

# INFRARED SPECTROSCOPY



**Presented By**

**Dr. T. VARAPRASAD.** M.Sc., M.Ed., M.Phil., P.hD  
**LECTURER IN CHEMISTRY**  
**HEAD OF THE DEPARTMENT**  
**DEPARTMENT OF CHEMISTRY**  
**P.R.GOVERNMENT COLLEGE(A), KAKINADA**

# Synopsis

- Introduction
- Theory and Instrumentation
- TERMS CONCERNING INFRARED SPECTROSCOPY
- ABSORPTION OF INFRARED RADIATION AND MOLECULAR VIBRATIONS
- FUNDAMENTAL VIBRATIONS AND OVERTONES
- NUMBER OF FUNDAMENTAL VIBRATIONS AND SELECTION RULES
- Bands resulting from Combination or Difference of vibrational frequencies or by the interaction of Overtone (or Combination Band) with the Fundamental Vibration (Fermi Resonance)
- SPECTRAL FEATURES OF MAJOR FUNCTIONAL GROUPS AND INTERPRETATION OF INFRARED SPECTRA OF SOME REPRESENTATIVE COMPOUNDS
- Question Bank

# INTRODUCTION

- Infrared spectroscopy is one of the most widely used techniques for the detection of functional groups in compounds.
- The spectrum is obtained in minutes using a few mg of the compound which can also be recovered.
- Infrared Spectroscopy gives information on molecular vibrations or more precisely on transitions between vibrational and rotational energy levels in molecules. This information is very helpful because it can be directly related to molecular structure.
- The infrared spectrum is the simplest, most rapid and often most reliable means for assigning a compound to its class.
- It can also provide a variety of information on structure, symmetry, purity, structural and geometrical isomers and hydrogen bonding.
- An infrared spectrum is obtained when the frequency of molecular vibration corresponds to the frequency of the infrared absorption.
- The position of absorption in the spectrum is usually expressed in terms of wave number ( $\text{cm}^{-1}$ ) of the absorbed light.

# BASIC THEORY AND INSTRUMENTATION

- A molecule contains electronic, vibrational and rotational energy levels. Each electronic level is associated with a number of vibrational levels with less energy separations and each vibrational level in turn is associated with a set of rotational levels with even less energy separations.
- When a molecule absorbs radiation, its energy increases in proportion to the energy of the photon as per the relation,

$$E = h\nu = hc / \lambda$$

Where  $h$  = Plank's constant,  
 $\nu$  = frequency,  
 $\lambda$  = wavelength and  
 $c$  = velocity of light

- Due to the relatively smaller amounts of energy associated with the infrared radiation, molecules are incapable of electronic excitations but induce transitions between vibrational and rotational energy levels of a molecule.
- Thus, the infrared spectrum of a molecule results from transitions between vibrational and rotational energy levels and is also called Vibrational-Rotational Spectrum of the molecule.

# INSTRUMENTATION

## Double-Beam Infrared Spectrometer

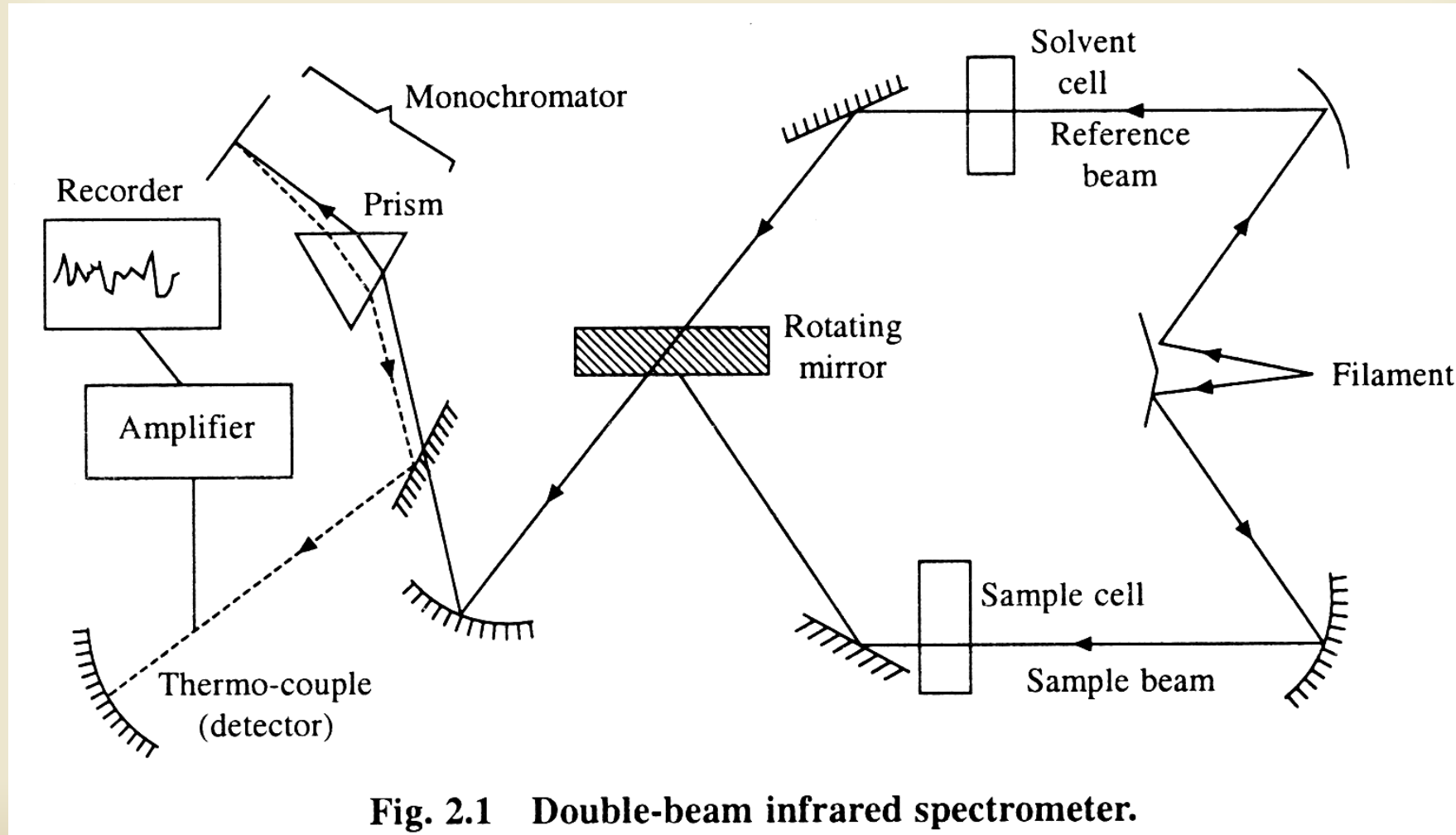


Fig. 2.1 Double-beam infrared spectrometer.

