

# 2

## CHAPTER

# INFRARED ABSORPTION SPECTROSCOPY

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### 2.1. INTRODUCTION

Infrared absorption spectroscopy concerns the absorption of radiation in the infrared range and is probably the single most widely used method for investigating the structures of organic substances. The instrument used for recording the infrared spectra is known as infrared spectrophotometer; most of infrared spectrophotometers having a range of  $2.5 \mu\text{m}$  (or  $4000 \text{ cm}^{-1}$ ) to  $17.2 \mu\text{m}$  (or  $580 \text{ cm}^{-1}$ ). The infrared region below  $2.5 \mu\text{m}$  is generally known as near infrared and that above  $17.2 \mu\text{m}$  is known as far infrared region. Since the organic molecules rarely undergo absorption of radiation in the near and far infrared regions, these are seldom used for spectroscopic purposes.

The various absorption bands in an infrared spectrum are referred to either by the wavelength (in  $\mu\text{m}$ ) or wave number (in  $\text{cm}^{-1}$ ) of the radiation absorbed.

Band intensity is expressed in terms of absorbance (A) or transmittance (T); the two being related to each other as :

$$A = \log \frac{1}{T}$$

### 2.2. BASIC THEORY OF IR SPECTROSCOPY : MOLECULAR VIBRATIONS

The atoms constituting a molecule are not held rigidly in fixed positions. They are continuously rotating and vibrating in a number of ways. To have an idea of molecular vibrations, let us compare a bond between two atoms in a molecule to a weightless spring connecting two balls together. Just as the spring can be compressed and stretched or bent, the bonds can be stretched or bent giving rise to vibrations in a molecule. There are two main kinds of molecular vibrations. These are :

(i) Stretching vibrations

(ii) Bending vibrations

These are described below :

#### 2.2.1. Stretching vibrations or bond stretching

In a simple diatomic molecule A—B, the only vibrations which can occur is a rhythmic compression and extension along the A—B bond. This type of periodic back and forth movement of the atoms along the covalent bond axis which can be compared to that of a coiled spring is known as stretching vibration or bond stretching (Fig. 2.1a)

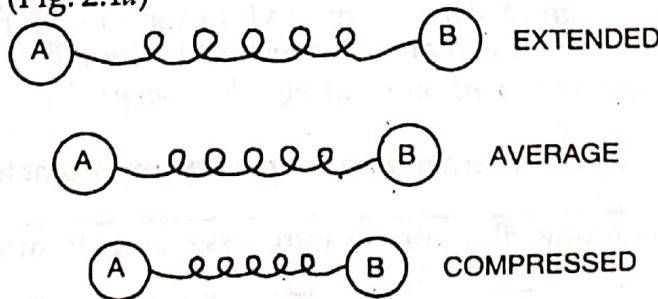
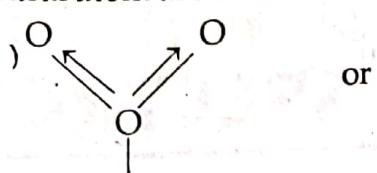


Fig. 2.1 (a) Bond stretching in a diatomic molecule

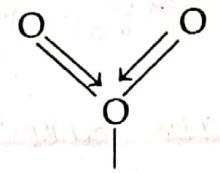
**Types of stretching vibrations.** In triatomic or higher molecules, the stretching vibrations can be of two types :

(i) **Symmetric stretching.** It is the stretching vibration in which the movement of the atoms with respect to a central atom in the molecule is in the same direction (Fig. 2.1b). In other words, all the bonds to the central atom are either stretched or compressed simultaneously.



Symmetric stretching

Fig. 2.1. (b)



Asymmetric stretching

Fig. 2.1. (c)

(ii) **Asymmetric stretching.** It is the stretching vibration in which one atom moves towards the central atom while the other moves away from it. (Fig. 2.1 c). In other words, one bond is being stretched and the other is being compressed.

