



# **IR Spectroscopy**

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# INTRODUCTION

- Infrared (IR) radiation refers to that part of the electromagnetic spectrum between the visible (400-800 nm) and microwave regions (1.0 -10 cm).
- IR spectrum contains a large number of absorption bands and it is impossible to assign all of them but those can be assigned correctly give a lot of information about the structure of the organic molecule.
- **Near IR** (14000-4000  $\text{cm}^{-1}$ ): **consists of overtones and combination bands** resulting from vibrations in the mid IR region of the spectrum.
- **Mid IR** (4000-400  $\text{cm}^{-1}$ ): **provides structural information for most organic molecules.**
- **Far IR** (400-33  $\text{cm}^{-1}$ ): it has been used with inorganic molecules.

# IR Regions

- IR region:  $2 \mu - 25 \mu = 2000 \text{ nm} - 25000 \text{ nm}$
- Organic compound generally absorb in the region:  $2.5 \mu - 15 \mu$ .
- In IR spectroscopy, units called wavenumbers are normally used to denote different types of light.

$$\bar{\nu} = \frac{1}{\lambda} \quad \text{where: } \bar{\nu} = \text{wavenumber}$$
$$\lambda = \text{wavelength}$$

$$\text{When } \lambda = 2.5 \mu, \bar{\nu} = \frac{1}{2.5 \mu} = \frac{1}{2.5 \times 10^{-4} \text{ cm}} = 4000 \text{ cm}^{-1}$$

$$\text{When } \lambda = 15 \mu, \bar{\nu} = \frac{1}{15 \mu} = \frac{1}{15 \times 10^{-4} \text{ cm}} = 667 \text{ cm}^{-1}$$

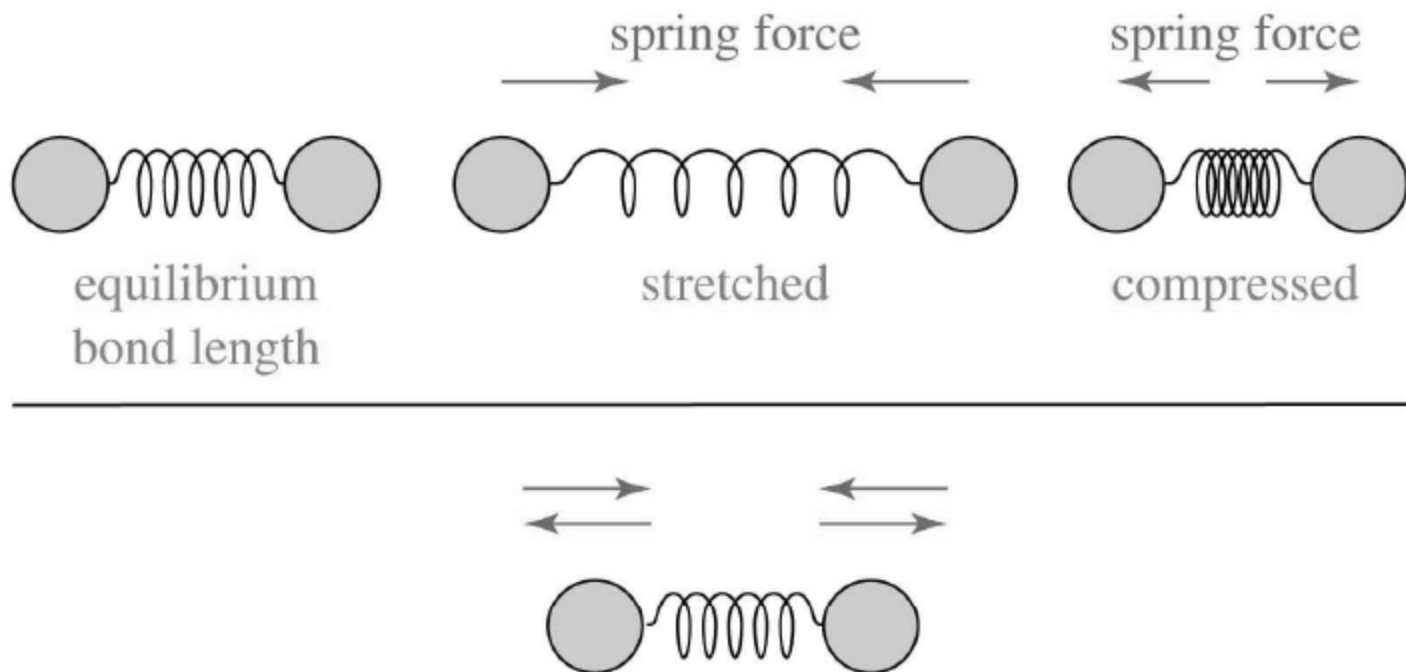
- IR region (in terms of wavenumber) for organic compounds:  
 $4000 \text{ cm}^{-1} - 667 \text{ cm}^{-1}$

# Theory of Molecular Vibration

- IR radiation is absorbed and converted by an organic molecule into energy of molecular vibration. This absorption is quantized, but **vibrational spectra appear as bands** rather than as lines because a single vibrational energy change is accompanied by a number of rotational energy changes. Each transition appears as a single line but the lines obtained from vibrational and rotational transitions are very closely spaced. Consequently the spectrum consists of a family of lines which are usually so closely spaced that they merge (for low resolution) into a broad band.
- **When a molecule absorbs IR radiation, its chemical bonds vibrate. The bonds can stretch, contract, and bend.** This is why IR spectroscopy is a type of vibrational spectroscopy.