The schematic diagram of Double-Beam Infrared Spectrometer and its essential features are described briefly as follows:

### **Radiation Source:**

The source of radiation is a small ceramic rod, heated electronically in the range 1100-1800°C and is made of either silicon carbide (Glowbar) or Nernst filament (a high-resistance, brittle element composed of mixture of oxides of Zirconium, Thorium and Cerium held together by a binding material). The radiation beam is divided into two beams, one is sample beam and the other is reference beam. These two beams are passed alternately into a monochromator at very short intervals by means of a rotating mirror.

### **Absorption Cells and Sample Preparation:**

The cells generally employed are made up of rock salt or potassium bromide (glass and quartz cells are unsuitable as these materials themselves absorb IR radiation).

A compound (0.55 mg) may be examined in solution in a suitable minimum absorbing solvent ( $\text{CCl}_4$ ,  $\text{CHCl}_3$ ,  $\text{CS}_2$  etc.) as a liquid film. In the case of solids not sufficiently soluble in these solvents, as a mull in Nujol (white mineral oil) or as a pellet obtained by pressing the sample in a hydraulic press.

### **Monochromator:**

The pulse beam enters the monochromator through an entrance slit and is dispersed by a grating. In the monochromator, the emergent beams are sorted out into individual wave lengths by means of a sodium chloride prism which is transparent to infrared radiation through out the range  $4000\text{-}650\text{ cm}^{-1}$ . In order to extend the operating range below  $650\text{ cm}^{-1}$ , prism made up of KBr (transparent upto  $400\text{ cm}^{-1}$ ) and Cesium Iodide (transparent upto  $200\text{ cm}^{-1}$ ) are employed.

### **Detector, Amplifier and Recorder:**

After the sorting out (dispersion), the beams are focused alternately at each particular wave length throughout the spectral range, by means of a mirror system on to the detector, usually a sensitive fast thermocouple. The signals from this are amplified electronically and by means of a mechanical arrangement, the spectrum which is really a measure of the difference in intensities of the reference and sample beams throughout the wave length range is recorded on a special graph paper.

### **Calibration of Spectral Chart:**

A very sharp band at  $1603\text{ cm}^{-1}$  found in the spectrum of polystyrene is often used to calibrate the spectral chart, immediately before or after the spectrum of a sample is recorded. This helps in determining whether the spectral chart is correctly mounted on the spectrometer or not. If necessary, corrections are made in reading the band positions on the chart.



## TERMS CONCERNING INFRARED SPECTROSCOPY

### Infrared Spectrum:

IR Spectrum of a compound represents its energy absorption pattern in the Infrared region and is obtained by plotting percent absorption or transmittance of Infrared radiation as a function of wavelength or wave number over a particular range.

Infrared Spectroscopy is usually divided into three regions,

Near Infrared  
(Overtone region)

Middle Infrared  
(Fundamental  
Vibrational region)

Far Infrared  
(Pure rotational region)

Functional  
Group region

Finger  
print region

---

12500 cm<sup>-1</sup>

4000 cm<sup>-1</sup>

1400 cm<sup>-1</sup>

900 cm<sup>-1</sup>

667 cm<sup>-1</sup>

50 cm<sup>-1</sup>

---



The normal Infrared region (middle infrared region) extends from  $4000\text{ cm}^{-1}$  to  $667\text{ cm}^{-1}$  and results from vibrational and rotational transitions. The vibrations induced in organic molecules are absorbed in this region.

The other regions are near infrared region ( $12,500$  to  $4,000\text{ cm}^{-1}$ ) and far infrared region ( $667\text{ cm}^{-1}$  to  $50\text{ cm}^{-1}$ ).

The near infrared region exhibits bands assignable to harmonic overtones of fundamental bands and combination bands, whereas the far infrared region deals with the pure rotational motion of the molecules.

### **Functional Group And Finger Print Region:**

The region of infrared spectrum from  $4000\text{ cm}^{-1}$  to  $1400\text{ cm}^{-1}$  exhibits absorption bands of a number of functional groups and is called functional region.

The region from  $1400\text{ cm}^{-1}$  to  $900\text{ cm}^{-1}$  is complex because it contains bands resulting from the sum or difference of their vibrational frequencies. This part of the spectrum is characteristic of a compound and is called-finger print region. Similar molecules may show very similar spectra in the functional group region but certainly exhibit discernible differences in the finger-print region.

# ABSORPTION OF INFRARED RADIATION AND MOLECULAR VIBRATIONS

## Absorption of Infrared Radiation:

The absorption of Infrared radiation corresponds to energy changes in the range from 2-10 k.cal/mol. Radiation in this energy range corresponds to the range encompassing the stretching and bending vibrational frequencies of the bonds in most covalent molecules.

Infrared light is absorbed when oscillating dipole moment (due to molecular vibration) interacts with the oscillating electric vector of the infrared beam. These vibrations absorb infrared light at certain quantized frequencies and give rise to characteristic bands. When infrared light of that frequency is incident on the molecule energy is absorbed and the amplitude of that vibration is increased.

## Molecular Vibrations

Molecule may be regarded as a system of balls (atoms) and springs (bonds). When it absorbs infrared radiation, it is set into vibrations resulting in excitation of bond deformations: stretching and bending.