## 2.2.2. Bending Vibrations or Deformations

In triatomic and higher molecules there can be another type of vibrations involving changes of bond angles. Such vibrational movements are referred to as bending vibrations or deformations. Bending vibrations may be defined as *periodic changes in bond angles between bonds formed by two atoms* (which are themselves not interlinked) with a central atom. (Fig. 2.2)

**Types of bending vibrations.** Bending vibrations can be of four types.

(i) **Scissoring.** This is an *in plane* bending vibration, in which the two atoms move towards each other. (Fig. 2.3. a)

(ii) **Rocking.** This is an *in plane* bending vibration in which the two atoms move in the same direction. (Fig. 2.3. b)

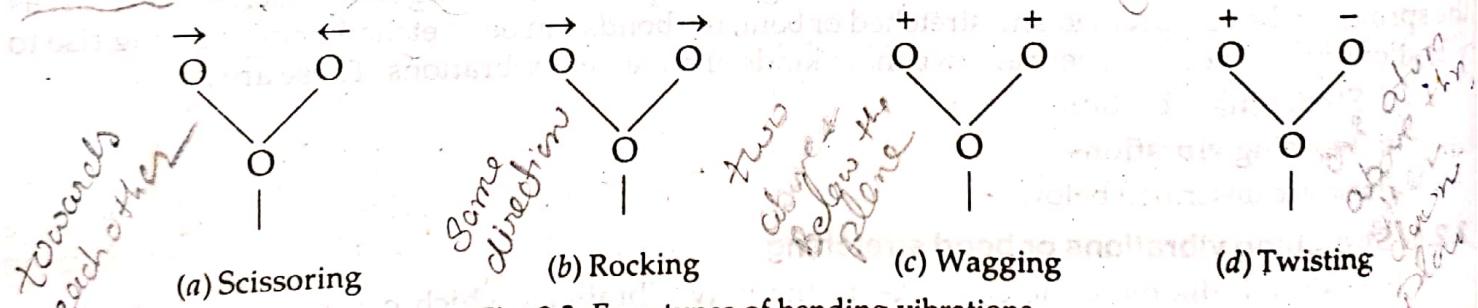


Fig. 2.3. Four types of bending vibrations.

(iii) **Wagging.** This is an *out of plane* bending vibration in which the two atoms move simultaneously either above or below the plane with respect to the central atom. (Fig. 2.3. c)

(iv) **Twisting.** This is an *out of plane* bending vibration in which one atom moves above the plane while the other moves down the plane with respect to the central atom. (Fig. 2.3. d)

*Scissoring and rocking represent in plane bending while wagging and twisting represent out of plane bending.*

The different types of vibrations in a molecule are very important for structure determination by infrared method.

It may be noted that bending vibrations require less energy than stretching vibrations because it is easier to bend a bond than to stretch it.

## 2.2.3. Origin of IR Spectra

The various modes of vibrations possible in a molecule depend primarily on the nature of the bonds themselves and to some extent on the nature of the entire molecule. Absorption of infrared radiation by a bond increases the amplitude of vibrations and also brings changes in rotational energy level. However, in the infrared range usually studied ( $2.5 \mu\text{m} - 15 \mu\text{m}$ ), the absorbed energy brings about predominant changes in the vibrational energy levels. It is obvious that a given bond or a part

of molecule can absorb only that wavelength of infra-red radiation which will provide the photon of that particular amount of energy which is required to raise the vibrational energy level to a permitted value. In other words, infrared spectra arise from the quantisation of vibrational energy levels.

The record of the amount of infrared radiations of different wavelengths absorbed to raise the vibrational energy levels constitutes the infrared spectrum of the molecule. Fig. 2.4 shows some of the stretching and bending vibrations possible for an alcohol group,  $\text{—C—O—H}$  and the characteristic wavelength absorptions due to these vibrations. A wavelength range is given for each of these vibrations because the actual value will also be determined by the nature of the rest of the molecule.