# Theory of Molecular Vibration

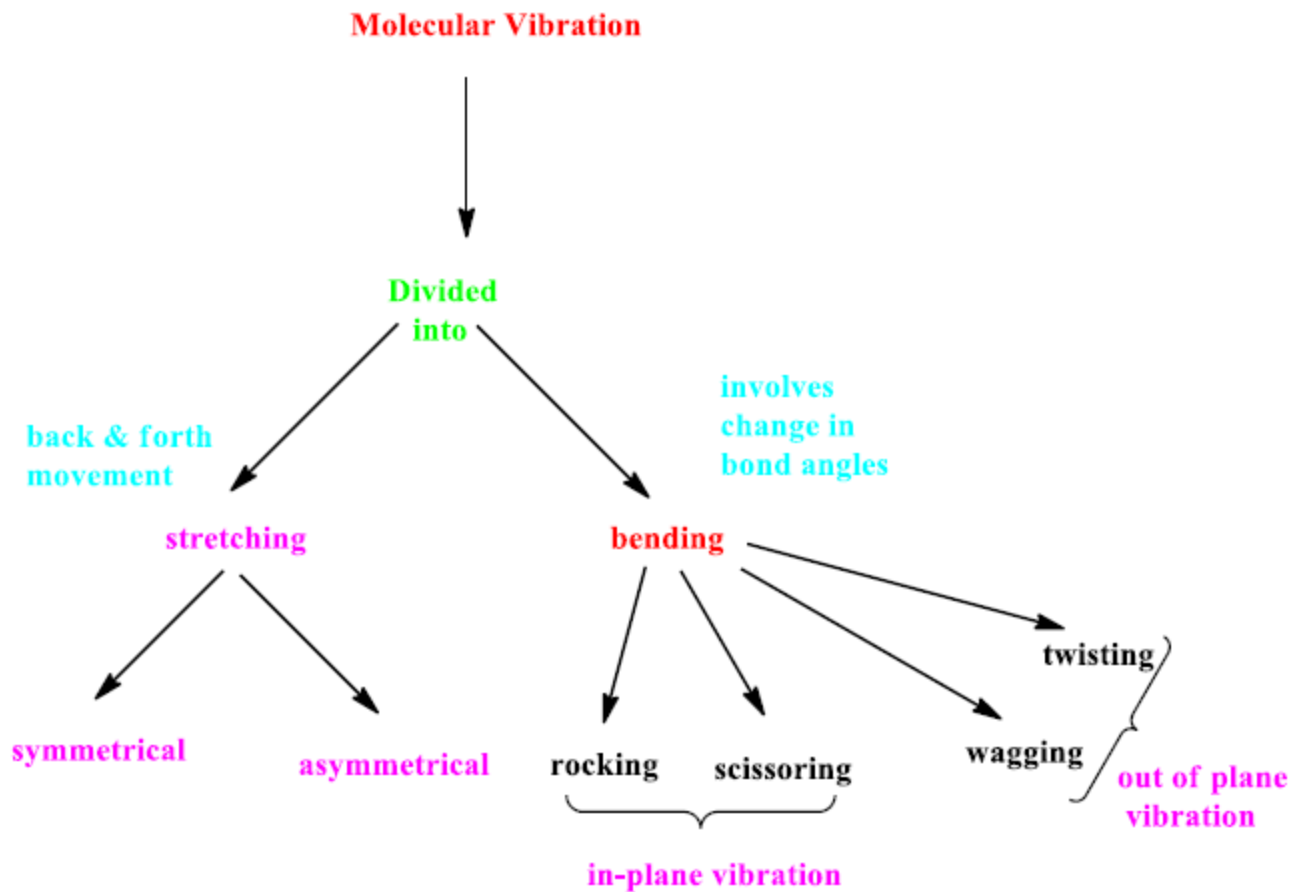
- A molecule is not a rigid assemblage of atoms. It can be said to resemble a system of balls of varying masses, corresponding to the atoms of a molecule, and springs of varying strengths, corresponding to the chemical bonds of a molecule (**'Ball-and-Spring' Model**). Therefore, several bonds in the molecule vibrate at a certain frequency.



- There are two types of molecular vibrations:
  - (i) Stretching
  - (ii) Bending
- More energy is required to stretch a bond than that required to bend it. Thus, stretching absorptions of a bond appear at high frequencies (higher energy) as compared to the bending absorptions of the same bond.

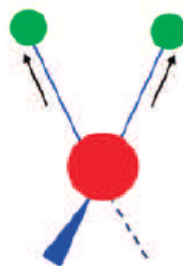
# Fundamental Vibrations

- Fundamental vibrations involve no change in the centre of gravity of the molecule.



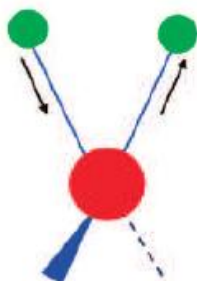
# Stretching Vibration

1. **Symmetric stretching:** In this type, the movement of the atoms with respect to a particular atom in a molecule is in the same direction. Therefore, in this mode of vibration both the bonds expand or contract at the same time.



Symmetric

2. **Asymmetric stretching:** In this vibrations, one atom approaches the central atom while the other departs from it. Therefore, in this mode of vibration, one bond expands while the other contracts.