## Stretching vibrations:

- During stretching vibrations, the distance between two atoms increases or decreases but the atoms remain in the same bond axis.
- Stretching vibrations require higher energy and occur at higher frequency.

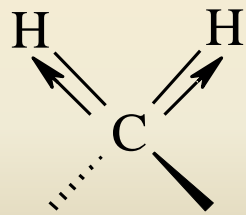
## Bending Vibrations (Deformations):

- During bending vibrations, the distance between the atoms remains constant but the position of the atoms changes relative to the original bond axis.
- Bending vibrations require lower energy and occur at lower frequency.

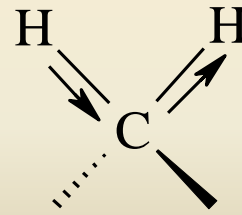
**Types of Stretching Vibrations:** They are of two types

**Symmetrical Stretching:-** In this mode, both the atoms move in and out simultaneously. Symmetrical stretching of  $>\text{CH}_2$  group is shown in the figure.

**Asymmetrical Stretching:-** In this mode, one atom moves in while the other moves out and is represented for  $>\text{CH}_2$  group in the figure.



Symmetrical Stretching



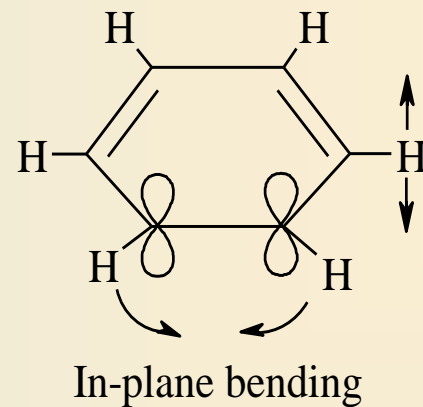
Asymmetrical Stretching

**Types of Bending Vibrations:** they are of two types:

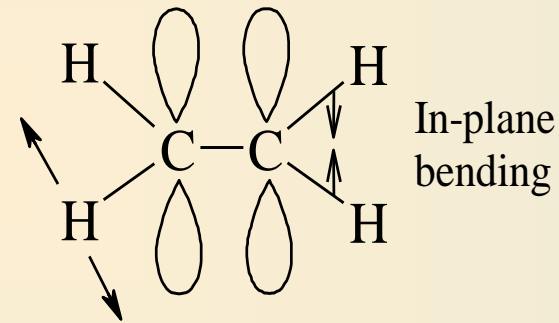
(i) In-plane bending

(ii) Out-of-plane bending

**(i) In-plane bending vibrations:-** A bending vibrational mode in which the atoms remain in the same plane as the nodal plane of the system, is called In-plane bending vibration.



Out-of-plane  
bending



In-plane bending vibrations are of two types:

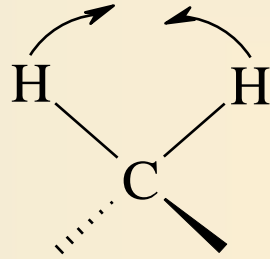
(a) In-plane scissoring deformation (b) In-plane rocking deformation.

**(a) In-plane scissoring deformation:**

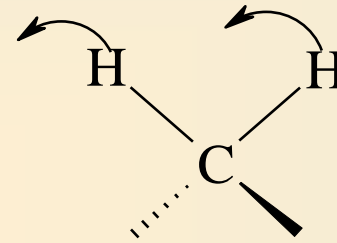
In this mode, both the atoms swing in concert toward opposite directions as represented for  $>\text{CH}_2$  group in the figure.

**(b) In-plane rocking deformation:**

In this mode, both the atoms swing to the same side and then both to the other side. This is shown for the  $>\text{CH}_2$  group in the figure.



In-plane bending (Scissoring)



In-plane bending (Rocking)

**(ii) Out-of-plane bending vibrations:**

When the atoms bend out of the nodal plane, the bending mode is called Out-of-plane bending. They are of two types:

(a) Out-of-plane wagging deformation

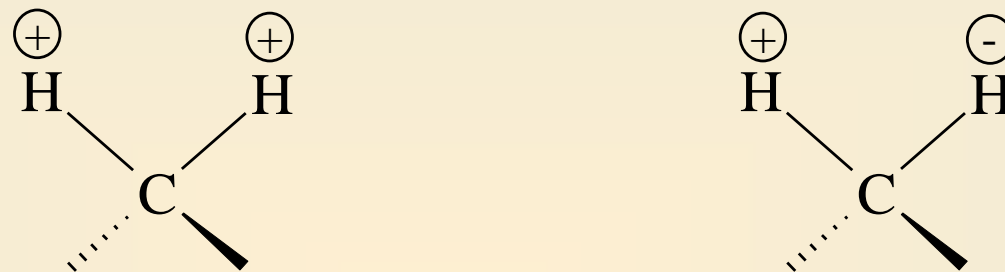
(b) Out-of-plane twisting deformation

**(a) Out-of-plane wagging deformation:**

In this deformation mode, both the atoms swing up and down out of the plane of the paper in unison. This is illustrated for the  $\text{CH}_2$  group in the figure.

## (b) Out-of-plane twisting deformation:

In twisting deformation, one atom swings up and the other swings down related to the plane of the paper as shown in the figure for CH<sub>2</sub> group.