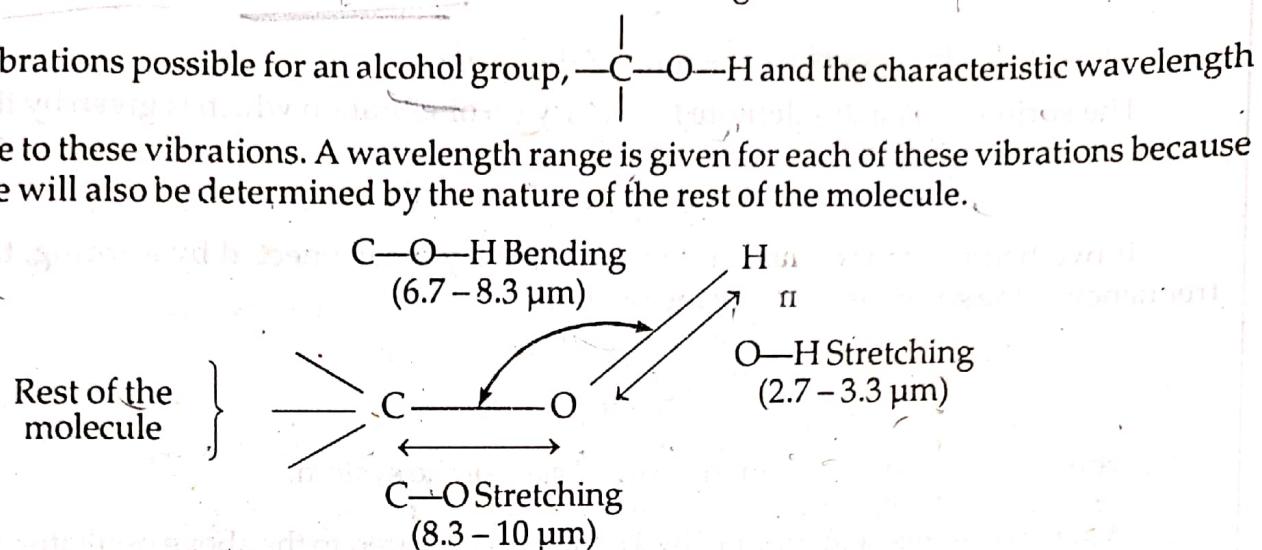


Fig. 2.4. Some modes of vibrations and characteristic absorption wavelengths for a  $\text{—C—OH}$  group.

## UNITS IN IR SPECTROSCOPY

The position of absorption of infrared radiations in IR spectroscopy is generally expressed in terms of wavelength (in micrometer,  $\mu\text{m}$ , or micron,  $\mu$ ) or in terms of wave number (in  $\text{cm}^{-1}$ ). However the wave number ( $\text{cm}^{-1}$ ) is usually treated as absorption band frequency.

The wave numbers corresponding to wavelengths of the infrared range usually studied are from  $4000 \text{ cm}^{-1}$  ( $\lambda = 2.5 \mu\text{m}$ ) to  $667 \text{ cm}^{-1}$  ( $\lambda = 15 \mu\text{m}$ ).

## 2.3. CALCULATION OF VIBRATIONAL FREQUENCY : HOOKE'S LAW

The molecules of organic compounds usually contain many  $\text{C—C}$  and  $\text{C—H}$  bonds and also some other bonds. Therefore, the analysis of various modes of vibrations for a molecule is very difficult because all the atoms present in the molecule contribute to the vibrational modes. However, it is still possible to calculate approximately where a particular vibrational mode will appear in the infrared spectrum by considering each bond present in the molecule one at a time and ignoring the other bonds.

Let us, for instance, consider the stretching vibrations of two bonded atoms. The stretching vibrations can be compared to the oscillations of two balls connected by a spring where the balls represent the atoms and the springs represent the bonds. As such the value of stretching vibrational frequency ( $v$ ) of the bond can be calculated fairly accurately by the application of Hooke's law which may be represented as :

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

But  $v = \frac{c}{\lambda}$  ( $\lambda = \bar{\nu}$ )  
 $\therefore v = c\bar{\nu}$

where  $k$  is called the force constant (in dynes  $\text{cm}^{-1}$ ) which is related to the strength of the bond,  $\mu$  is termed the reduced mass (in grams per atom) of the diatomic system. It is calculated from the expression,  $\mu = \frac{m_1 m_2}{m_1 + m_2}$  where  $m_1$  and  $m_2$  are the actual masses of the two atoms in grams.