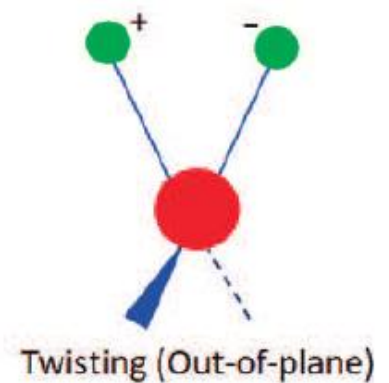
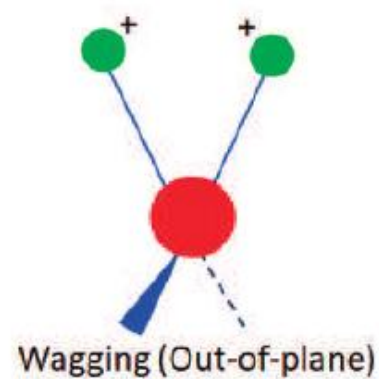
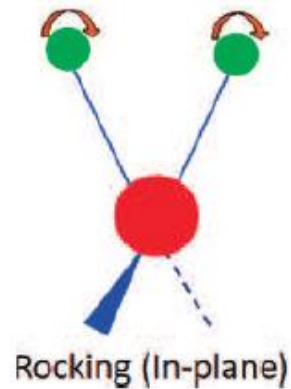
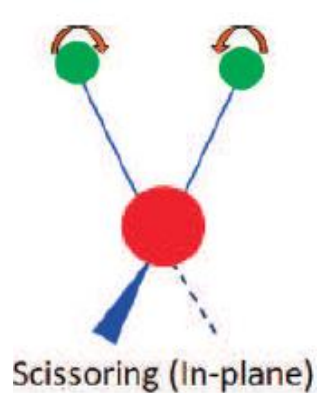


Antisymmetric



# Bending Vibration

1. **Scissoring**: In this type, two atoms approach each other.
2. **Rocking**: In this type, the movement of the atoms takes place in the same direction.
3. **Wagging**: Two atoms move 'up and down' the plane with respect to the central atom.
4. **Twisting**: In this type, one of the atoms moves up the plane while the other moves down the plane with respect to the central atoms.



## Modes of vibrations (normal modes)

- A molecule has as many degrees of freedom as the total degrees of freedom of its individual atoms. Each atom has three degrees of freedom corresponding to the Cartesian coordinates (x, y, z) necessary to describe its position relative to other atoms in the molecule. A molecule of  $n$  atoms therefore has  $3n$  degrees of freedom.
- For nonlinear molecules, three degrees of freedom describe rotation and three describe translation; the remaining  $3n - 6$  degrees of freedom are vibrational degrees of freedom or fundamental vibrations. Linear molecules have  $3n - 5$  vibrational degrees of freedom, for only two degrees of freedom are required to describe rotation.

## Number of Fundamental Vibration

- A normal 3-atom molecule such as carbon dioxide ( $\text{CO}_2$ ) has  $(3 \times 3) - 4 = 4$  normal modes. The normal modes of  $\text{CO}_2$  are a symmetric stretch, an asymmetric stretch, and two bending vibrations.
- Water is a nonlinear molecule, and has  $(3 \times 3) - 6 = 3$  normal modes. The normal modes of  $\text{H}_2\text{O}$  consists of a symmetric stretch, an asymmetric stretch, and one bending vibration.
- When a molecule absorbs IR light and begins vibrating, it gives rise to an absorption band in the IR spectrum of the molecule at the wavenumber of light absorbed.

# Selection Rules

## (Active and Forbidden Vibrations)

- **The first necessary condition** for a molecule to absorb IR light is that **the molecule must have a vibration during which the change in dipole moment with respect to distance is non-zero, i.e.,**

$$\partial\mu/\partial x \neq 0$$

Where:  $\partial\mu$  = change in dipole moment

$\partial x$  = change in bond distance

- **The second necessary condition** for IR absorption to take place is that **the energy of the light entering on a molecule must equal a vibrational energy level difference within the molecule, i.e.,**

$$\Delta E_{\text{vib}} = h\nu = hc\bar{\nu}$$

Where:  $\Delta E_{\text{vib}}$  = vibrational energy level difference in a molecule

$h$  = Planck's Constant ( $6.626 \times 10^{-34}$  J.s)

$c$  = The speed of light ( $3 \times 10^{10}$  cm/s)

$\bar{\nu}$  = Wavenumber in  $\text{cm}^{-1}$

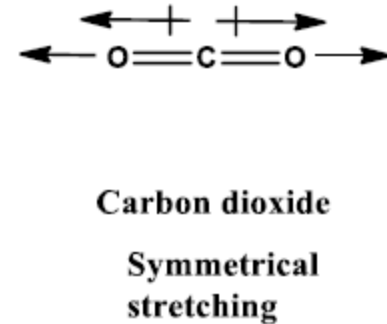
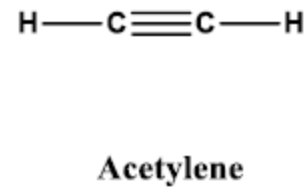
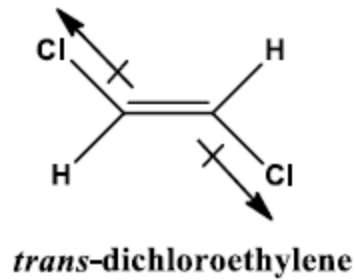
# IR Active Molecules

- Molecular vibration which will lead to a change in the dipole moment of the molecule will give rise to absorption bands in the IR. Otherwise, they are said to be IR inactive and will show no absorption.
- If a molecule has a centre of symmetry, then the vibrations are centrosymmetric and are inactive in the IR.
- The vibrations which are not centrosymmetric are active in the IR.
- The intensity of a fundamental absorption depends upon the difference between the dipole moments of the molecule in the ground state and the vibrational excited state. Greater the difference, more is the intensity of absorption.