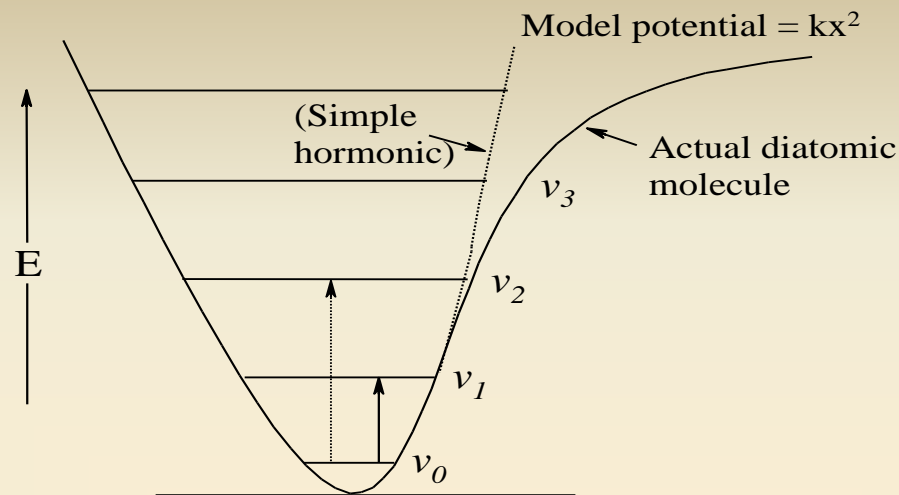
Out-of-plane bending (Wagging)

Out-of-plane bending (Twisting)

The + and - signs signify the movement of hydrogens in a direction perpendicular to the plane of the paper

## FUNDAMENTAL VIBRATIONS AND OVERTONES

The fundamental vibrations correspond in the quantum treatment to the first vibrational transition from the zeroth vibrational level to the first,  $\nu_0 \rightarrow \nu_1$  (at the room temperature most of the molecules are in the zeroth level).



Potential energy curves for a model and an actual diatomic molecule, showing fundamental transition ( $\nu_0 \rightarrow \nu_1$ ) and overtone transition ( $\nu_0 \rightarrow \nu_2$ ).

### Overtone:

- The term overtone is used in a general sense to apply to any multiple of a given fundamental frequency.
- The transitions from  $\nu_0 \rightarrow \nu_2$  and  $\nu_0 \rightarrow \nu_3$  are the first and second overtones of the fundamental and require radiation of twice and thrice its frequency. For example, the first overtone  $2 \nu_{\text{C=O}}$  for the carbonyl fundamental  $\nu_{\text{C=O}}$  at  $1700 \text{ cm}^{-1}$  will be  $3400 \text{ cm}^{-1}$ .
- In infrared spectroscopy, most overtones are found in the near infrared region beyond  $4000 \text{ cm}^{-1}$ . Such absorptions are much weaker than the fundamental.
- For example, Aromatic compounds exhibit overtone absorptions in the region  $2000\text{--}1667 \text{ cm}^{-1}$  which are characteristic of the aromatic substitution.



## NUMBER OF FUNDAMENTAL VIBRATIONS AND SELECTION RULES

### Number of Fundamental Vibrations:

- A molecule containing  $n$  atoms has  $3n$  degrees of freedom; three of which are assigned to translational, another three to rotational (two in case of linear molecules such as CO<sub>2</sub> or Acetylene) and the remaining  $3n-6$  ( $3n-5$ , if linear) to vibrational motions.
- For example, non-linear molecules such as methane and benzene should have, theoretically, 9 and 30 possible fundamental absorption bands respectively whereas CO<sub>2</sub>, a linear molecule, should exhibit only 4 fundamental absorptions.

### Infrared Vibrations—Active and Forbidden (Selection Rules):

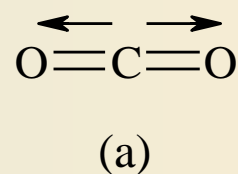
Infrared light is absorbed when a change in the dipole character of the molecule takes place. Total symmetry about a bond will eliminate certain absorption bands so that the number of absorption bands does not coincide exactly with the number of fundamental vibrations and the molecules display somewhat simplified spectra. Thus, some of the fundamental vibrations are infrared active while the others are not. This is governed by the selection rules which may be stipulated as follows:

- In a molecule with a centre of symmetry, the vibrations symmetrical about the centre of symmetry are inactive in the Infrared but active in the Raman.
- The vibrations, without a centre of symmetry, are active in Infrared but inactive in the Raman.

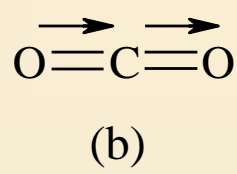
S.No.	Type of Vibrations	Infrared	Raman
1.	Centrosymmetric	Inactive	Active
2.	Non-Centrosymmetric	Active	Inactive

It means that the two types of spectra are complementary and the more easily obtained, the infrared, is most informative for organic chemists because most of the fundamental groups are not Centrosymmetric.

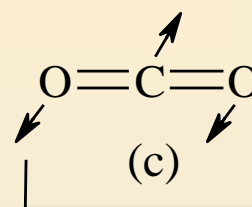
For example, CO<sub>2</sub> can have the following vibrations:



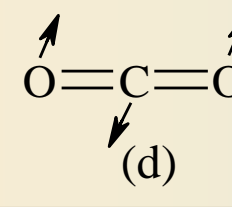
Symmetrical  
stretching  
(IR-Inactive)



Asymmetrical  
stretching  
 $\lambda_{\max} = 2350 \text{ cm}^{-1}$



Bendingvibration  
(identical motion)  
 $\lambda_{\max} = 667 \text{ cm}^{-1}$



### Fundamental vibrations of Carbon dioxide

- These four vibrations (a–d) are the fundamental vibrations of CO<sub>2</sub>.
- The symmetric C=O stretching vibration (a) of CO<sub>2</sub> does not give rise to a change in the dipole moment of the molecule and consequently remains inactive.
- In the asymmetric stretching (b), the two C=O bonds are of different length and hence the molecule has a net charge in the dipole character (infrared active) and consequently absorbs at 2350 cm<sup>-1</sup>.
- The bending of O=C=O bonds (c and d) are identical motions but they occur in perpendicular planes. Such vibrations are called degenerate and appear in the same position in the spectrum.
- Thus the two bands at 2350 cm<sup>-1</sup> and 667 cm<sup>-1</sup> pertaining to asymmetric stretching (b) and bending vibrations (c and d) constitute the fundamental spectrum of CO<sub>2</sub>.

### **Intensity and Position of Infrared Absorption Bands**

- The intensity of a particular fundamental absorption depends upon the difference between the dipole moments of the molecule in the ground state and the vibrational excited state.
- The greater the difference in these dipole moments, the more intense the absorption. If no change in the dipole moment accompanies the vibrations, then that mode is infrared inactive.
- The intensity of absorption bands in infrared spectroscopy cannot be measured with the same accuracy as in ultraviolet spectroscopy.