Since  $\bar{\nu} = \frac{v}{c}$  where  $c$  is the velocity of light, Hooke's law may also be expressed as:

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

$$c = 3 \times 10^{10} \text{ cm/sec}$$

**Hooke's Law.** If a body of mass  $m$  is hung on a spring and given a pull downwards, it begins to undergo simple harmonic oscillations. According to Hooke's law the force ( $F$ ) which tends to restore the body to its original position is proportional to the displacement ( $x$ ) of the body from that position. That is :

$$F = -kx$$

where  $k$  is called the **force constant** of the spring.

The spring will have a definite frequency ( $v$ ) of vibration which is given by the relation :

$$v = \frac{1}{2\pi} \sqrt{\frac{k}{m}}$$

If two bodies of masses  $m_1$  and  $m_2$  respectively are connected by a spring, the vibrational frequency of the spring is given by the relation :

$$v = \frac{1}{2\pi} \sqrt{\frac{k}{u}}$$

where  $u = \frac{m_1 m_2}{m_1 + m_2}$  is called the *reduced mass* of the system.

When two atoms held together by a bond are compared to the above oscillator, the vibrational frequency of the bond  $v$  can be calculated by applying the same relationship as given above.

**Factors which determine the vibrational frequency.** The simple analogy between two bonded atoms and a simple oscillator helps us in knowing the frequency (or wavelength) of various absorption bands in the infrared spectrum from the nature of atoms and strengths of the bonds between them as illustrated below.

(i) *The smaller the mass of bonded atoms, the smaller is the reduced mass and, therefore, higher its vibrational frequency.*

In other words, **vibrational frequency is inversely proportional to reduced mass.**

The bonds between hydrogen and other atoms have the highest known fundamental frequencies, but covalent compounds of halogens or most metals show infrared absorptions of very low frequencies which are too low to be recorded on a routine spectrophotometer.

(ii) *The force constant ( $k$ ) is a measure of the strength of the bond and, therefore, its value increases with the increase in bond order.* It is taken as approximately  $5 \times 10^5$  dynes  $\text{cm}^{-1}$  for a **single bond** between any two atoms. For **double** and **triple** bonds the values are  $10 \times 10^5$  and  $15 \times 10^5$  dynes  $\text{cm}^{-1}$ , respectively. (In SI system, the values of  $k$  are approximately  $500 \text{ Nm}^{-1}$ ,  $1000 \text{ Nm}^{-1}$  and  $1500 \text{ Nm}^{-1}$ ).

With the increase in the value of  $k$  corresponding to the increase in bond strength, vibrational frequency also increases.

In other words, **vibrational frequency is directly proportional to bond strength.**

It must be noted, however, that the **intensity of absorption depends mainly on the polarity of the bond.**

**Simplified form of Hooke's Law.** For computing the values of  $v$ , a simplified form of Hooke's law may be obtained as follows.

Actual mass of an atom =  $\frac{\text{gram atomic mass of the atom}}{6.02 \times 10^{23}}$  g where  $6.02 \times 10^{23}$  is the Avogadro number.

*If the gram atomic masses of two atoms are taken as  $M_1$  and  $M_2$  their actual masses in grams would be  $m_1 = \frac{M_1}{6.02 \times 10^{23}}$  g and  $m_2 = \frac{M_2}{6.02 \times 10^{23}}$  g respectively.*

$$\text{Reduced mass, } \mu = \frac{m_1 m_2}{m_1 + m_2} = \frac{M_1 / 6.02 \times 10^{23} \times M_2 / 6.02 \times 10^{23}}{(M_1 + M_2) / 6.02 \times 10^{23}}$$