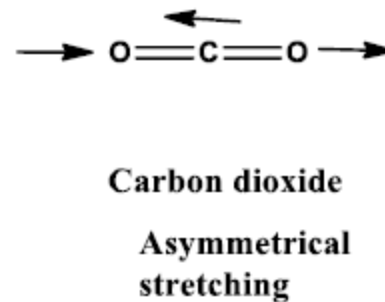
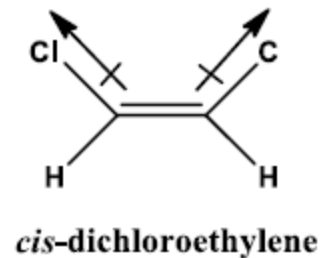
## IR Active Molecules

- The symmetrical stretching of the C=C bond in ethylene (a molecule with a centre of symmetry) will not produce a change in the dipole moment of the molecule. This mode of vibration is IR inactive. Therefore, *trans*- dichloroethylene shows no C=C stretching vibration whereas *cis*-isomer shows this band.
- The symmetrical stretching mode of carbon dioxide produces no change in the dipole moment ( $\mu$ ) of the molecule and is, therefore, 'inactive' in the IR. The asymmetrical stretching mode produces a change in the dipole moment, is thus IR active.
- A large change in dipole moment will usually give rise to strong absorption. So, bands of hydrocarbons which are only composed of carbon and hydrogen atoms are weak.

# Examples of IR Active/Inactive Molecules/Modes



IR Inactive ( $\mu = 0$ )



IR Active ( $\mu \neq 0$ )

## Vibrational Frequency

- The value of a stretching vibrational frequency of a bond can be calculated fairly accurately by the application of Hooke's law. In the application of the law, two atoms and their connecting bond are treated as a simple harmonic oscillator composed of two masses joined by a spring (ball-and-spring model). The value of vibrational frequency or wave number depends upon:
  1. The stiffness of the bond expressed as the force constant ( $k$  or  $f$ )
  2. The masses of the atoms at each end of the bond.
- A molecule with a large force constant (a stiff or strong chemical bond) will absorb at a high wavenumber, and a molecule with heavy atoms (a large reduced mass) will absorb at low wavenumber.



# HOOKE'S LAW

- The following equation, derived from Hooke's law, states the relationship between frequency of vibration, atomic masses, and the force constant of the bond.
- The vibrational frequency of a bond will increase as 1) the strength of the bond increases and/or 2) the reduced mass ( $\mu$ ) decreases.

$$\bar{\nu} = \frac{1}{2\pi c} \left[ \frac{k}{m_x m_y / (m_x + m_y)} \right]^{1/2}$$

where,  $\bar{\nu}$  = wave number (in  $\text{cm}^{-1}$ )

$c$  = velocity of light (in  $\text{cm/s}$ )

$k$  = force constant of the bond (in  $\text{dyne/cm}$ )

$$\bar{\nu} = \frac{1}{2\pi c} \left[ \frac{k}{\mu} \right]^{1/2}$$

$m_x$  and  $m_y$  = masses (in  $\text{g}$ ) of the atoms  $x$  and  $y$ ,  
respectively in a particular bond

$\mu$  = reduced mass =  $m_x m_y / (m_x + m_y)$

# A hypothetical plot of the molecular potential energy versus bond distance

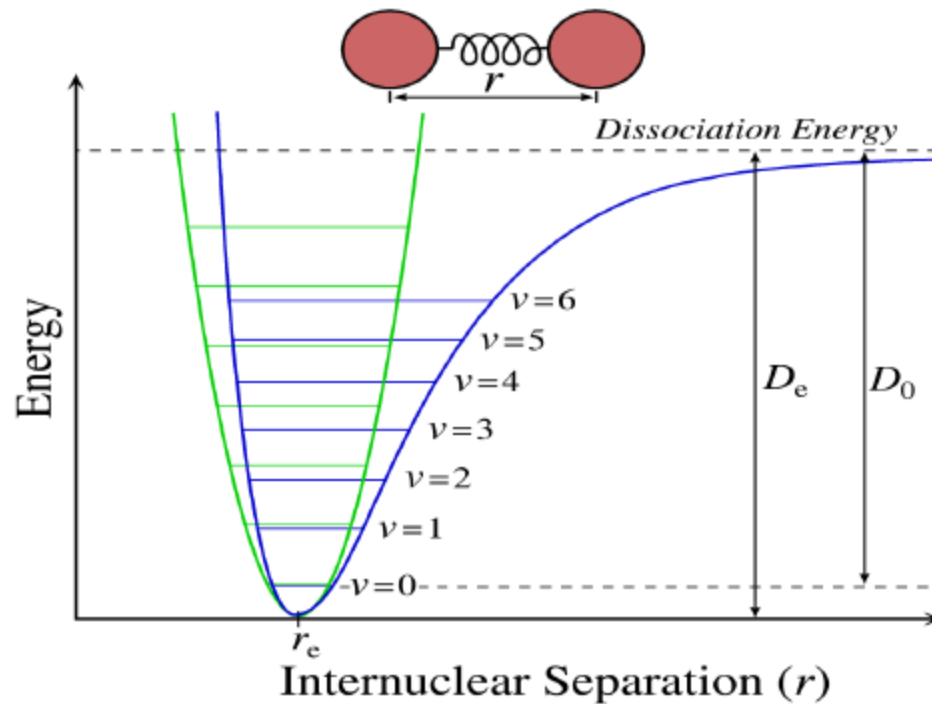


Figure 1: Harmonic Oscillator approximation (green parabola) superimposed on the anharmonic oscillator (blue curve)