- It is usually sufficient for an organic chemist to know that a band is of strong, medium, weak or variable intensity. This may be estimated by assigning the most intense peak (say base peak), in the infrared spectrum, a relative intensity of 100% and the intensities of other peaks are expressed as very strong (intensity is 80% to that of the base peak), strong (80 to 60%), medium (60 to 50%), weak (50 to 30%) and very weak if the intensity is less than 30% to that of the base peak.
- Either the wavelength ( $\mu$ ) or wave number ( $\text{cm}^{-1}$ ) is used to measure the position of a given infrared absorption.
- Frequencies are usually expressed in terms of wave numbers ( $\text{cm}^{-1}$ ), since wave number is proportional to the frequency and therefore to the energy, while wavelength is inversely proportional to the energy.

### **Bands resulting from Combination or Difference of vibrational frequencies or by the interaction of Overtone (or Combination Band) with the Fundamental Vibration (Fermi Resonance)**

#### **Combination Bands:**

A number of weak absorptions occurs in the infrared spectra due to the sum of two or more fundamental vibrational frequencies. The combination modes arise from the anharmonicity of the oscillators which lead to an interaction of the vibrational states in polyatomic molecules. The resulting absorptions are weak compared to the fundamental vibrations and Overtones.

## **Deference Modes:**

Some of the absorptions recorded in the infrared spectra correspond to the difference between two vibrational frequencies. In these cases, the molecule already existing in one excited vibrational state absorbs enough additional radiant energy to raise it to another vibrational level in a different vibrational mode. The measured absorption is then the difference between the two.

## **Fundamental–Overtone interaction (Fermi Resonance):**

When an overtone or combination band falls near a strong fundamental vibration, it causes a decrease in the intensity of the fundamental vibration and a large increase in the intensity of the overtone or combination vibration. Such an interaction between fundamental and overtone or combination vibration is known as Fermi Resonance.

For example in Aldehydes, the appearance of two moderately intense bands in the region 2830–2695  $\text{cm}^{-1}$  is due to the interaction between the aldehydic C–H stretch and the first overtone of aldehydic C–H in-plane bending which appears near 1390  $\text{cm}^{-1}$ .

## Frequency of Vibration of a Diatomic Molecule and its Variation with Force Constant and Relative Masses of the Bonded Atoms

### Frequency of Vibration of a Diatomic Molecule:

A vibrating diatomic molecule or less precisely a diatomic grouping (O–H, N–H, C=O etc) in a more complex molecule behaves as a simple harmonic oscillator, oscillating with the frequency  $\nu$  as per the equation,

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

Where,

$k$  = Force constant (dynes/cm) of the bond

$\mu$  = Reduced mass, that is, harmonic mean  $m_1 \times m_2 / m_1 + m_2$  or the masses of  $m_1$  and  $m_2$

$c$  = Velocity of light.

Thus, the frequency of vibration of a bond is a function of

- i. Force constant of the bond which is a measure of the binding force between atoms or restoring force per unit displacement of the point masses  $m_1$ , and  $m_2$  and
- ii. Masses of the atoms involved in the bonding.

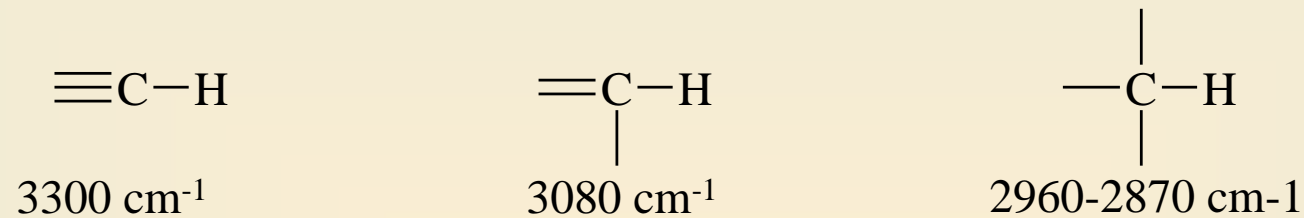
### Variation of Vibrational Frequency of a Bond with Force Constant:

The Force Constant of a bond increases numerically with bond order and consequently decreases with the increase in bond length. It has been shown that the stretching frequencies in the following series also increase in the anticipated sequence:

Hydrocarbon Series	Force Constant $k$ (dynes/cm)	Bond order	Bond length (Å)	Stretching Frequency $\nu_{\max}$ (cm <sup>-1</sup> )
—C—C— (Alkane)	$5 \times 10^5$	1	1.54	1300-800
>C=C< (Alkene)	$10 \times 10^5$	2	1.33	1640-1600
—C≡C— (Alkyne)	$15 \times 10^5$	3	1.20	2300-2100



Hybridization affects the force constant  $k$  of the bond. Bonds are stronger in the order  $sp > sp^2 > sp^3$  (order of decreasing electronegativity of carbon atoms) and is illustrated by the observed C–H stretching frequencies in the following partial structures of hydrocarbons.



### Vibration of Frequency with Masses of the Bonded Atoms:

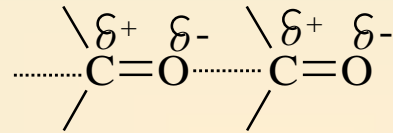
Bonds between atoms of higher masses will vibrate at lower frequencies than the bonds bearing the lighter atoms. This is illustrated by the following examples:

- (a) The O–H bond absorbs near  $3600\text{ cm}^{-1}$  while the O–D bond absorbs near  $2630\text{ cm}^{-1}$ .
- (b) The C–H stretching occurs at  $2960\text{ cm}^{-1}$ . As the atom bonded to carbon increases in mass, the factor  $\mu$  increases and consequently the frequency decreases. This is shown as follows:



## Frequency Shifts by Change of Phase and Solvents

- Variations in the physical state influence the infrared frequencies by means of association effects.
- Shifts of absorption bands occurring as a result of changes of solvents or phase can be of definite use in qualitative analysis. Apart from band frequency shifts, band splitting or coalescence may occur. For example, the carbonyl stretching frequency of acetone occurs at 1742 cm<sup>-1</sup> in the vapour phase, whereas in the liquid phase dipole-dipole association of the type,



lowers the frequency to 1718 cm<sup>-1</sup> and In solution it occurs at 1726 cm<sup>-1</sup> in hexane, at 1713 cm<sup>-1</sup> in chloroform and at 1709 cm<sup>-1</sup> in ethanol.