$$= \frac{M_1 \times M_2}{6.02 \times 10^{23} (M_1 + M_2)}$$

$$\bar{v} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} = \frac{1}{2\pi c} \sqrt{\frac{k \times 6.02 \times 10^{23} (M_1 + M_2)}{M_1 \times M_2}}$$

$$= \frac{7.76 \times 10^{11}}{2\pi c} \sqrt{\frac{k(M_1 + M_2)}{M_1 M_2}}$$

Further substituting the values of  $\pi$  and  $c$ , we get :

$$\bar{v} \text{ (in } \text{cm}^{-1}) = \frac{7.76 \times 10^{11}}{2 \times 3.14 \times 3 \times 10^{10}} \sqrt{\frac{k(M_1 + M_2)}{M_1 M_2}}$$

$$\text{or } \bar{v} \text{ (in } \text{cm}^{-1}) = 4.12 \sqrt{\frac{k(M_1 + M_2)}{M_1 M_2}}$$

(We can compute the value of  $\bar{v}$  by just substituting the values of  $k$  and  $M_1$  and  $M_2$  in the above relationship)

**Example 2.1.** Calculate the wave number for the stretching vibration of a single bond between carbon ( $^{12}\text{C}$ ) and hydrogen ( $^1\text{H}$ ). Given that  $k = 5 \times 10^5$  dynes  $\text{cm}^{-1}$  and Avogadro number ( $N_A$ ) is  $6.02 \times 10^{23}$ .

**Solution.** Mass of a hydrogen atom,  $m_1 = \frac{1}{N_A} \text{ g}$  (Gram atomic mass of H = 1 g)

Mass of a carbon atom,  $m_2 = \frac{12}{N_A} \text{ g}$  (Gram atomic mass of C = 12 g)

$$\therefore \text{For C-H stretching, reduced mass, } \mu = \frac{m_1 m_2}{m_1 + m_2} = \frac{1 \times 12}{N_A^2} \times \frac{N_A}{1 + 12} \text{ g atom}^{-1}$$

$$= \frac{12}{13 N_A} \text{ g atom}^{-1} = \frac{12}{13 \times 6.02 \times 10^{23}} \text{ g atom}^{-1}$$

Force constant for a single bond,  $k = 5 \times 10^5$  dynes  $\text{cm}^{-1}$

Velocity of light,  $c = 3 \times 10^{10} \text{ cm s}^{-1}$

Substituting these values in Hooke's law :

$$\bar{v} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}$$

$$= \frac{1}{2 \times 3.142 \times 3 \times 10^{10}} \times \sqrt{\frac{5 \times 10^5 \times 13 \times 6.02 \times 10^{23}}{12}} = 3.03 \times 10^3 \text{ cm}^{-1}$$

**Alternate solution.**

Substitute the values of  $k = 5 \times 10^5$  dynes  $\text{cm}^{-1}$ , gram atomic mass of hydrogen and gram atomic mass of carbon in the simplified form of Hooke's law :

$$\bar{v} = 4.12 \sqrt{\frac{k(M_1 + M_2)}{M_1 M_2}}$$

$$= 4.12 \sqrt{\frac{5 \times 10^5 (1+12)}{1 \times 12}}$$

$$= 3.03 \times 10^3 \text{ cm}^{-1}$$

**Problem 2.1.** Compute the wave number for the stretching vibration of a carbon-carbon single bond ( $^{12}\text{C}$ ). Assume the force constant to be  $5 \times 10^5$  dynes  $\text{cm}^{-1}$ . [Ans.  $1188 \text{ cm}^{-1}$ ]

## 2.4. NUMBER OF FUNDAMENTAL VIBRATIONS

It has been stated earlier that absorption of infrared radiation having energy equal to the difference between two vibrational energy levels will lead to a vibrational transition. In the transition from ground state to the first excited state, light is absorbed strongly and as a result intense bands called **fundamental absorption bands**, are produced.