# Overtone Bands

- In **Figure 1**, vibrational energy levels with vibrational quantum numbers of 0, 1, 2 and so on are seen. At room temperature, the vast majority of molecules are in the  $\nu=0$  or ground vibrational state. When a molecule absorbs IR light and is excited to the first vibrational energy level ( $\nu = 1$ ), it undergoes a **fundamental transition**.
- When a molecule is in the  $\nu=1$  level, it is said to contain one quantum of vibrational energy. Fundamental vibrational frequencies of a molecule corresponds to transition from  $\Delta\nu = \pm 1$ .
- **Figure 1**, also, shows that a molecule can be excited from the  $\nu = 0$  level to the  $\nu = 2, 3, 4$  and higher levels. **This type of transition is called an overtone transition**. If the molecule is excited to the  $\nu = 2$  level, it contains two quanta of vibrational energy; if it is excited to the  $\nu=3$  level, it contains 3 quanta of vibrational energy.

- In vibrational spectroscopy, an overtone band is the spectral band that occurs in a vibrational spectrum of a molecule when the molecule makes a transition from the ground state ( $\nu = 0$ ) to the first ( $\nu = 1$ ), second ( $\nu = 2$ ) or higher excited vibrational energy level.
- Overtones give rise to very weak absorbance bands. A  $\nu = 0$  to  $\nu = 2$  transition is typically 10 times weaker than a fundamental band; a  $\nu = 0$  to  $\nu = 3$  transition is typically 100 times weaker than a fundamental band.
- Overtone bands (harmonics) appear at integer multiples of fundamental vibrations, so that strong absorptions at, say,  $750\text{ cm}^{-1}$  and  $1725\text{ cm}^{-1}$  will also give rise to weaker absorptions at about  $1500\text{ cm}^{-1}$  and  $3450\text{ cm}^{-1}$ , respectively.

**Combination Bands:** Combination bands are observed when two or more than two fundamental vibrations are excited simultaneously. If there are two fundamental vibrations at  $x$  and  $y$   $\text{cm}^{-1}$  then it may also give rise to absorption bands at  $(x+y)$ ,  $(x+2y)$ ,  $(2x+y)$   $\text{cm}^{-1}$ .

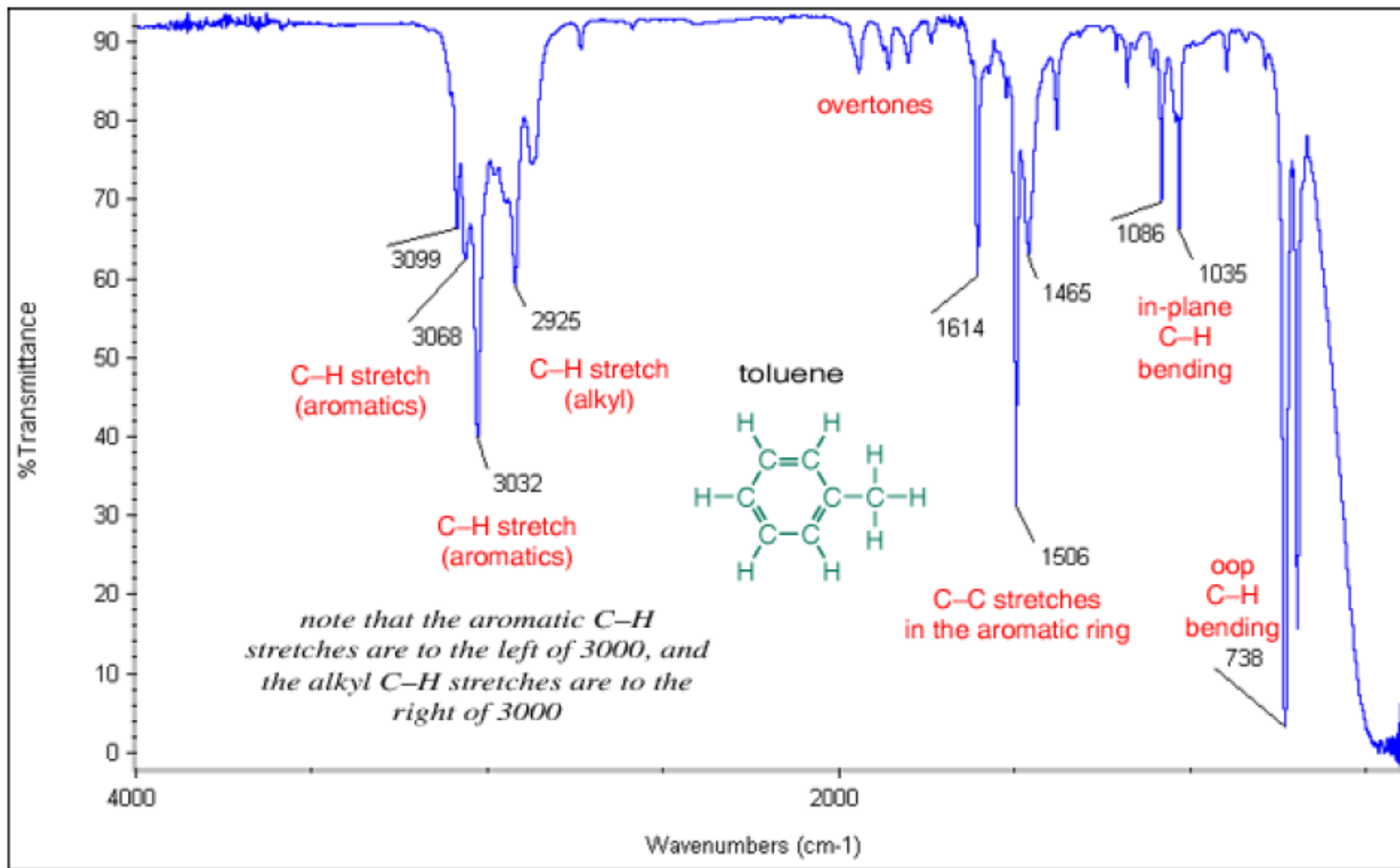
**Difference bands:** It is also possible to have a difference band where the frequencies of two fundamental bands are subtracted, i.e.  $(x-y)$ ,  $(x-2y)$ ,  $(2x-y)$   $\text{cm}^{-1}$ .