- Similarly cyclopentanone shows in the vapour phase a carbonyl absorption band at 1772 cm<sup>-1</sup> but as a liquid film absorbs at 1746 and 1732 cm<sup>-1</sup>. In solution the two absorption bands occur at 1750-1740 and at 1731-1725 cm<sup>-1</sup>.
- When the infrared of crystalline solids are examined, the absorption frequencies of polar groups are modified by means of strong interactions between the polar groups of adjoining molecules in the crystal. Hence the stretching frequencies of the groups in the condensed phase are lowered by 10-20 cm<sup>-1</sup> as compared to the corresponding values in dilute solution.

- The effect of change of phase or solvent on the degree of hydrogen bonding is illustrated by simple primary (1o) amides. When examined in the solid state, they exhibit only one band at 1680-1600 cm<sup>-1</sup>, which is split into amide I and II bands when the spectra are measured as dilute solutions.
- When the compound is a pure liquid, the same intermolecular forces operate, although the molecules are more randomly oriented. This is illustrated by simple 2o amides. The amide I band of N-methyl and N-ethyl acetamide occurs at 1650 cm<sup>-1</sup> in the condensed liquid state, at 1700 cm<sup>-1</sup> in dilute solution and at 1720-1715 cm<sup>-1</sup> in the vapour phase.
- Solute-solvent interactions, as well as intermolecular interactions, are minimal if the spectrum of a very dilute solution of the compound is run in an inert, non-polar solvent such as *n*-hexane.

## **SPECTRAL FEATURES OF MAJOR FUNCTIONAL GROUPS AND INTERPRETATION OF INFRARED SPECTRA OF SOME REPRESENTATIVE COMPOUNDS**

### ***(I) Hydrocarbons (Saturated and Unsaturated)***

#### ***(i) Alkanes and Cycloalkanes:***

##### ***Alkanes (Paraffins):***

The spectrum of alkanes is usually simple and displays the following characteristic bands:

**(a) C–H stretching Vibrations:**

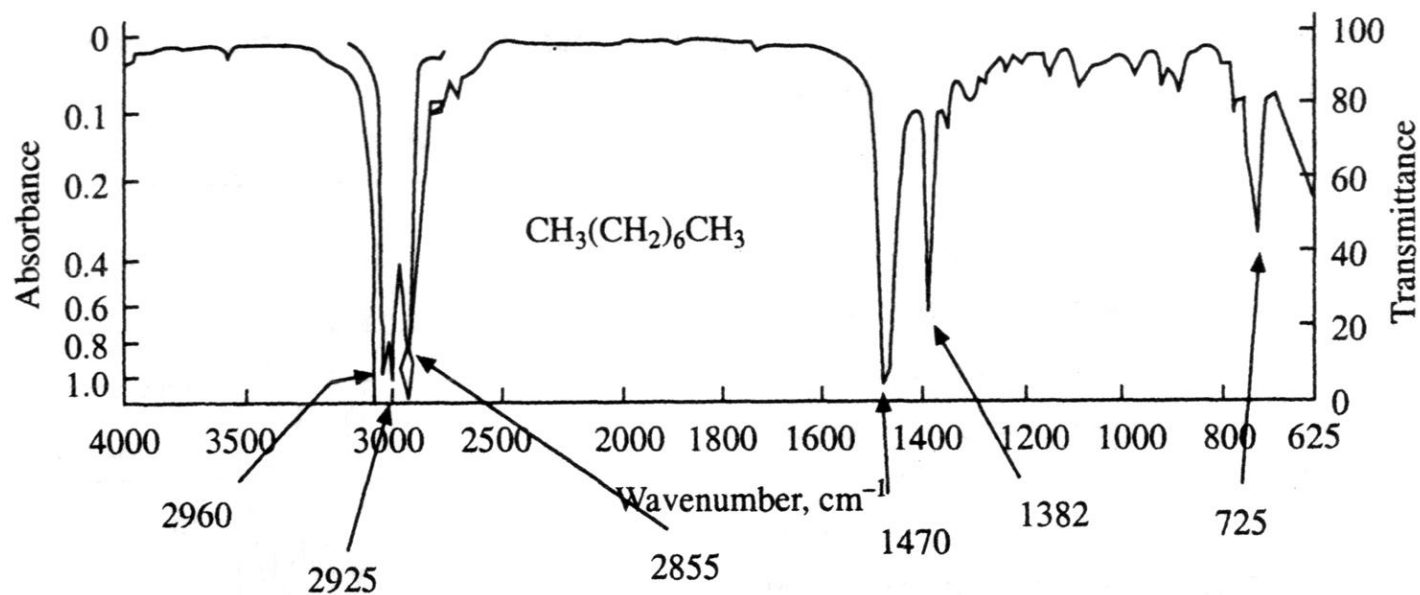
- The C–H stretching frequencies of alkanes occur just below 3000  $\text{cm}^{-1}$ , in contrast to those of unsaturated compounds; typical exceptions being cyclopropane ( $\nu_{\text{asym}} = 3060\text{-}3040 \text{ cm}^{-1}$ ) and methyl halides ( $\nu_{\text{asym}} = 3060 \text{ cm}^{-1}$ ).
- Two strong and distinct C–H stretching bands generally appear for methyl group near 2962 (asymmetric stretching) and 2872  $\text{cm}^{-1}$  (symmetric stretching). The methylene group, however, exhibits the two bands near 2930 and 2850  $\text{cm}^{-1}$  respectively. The presence of several methyl groups in a molecule results in strong absorptions at these positions.