The number of fundamental absorption bands exhibited by a molecule is related to the fundamental ways of vibrating or **vibrational modes** available to a molecule. In general;

$$\frac{\text{Number of fundamental absorption bands}}{\text{vibrational modes}} = \frac{\text{Number of fundamental}}{\text{vibrational modes}}$$

Since a diatomic molecule has only one fundamental vibrational mode (i.e. stretching vibrations), it gives rise to one fundamental absorption band. However, polyatomic molecules can have more than one kind of vibrational movement, they exhibit more than one fundamental absorption band as given below :

(a) **Non-linear polyatomic molecules.** It has been found that a non-linear polyatomic molecule can have  $3n-6$  modes of fundamental vibrations, where  $n$  is the number of atoms present in the molecule. For example, water ( $n=3$ ) has three vibrational modes (i.e.  $3 \times 3 - 6$ ), each of which can give an absorption band.

(b) **Linear polyatomic molecules.** A linear polyatomic molecule having  $n$  atoms can have  $3n - 5$  fundamental vibrations. For example, carbon dioxide ( $n=3$ ) has four vibrational modes (i.e.  $3 \times 3 - 5$ ).

In case of larger molecules, the number of fundamental vibrations goes on increasing very rapidly with the increase in the value of  $n$ . But it has been observed that the number of fundamental bands actually obtained is usually less than that expected from the theoretical number of fundamental vibrations. This may be due to the following reasons :

(i) Some of the fundamental vibrations may be very weak and, therefore, may not be recorded as bands.

(ii) Some of the fundamental vibrations may be very close and as a result overlapping of bands may take place.

(iii) Some of the fundamental vibrations may involve energy changes which fall outside of usual IR range (i.e.  $2.5 \mu\text{m}$  to  $15 \mu\text{m}$ )

It is also interesting to note that sometimes additional bands (of very low intensity) such as **combination bands, difference bands and overtones** may also be exhibited (as discussed a little later).

## 2.5. SELECTION RULES

Most of the molecules possess dipole moment due to presence of polar bonds linking the constituent atoms. When a polar bond undergoes stretching vibration along the internuclear axis, a change in electron distribution of the bond takes place. As a result dipole moment also undergoes a change. In other words, a vibration produces a fluctuating dipole moment. Interaction between the oscillating dipole moment and the infrared radiation leads to the absorption of energy from the radiation so that the energy of vibration increases (i.e. amplitude of oscillation increases). This interaction and absorption of energy can occur only if the dipole moment at one extreme of the vibration is different from the dipole moment at the other extreme of the vibration in a molecule.

It is evident from the above discussion that a bond vibration can lead to absorption of infrared radiation only if it is accompanied by a change of dipole moment. As a result of comprehensive studies in the field of spectroscopy, certain generalisations have been made which determine whether a vibration would be effective for a particular type of spectrum or not. These are known as **selection rules**.

For infrared spectrum, the rule is that *only those vibrations are effective in causing absorption which are not centro-symmetric* (i.e. the vibrations are not symmetrical about the centre of the molecule). For example, symmetric stretching vibrations of  $\text{CO}_2$  are centro symmetric and are not effective in infrared spectroscopy while the asymmetric stretching vibrations are not centro symmetric and give rise to absorption in infrared region. Since most of the functional groups in organic chemistry such as  $\text{C}=\text{O}$ ,  $\text{O}-\text{H}$  and

N - H undergo vibrations which are not centro symmetric, they respond very well to infrared spectroscopy.

## 2.6. POSITION AND INTENSITY OF BANDS

### 2.6.1. Position of Absorption Bands

P Depending upon the types of bonds present in a molecule, various wavelengths are found to be absorbed in the infrared spectrum of the molecule giving rise to absorption bands. The position of absorption band depends upon the nature of the bond or group. Absorption band characteristic of a particular bond or group indicates the presence of that bond or group in the molecule. For instance, in the spectrum recorded in Fig. 2.6. the absorption band at  $3 \mu\text{m}$  ( $3333 \text{ cm}^{-1}$ ) clearly establishes the presence of hydroxyl group in the molecule. Similarly the absence of characteristic absorption band of a bond or group guarantees the absence of that particular bond or group. It may be noted, however, that the actual absorption pattern of a bond or group may vary slightly from one type of molecule to another. This is because the exact position of absorption band is also determined, to a very small extent, by the nature of the rest of the molecule.