**Fermi Resonance:** When a fundamental vibration couples with overtone or combination band, the coupled vibration is called a Fermi resonance. These two vibrational modes (or frequencies) having close vibrational frequencies, resonate and exchange energy resulting in two new frequencies, one higher and one lower than the original frequency. This phenomenon was explained by the Italian physicist Enrico Fermi.

Example of Fermi resonance can be found in  $\text{CO}_2$ , the symmetrical stretching band of  $\text{CO}_2$  appears at  $1340$   $\text{cm}^{-1}$ . The fundamental bending vibration occurs at  $667$   $\text{cm}^{-1}$  and the first overtone of this vibration occurs at  $1334$   $\text{cm}^{-1}$  ( $2 \times 667$   $\text{cm}^{-1}$ ). The coupling between the fundamental stretching vibration ( $1340$   $\text{cm}^{-1}$ ) and the first overtone of the bending vibration ( $1334$   $\text{cm}^{-1}$ ) takes place to give two bands at frequencies  $1285$   $\text{cm}^{-1}$  and  $1385$   $\text{cm}^{-1}$ .

# Fingerprint Region

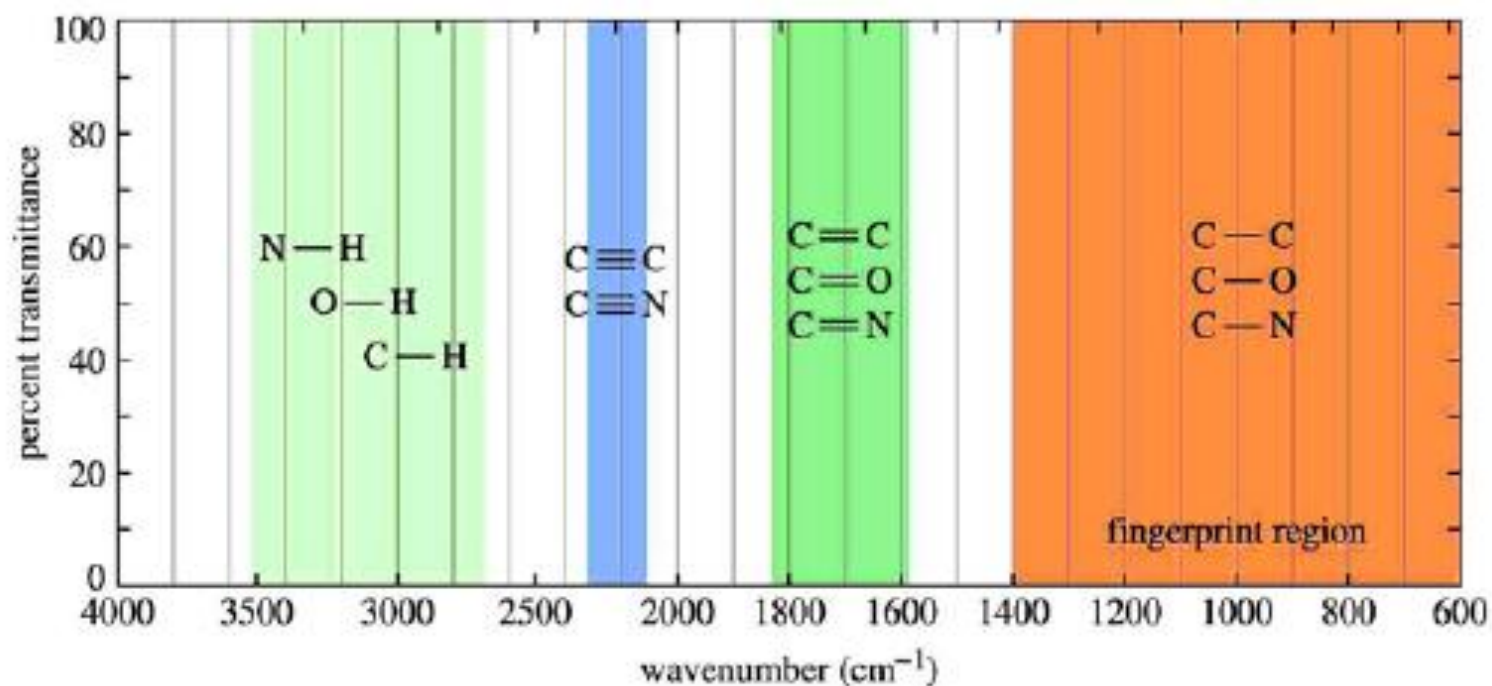
- The region  $1470\text{-}910\text{ cm}^{-1}$  in the IR spectra of a compound is known as *Fingerprint region*. This region of the spectrum is particularly rich in absorption bands and shoulders.
- This region contains many important absorptions caused by bending vibrations (particularly C-H) as well as absorptions caused by C-C, C-O, and C-N single bond stretching vibrations. Some absorption bands due to benzene rings are also found in this wavenumber region.
- The utility of the fingerprint region is that the many bands there provide a fingerprint for a molecule. **No two molecules, except the enantiomers, in the universe have the same IR spectrum**, and there is no better way to determine whether two samples are the same than by comparing their fingerprint regions.