**(b) C–H in-plane bending vibrations:**

- Two absorption bands, due to C–H in-plane bending vibrations, appear for the methyl group at 1460  $\text{cm}^{-1}$  (asymmetric bending) and 1380  $\text{cm}^{-1}$  (symmetric bending). The band at 1380  $\text{cm}^{-1}$  is due only to a methyl group and is sensitive to the electro negativity of the substituents attached to it. It can shift from as high as 1475  $\text{cm}^{-1}$  in  $\text{CH}_3\text{-F}$  to as low as 1150  $\text{cm}^{-1}$  in  $\text{CH}_3\text{-Bi}$ . However, this band is extremely useful in detecting the presence of methyl group because this sharp and medium intensity band is rarely overlapped by absorptions due to methylene and methane deformations.
- The presence of two or more methyl groups, attached to the same carbon atom results in splitting of the C–H symmetric bending vibrations. For example, the isopropyl group gives rise to two bands at 1397 and 1370  $\text{cm}^{-1}$  and in t-butyl group the two bands appear at 1385 and 1370  $\text{cm}^{-1}$  (skeletal vibrational bands).

- The band at 1460 cm<sup>-1</sup> indicates C–H asymmetric bending of both methyl and methylene groups whereas the band at 1380 cm<sup>-1</sup> represents symmetric bending of methyl group only.
- The methane group C–H exhibits C–H stretching and bending vibrations at 2890 and 1340 cm<sup>-1</sup> respectively and are very weak having no practical utility in structural elucidation.

The spectrum of n-octane illustrates most of the important absorptions characteristic for Alkanes.



**Fig. 2.4 Infrared spectrum of n-Octane**

- The lack of absorption above 3000  $\text{cm}^{-1}$  excludes the presence of groups such as OH,  $-\text{NH}_2$ ,  $-\text{NHR}$ ,  $\text{HC}\equiv\text{C}-\text{R}-$ ,  $\text{R}_2\text{C}=\text{CHR}_1$  and an aromatic system. The absence of the double bond is further supported by the lack of moderate intensity C–H out-of-plane bending band near 900  $\text{cm}^{-1}$ .
- The band at 2960 and 2870  $\text{cm}^{-1}$  represent asymmetric and symmetric  $\text{Csp}^3-\text{H}$  stretching vibrations due to methyl group whereas the bands at 2925 and 2855  $\text{cm}^{-1}$  exhibit asymmetric and symmetric  $\text{Csp}^3-\text{H}$  stretching vibrations for the methylene group respectively.
- The absorption at 1470  $\text{cm}^{-1}$  is due to the methylene scissoring and methyl asymmetric bending modes. The molecule, therefore contains both methyl and methylene groups.
- The sharp, symmetric methyl bending vibration at 1382  $\text{cm}^{-1}$  indicates the absence of isopropyl and t-butyl groups.
- The prominent band at 725  $\text{cm}^{-1}$  indicates the rocking vibrational mode of a chain of methylenes longer than four carbon atoms.

### *Cycloalkanes (Cycloparaffins)*

#### **(a) C–H Stretching Vibrations:**

- The C–H stretching frequencies in unstrained cyclic alkanes are much the same as those observed for acyclic alkanes.
- Increasing ring strain moves the C–H stretching bands progressively to higher frequencies. For example, the ring  $\text{CH}_2$  and  $\text{CH}$  groups in a monoalkylcyclopropane ring absorb in the range of 3100-2990  $\text{cm}^{-1}$ .



**(b) *C–H in-plane bending vibrations:***

Methylene scissoring bands in cyclic alkane shift slightly to smaller wavenumber as compared to their acyclic counterpart. For example, cyclohexane absorbs at 1452  $\text{cm}^{-1}$  whereas n-hexane absorbs at 1468  $\text{cm}^{-1}$ .

**(c) *C–C stretching vibrations:***

The C–C stretching vibrations in cyclic alkanes appear as weak bands in the region from 1200 to 800  $\text{cm}^{-1}$  and consequently are of little value for structural study.

***(ii) Aromatic Compounds***

Aromatic compounds display the following modes of vibrations due to aromatic residues in their IR spectra.

**(a) *Aromatic C–H Stretching Vibrations (3100-3000  $\text{cm}^{-1}$ ):***

Aromatic compounds commonly exhibit multiple weak bands (appear merely as a shoulder on the stronger alkane C–H stretching bands) in the region 3100-3000  $\text{cm}^{-1}$  due to aromatic C–H stretching vibrations.



**(b) *Overtones and Combination Bands (2000-1667 cm<sup>-1</sup>):***

- Overtones and combination bands of C–H out-of-plane bending vibrations form a group of weak bands (concentrated solutions give sufficiently intense bands) which appear between 2000 and 1667 cm<sup>-1</sup> and is a function of the substitution pattern on the ring.
- If the compound has a high frequency carbonyl group, then the carbonyl absorption will overlap the weak overtone bands so that no useful information can be obtained from the region 2000-1667 cm<sup>-1</sup>.

**(c) *Vibrations due to Ring Carbons (Skeletal Vibrations):***

- There are six equivalent C=C bonds in benzene and consequently there will be six C=C stretching vibrations. In addition there are several in-plane and out-of-plane bending vibrations of the ring carbons.
- Due to high symmetry of benzene, many modes of vibrations are infrared inactive. For example, carbons which are para to each other move in opposite directions in the stretching and out-of-plane bending vibrations and consequently remain infrared inactive.

The most important infrared vibrations due to ring carbons in substituted benzenes are explained as follows:

**(i) *Quadrant and Semi-Circle Stretching Vibrations:***

- Quadrant stretching vibrations at 1600 and 1580  $\text{cm}^{-1}$ : The band at 1600  $\text{cm}^{-1}$ , resulting from quadrant stretching vibrations of ring carbons, has two components which may sometimes be resolved into a doublet absorbing near 1620-1585 and 1585-1565  $\text{cm}^{-1}$ , particularly when the ring is conjugated with unsaturated group (C=C, C=O, C=N, NO<sub>2</sub> etc.) or a group with a lone pair of electrons (Cl, S, P etc.).
- Semi-Circle stretching vibrations at 1500 and 1450  $\text{cm}^{-1}$ : The band at 1500  $\text{cm}^{-1}$ , resulting from semicircle stretching vibrations of ring carbons, also has two components, one absorbing near 1465-1430  $\text{cm}^{-1}$  for others (p-disubstituted benzene) absorbs near 1420-1400  $\text{cm}^{-1}$ . The intensity of the band near 1500  $\text{cm}^{-1}$  is strong for electron donor groups and may be very weak for rings conjugated with carbonyl groups.