Infrared spectrum can be usually divided into two regions for the purpose of its interpretation.

(i) **Functional group region.** In general, absorption bands from  $2.5$  to  $8 \mu\text{m}$  (or  $4000$  to  $1250 \text{ cm}^{-1}$ ) are associated with the changes in the vibrational states of the various bonds. Accordingly this region is characteristic of the types of bonds present and may be termed as functional group region of the infrared spectrum.

(ii) **Finger print region.** Absorption bands in the region  $8 \mu\text{m}$  (i.e. less than  $1250 \text{ cm}^{-1}$ ) are generally associated with complex vibrational and rotational energy changes of the molecule as a whole. This region is very useful for establishing whether two compounds are identical or different from each other. It is, therefore, referred to as the finger print region. There are so many absorption bands in the finger print region that no two compounds, however, closely related, can have identical IR spectrum in all details including intensity. On the other hand, if two given samples have exactly the same infrared spectrum, it is a conclusive proof of the identity of the two samples.

### 2.6.2 INTENSITY OF ABSORPTION BANDS

Different absorption bands in infrared spectrum have different intensities. The intensity of absorption bands is mainly dependent on the magnitude of change in dipole moment. The more the polar character of a bond, the greater the change in dipole moment and greater the intensity of absorption. For example, a carbonyl group has a much higher dipole moment than C = C double bond and, therefore, it gives rise to stretching absorption bands of much higher intensity than C = C stretching absorption band.

The intensity of absorption band also increases to a small extent with the increase in the concentration of molecules in the sample and the number of absorbing groups in a molecule.

## 2.7. FACTORS INFLUENCING VIBRATIONAL FREQUENCY

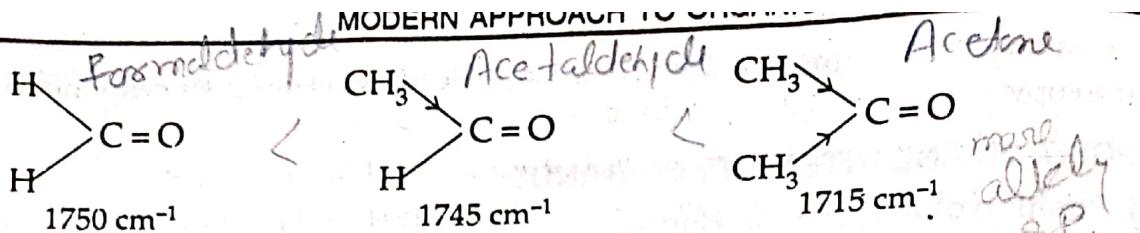
We have seen that the probable frequency of a bond in its IR spectrum can be calculated with the help of Hooke's law. However, it has been found that the calculated value for a bond is only in tolerable agreement with the experimental value but never equal to it. This is because the vibration of each group is influenced by the structure of the rest of the molecule in its immediate neighbourhood. The important factors responsible for the vibrational shift are as follows :

1. **Electronic effect.** When the substituents in the neighbourhood of a particular group are changed, it brings about changes in the absorption frequency of that group due to electronic effects such as inductive effect and resonance effect. Due to these effects, the force constant or bond strength changes which causes the absorption frequency shift from its normal value as illustrated below :

(i) **Inductive effect.** The presence of alkyl group in the vicinity of a particular group causes + I effect. As a result the bond length of that group tends to increase or the bond strength decreases. Consequently, the force constant is lowered and the frequency or wave number of absorption decreases. This is clear from the following examples showing the absorption wave numbers of carbonyl group in different compounds.