## Group frequency


Absorption bands in the **4000 to 1450  $\text{cm}^{-1}$  region** are usually due to stretching vibrations of diatomic units, and this is sometimes called the group frequency region.

The typical IR absorption range for covalent bonds is **600 - 4000  $\text{cm}^{-1}$** . The graph shows the regions of the spectrum where the following types of bonds normally absorb. For example a sharp band around 2200-2400  $\text{cm}^{-1}$  would indicate the possible presence of a C-N or a C-C triple bond.





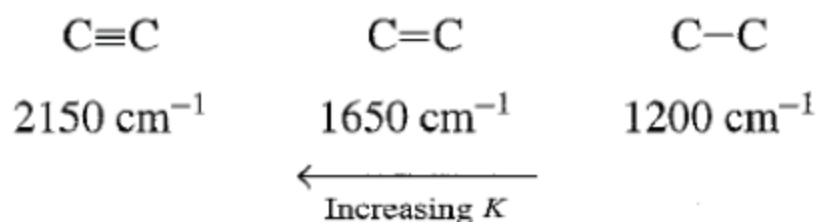
**Table 1** Important IR Stretching Frequencies

Type of bond	Wavenumber ( $\text{cm}^{-1}$ )	Intensity
$\text{C}\equiv\text{N}$	2260–2220	medium
$\text{C}\equiv\text{C}$	2260–2100	medium to weak
$\text{C}=\text{C}$	1680–1600	medium
$\text{C}=\text{N}$	1650–1550	medium
	~1600 and ~1500–1430	strong to weak
$\text{C}=\text{O}$	1780–1650	strong
$\text{C}-\text{O}$	1250–1050	strong
$\text{C}-\text{N}$	1230–1020	medium
$\text{O}-\text{H}$ (alcohol)	3650–3200	strong, broad
$\text{O}-\text{H}$ (carboxylic acid)	3300–2500	strong, very broad
$\text{N}-\text{H}$	3500–3300	medium, broad
$\text{C}-\text{H}$	3300–2700	medium

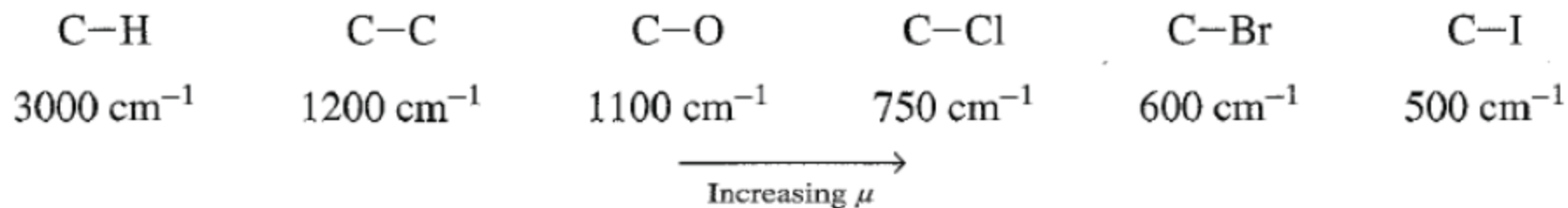
## The position of an IR-Absorption Band

The force constant is a measure of the strength of a bond. Thus the value of stretching frequency of a bond increases with increasing the bond strength and decreasing the reduced mass of the bonded atoms.

The triple bonds are stronger than the double bonds followed by single bonds between the same two atoms and hence vibrational frequency is in the order of triple > double > single.



As the atom attached to carbon a particular atom say carbon increases in mass, the reduced mass increases and hence the frequency of vibration decreases.



## Factors Influencing Vibrational Frequencies

### Effect of Bond Order

Bond order affects the position of absorption bands. Higher the bond order larger is the band frequency. A C-C triple bond is stronger than a C=C bond, so a C-C triple bond has higher stretching frequency than does a C=C bond. The C-C bonds show stretching vibrations in the region from  $1200\text{-}800\text{ cm}^{-1}$  but these vibrations are weak and of little value in identifying compounds. Similarly, a C=O bond stretches at a higher frequency than does a C-O bond and a C-N triple bond stretches at a higher frequency than does a C=N bond which in turn stretches at a higher frequency than does a C-N bond.

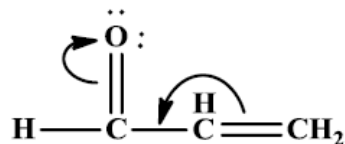
**Electronic effects:** The absorption frequency of particular group changes, when the neighboring structural environment of that particular bond is changed. The electronic effect including inductive effect, mesomeric effect, field effect can cause changes in force constant or bond strength which leads to the shift in absorption frequency from the normal value.