**(ii) *C $\equiv$ C Out-of-plane Bending Vibrations by Sextants and Quadrants:***

**1) Out of plane ring ( C $\equiv$ C ) bending vibrations by sextants (700  $\text{cm}^{-1}$ ) (Ring puckering vibrations):**

The band occurring near 710-675  $\text{cm}^{-1}$  and resulting from ring bending vibrations by sextants is shown by monosubstituted benzene, m-disubstituted benzene, 1,2,3-trisubstituted benzene and 1,3,5-trisubstituted benzene.

The intensity of the band is generally weaker in vicinal and unsymmetrical trisubstituted benzenes, ortho and para isomers when substituents are different; the bands become infrared inactive for identical substituents.

## 2) Out of plane bending vibrations by Quadrants (450 cm<sup>-1</sup>):

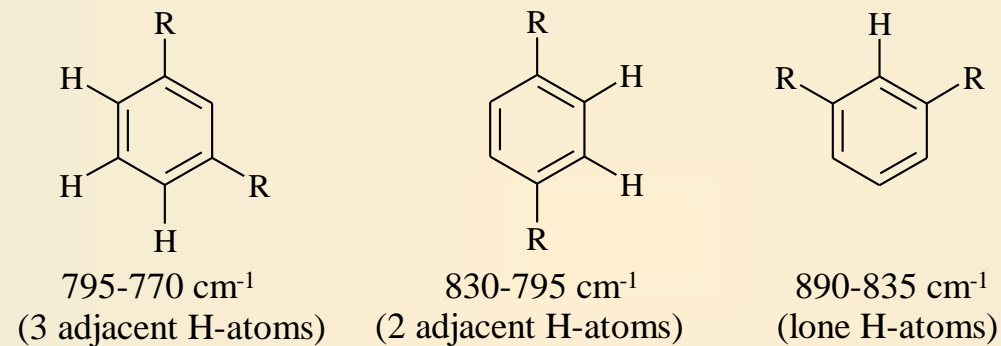
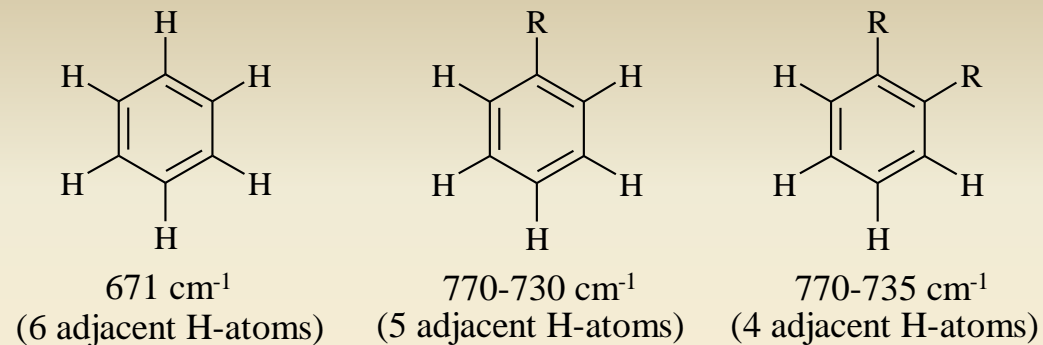
The band, resulting from out-of-plane bending vibrations by quadrants, occurs for the phenyl ring near 580-450 cm<sup>-1</sup>; o-disubstituted benzene near 490-430 cm<sup>-1</sup>; m-disubstituted benzene near 470-430 cm<sup>-1</sup> and p-disubstituted benzene near 580-470 cm<sup>-1</sup>.

### (d) *C–H in-plane Ring Bending Vibrations (1300-1000 cm<sup>-1</sup>):*

- The bands due to C–H in-plane ring bending vibrations interact somewhat with C–C stretching vibrations, are observed as a number of m–w intensity sharp bands in the region 1300-1000 cm<sup>-1</sup>.
- When there is in-plane interaction above 1200 cm<sup>-1</sup>, they move in the same direction.
- These bands are of little diagnostic value because of the overlapping with other stronger absorptions which generally occur in this region.

### (e) *C–H Out-of-Plane Bending Vibrations (900-667 cm<sup>-1</sup>):*

- The C–H out-of-plane bending vibrations are strongly coupled vibrations (strong coupled vibrations (strong coupling between adjacent hydrogens and much weaker coupling between hydrogens separated by other substituting groups) and occur in the region 900-667 cm<sup>-1</sup>. these extremely intense absorptions are used to assign the position of substituents on the aromatic ring (the pattern of absorption is a function of the substitution on the ring).
- The in-plane, out-of-plane C–H wagging vibrations of adjacent hydrogens on the aromatic ring are illustrated in the figure.



**In-plane, out-of-plane C - H Wagging vibrations of adjacent hydrogens on aromatic ring**

- Six adjacent hydrogens in benzene give rise to a single in-plane, out-of-plane bending vibration at 671 cm<sup>-1</sup>.
- Five adjacent hydrogens in mono substituted benzene exhibit a single in-plane, C–H out-of-plane bending vibration at 770-730 cm<sup>-1</sup> and a second band near 700 cm<sup>-1</sup> appears due to the absorption of C–C out-of-plane bending vibration.
- Four adjacent hydrogens in o-disubstituted benzenes absorb in the region 770-735 cm<sup>-1</sup>.

# Question Bank

- Explain important spectral regions in infrared spectrum.
- Explain about modes of vibrations in polyatomic molecules.
- Characteristic absorption bands of various functional groups.
- Explain interpretation of IR Spectra with example.

**THANK YOU**