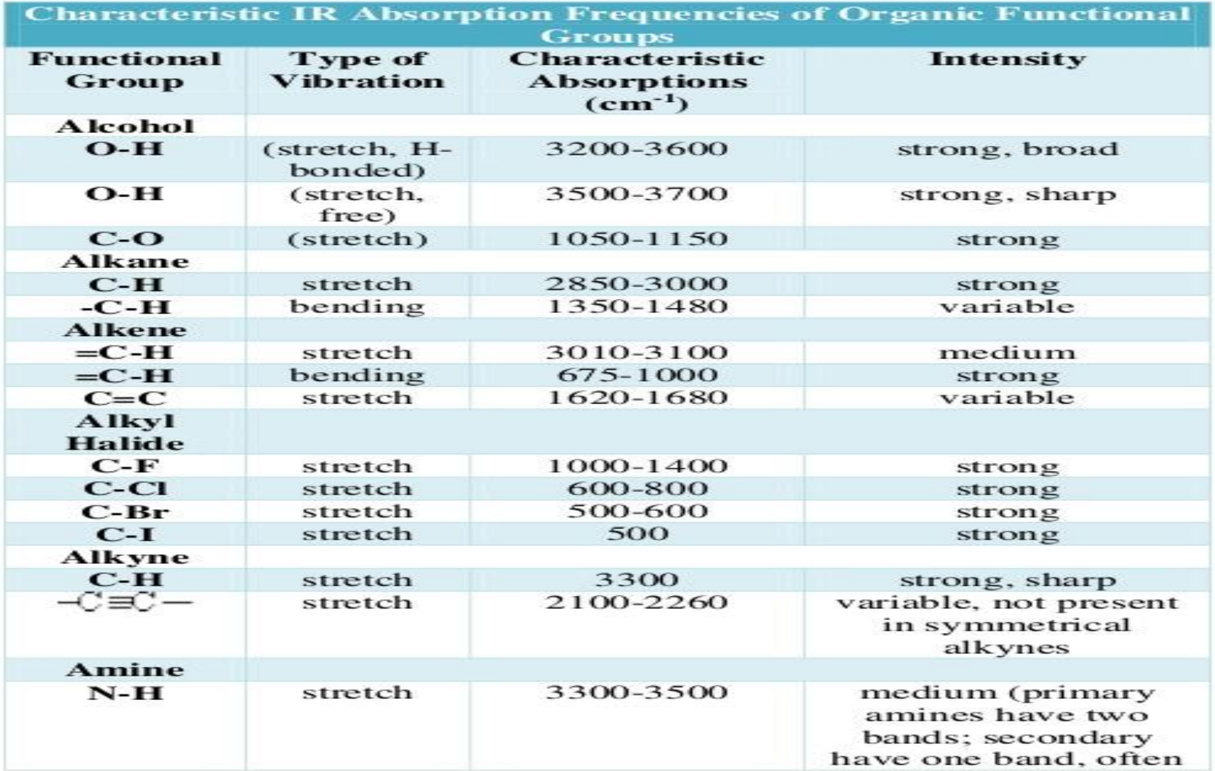
- Characteristic strong bands due to C-O stretching are present.

Compound	IR region
Ethers	1150- 1070 cm-1
Primary alcohols	1350- 1260 cm-1 and Near 1050 cm-1
Esters	1380- 1050 cm-1
Phenols	Near 1200 cm-1

iii. Less than 1000 cm-1

- Absorption band in the region 750- 700 cm-1 indicates the presence of mono substituted benzenes.
- Geometrical isomers of olefins can be distinguished in the region 970 – 700 cm-1.
- Cis- isomer shows strong intensity absorption band at 700 cm-1 and trans- isomer at 970-960 cm-1.

IR Absorption Frequencies of Organic Functional Groups



Characteristic IR Absorption Frequencies of Organic Functional Groups

Functional Group	Type of Vibration	Characteristic Absorptions (cm^{-1})	Intensity
Alcohol			
O-H	(stretch, H-bonded)	3200-3600	strong, broad
O-H	(stretch, free)	3500-3700	strong, sharp
C-O	(stretch)	1050-1150	strong
Alkane			
C-H	stretch	2850-3000	strong
-C-H	bending	1350-1480	variable
Alkene			
=C-H	stretch	3010-3100	medium
=C-H	bending	675-1000	strong
C=C	stretch	1620-1680	variable
Alkyl Halide			
C-F	stretch	1000-1400	strong
C-Cl	stretch	600-800	strong
C-Br	stretch	500-600	strong
C-I	stretch	500	strong
Alkyne			
C-H	stretch	3300	strong, sharp
$-C\equiv C-$	stretch	2100-2260	variable, not present in symmetrical alkynes
Amine			
N-H	stretch	3300-3500	medium (primary amines have two bands; secondary have one band, often

			very weak)
C-N	stretch	1080-1360	medium-weak
N-H	bending	1600	medium
Aromatic			
C-H	stretch	3000-3100	medium
C=C	stretch	1400-1600	medium-weak, multiple bands
Analysis of C-H out-of-plane bending can often distinguish substitution patterns			
Carbonyl	Detailed Information on Carbonyl IR		
C=O	stretch	1670-1820	strong
(conjugation moves absorptions to lower wave numbers)			
Ether			
C-O	stretch	1000-1300 (1070-1150)	strong
Nitrile			
CN	stretch	2210-2260	medium
Nitro			
N-O	stretch	1515-1560 & 1345-1385	strong, two bands

IR Absorption Frequencies of Functional Groups Containing a Carbonyl (C=O)

Functional Group	Type of Vibration	Characteristic Absorptions (cm-1)	Intensity
Carbonyl			
C=O	stretch	1670-1820	strong
(conjugation moves absorptions to lower wave numbers)			
Acid			
C=O	stretch	1700-1725	strong
O-H	stretch	2500-3300	strong, very broad
C-O	stretch	1210-1320	strong
Aldehyde			
C=O	stretch	1740-1720	strong
=C-H	stretch	2820-2850 & 2720-	medium, two

		2750	peaks
Amide			
C=O	stretch	1640-1690	strong
N-H	stretch	3100-3500	Un substituted have two bands
N-H	bending	1550-1640	
Anhydride			
C=O	stretch	1800-1830 & 1740-1775	two bands
Ester			
C=O	stretch	1735-1750	strong
C-O	stretch	1000-1300	two bands or more
Ketone			
acyclic	stretch	1705-1725	strong
cyclic	stretch	3-membered - 1850 4-membered - 1780 5-membered - 1745 6-membered - 1715 7-membered - 1705	strong
┌,┐-unsaturated	stretch	1665-1685	strong
aryl ketone	stretch	1680-1700	strong

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