In case of inductive effect, the +I effect **decreases wave number** (lengthening or weakening of bond occurs due to which force constant is decreased) and -I effect causes **increase in wavenumber** due to increase in force constant and decrease in bond length.

Example:  $\nu(\text{C}=\text{O})$  of formaldehyde  $\text{HCHO}$  occurs at higher wavenumber  $1750\text{ cm}^{-1}$  than acetaldehyde ( $1745\text{ cm}^{-1}$ ) due to +I effect of  $\text{CH}_3$  group.

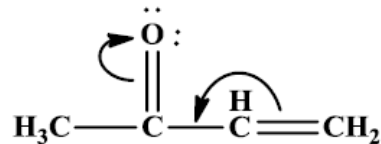
Due to -I effect of chloro group,  $\nu(\text{C}=\text{O})$  of chloroacetone ( $1725\text{ cm}^{-1}$ ) occurs at higher wave number than acetone ( $1715\text{ cm}^{-1}$ ).

Mesomeric effect causes lengthening of bond or weakening of bond resulting in decrease in wavenumber. For, example, conjugation of  $\text{C}=\text{O}$  group with olefinic or phenyl group causes a shift in  $\text{C}=\text{O}$  absorption to lower frequency. Consider the following compounds:



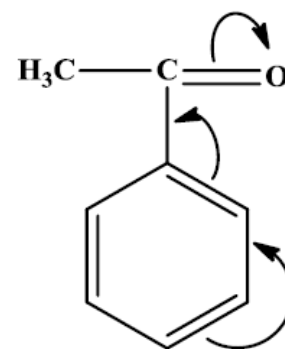
2-Butenal

$\nu\text{C}=\text{O}$   $1690\text{ cm}^{-1}$



Methyl Vinyl Ketone

$\nu\text{C}=\text{O}$   $1686\text{ cm}^{-1}$

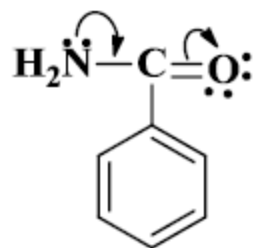


Acetophenone

$\nu\text{C}=\text{O}$   $1693\text{ cm}^{-1}$

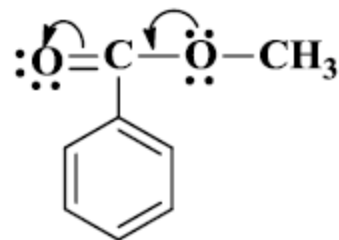
$\nu(\text{C}=\text{O})$  of acetone ( $\text{CH}_3\text{COCH}_3$ ) occurs at  $1715\text{ cm}^{-1}$ .

Now, let us consider the C=O stretching frequency of amide and ester:



Benzamide

$\nu_{\text{C=O}}$  1663  $\text{cm}^{-1}$



Methyl benzoate

$\nu_{\text{C=O}}$  1730  $\text{cm}^{-1}$

Oxygen atom of ester is more electronegative than nitrogen of amide. Therefore, lone pair of electrons on nitrogen atom of amide participates more in conjugation resulting in the decrease in absorption frequency of  $\nu_{\text{C=O}}$  in amide as compared to that of ester.

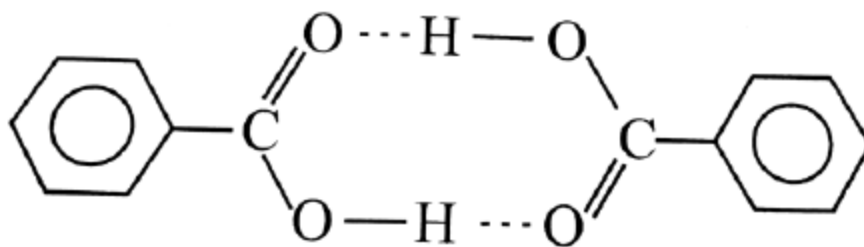
## Hydrogen bonding:

The presence of hydrogen bonding in the molecule changes the absorption frequency as well as shape of absorption band. Stronger the hydrogen bonding, greater the absorption shift towards lower wave number from normal value. The two types of hydrogen bonding (intramolecular and intermolecular) can be distinguished by the use of infrared spectroscopy.

Intermolecular hydrogen bonding is concentration dependent and the absorption band shift on dilution. On the other hand intramolecular H-bonding is concentration independent. The intermolecular bonding gives rise to broad bands while the bands due to intra-molecular hydrogen bonding are sharp and well defined.

A free (unassociated) O-H bond (in vapour phase or in very dilute solutions) gives rise to stretching absorption at about  $3610\text{ cm}^{-1}$ . While in dimeric or polymeric association the hydroxyl group absorbs as broad bands at lower frequency at around  $3350\text{ cm}^{-1}$ .

Benzoic acid exists as dimer. The bridges formed are stabilized by resonance. The formation of dimer causes lowering in the force constant and lengthening of bonds. As a result absorption frequency for  $\nu_{\text{C=O}}$  and  $\nu_{\text{O-H}}$  decreases. The spectrum of benzoic acid displays broad and strong O-H stretching band at about  $3000\text{-}2500\text{ cm}^{-1}$  and C=O stretching frequency at about  $1685\text{ cm}^{-1}$ .



Dimerization in benzoic acid