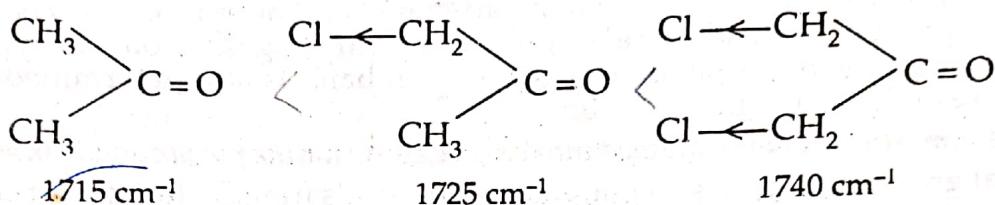
+ I B.L. m. B.S. m. + I B.L. m. B.S. m. + I B.L. m. B.S. m. + I B.L. m. B.S. m.

- I B.L. m. B.S. m. - I B.L. m. B.S. m. - I B.L. m. B.S. m. - I B.L. m. B.S. m.



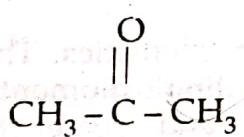
It is obvious that greater the + I effect, smaller the wave number.

If, on the other hand, a group having - I effect is present in the neighbourhood of a particular group, it increases the value of the force constant. As a result the absorption shifts to higher wave number as shown below in terms of absorption wave numbers of carbonyl groups in acetone, chloroacetone and dichloroacetone.

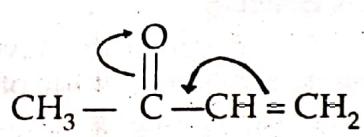


It is apparent that greater the -I effect, higher the wave number.

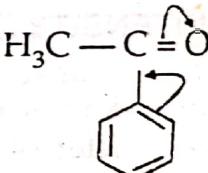
**(ii) Resonance effect.** Resonance effect has significant influence on the absorption frequencies in the infrared spectra of many compounds. For instance conjugation lowers the absorption frequency or wave number of ethylenic bond in conjugated dienes and of the carbonyl group in conjugation with ethylenic bond or aromatic ring. This is because conjugation tends to increase the bond length of the group so that its bond strength decreases. This in turn lowers the force constant of the bond and the absorption frequency decreases. This is evident from the absorption frequency of C = O stretching in the following compounds :



Acetone ( $1715 \text{ cm}^{-1}$ )



Methyl vinyl ketone ( $1690 \text{ cm}^{-1}$ )



Acetophenone ( $1693 \text{ cm}^{-1}$ )

It may be noted that in case of compounds where both the resonance effect and the inductive effect operate but in opposite directions, the resonance effect may dominate over the inductive effect or the reverse may be true. For example, in acetophenone conjugation tends to lower the absorption frequency of C = O stretching while -I effect (due to  $\text{C}_6\text{H}_5$ - group) tends to increase the value. But resonance effect dominates the - I effect, so that there is a decrease in absorption frequency.

**2. Hydrogen bonding.** The infrared spectra of organic compounds such as alcohols, phenols, carboxylic acids and amines which exhibit hydrogen bonding are strongly influenced by the presence of hydrogen bonds. Hydrogen bonding results in the weakening of the bonds involved so that the force constant decreases and absorption shifts towards lower frequency or wave number.

Some important generalisations about the role of hydrogen bonding in infra-red spectroscopy are as follows :

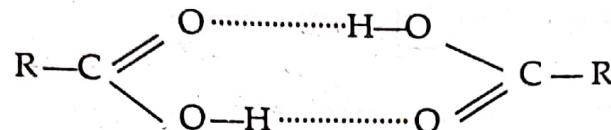
- (i) The stronger the hydrogen bonding the greater the downward shift in absorption frequency.
- (ii) Intermolecular hydrogen bonding gives rise to broader bands while intramolecular hydrogen bonding gives rise to sharp and well-defined bands.
- (iii) The intensity of absorption bands in intermolecular hydrogen bonding is concentration dependent and decreases with dilution. In contrast, concentration has no effect on the intensity in case of intramolecular hydrogen bonding because it takes place within the same molecule.

(iv) The downward shift is more pronounced in case of intermolecular hydrogen bonding than in intramolecular hydrogen bonding.

Let us illustrate the above generalisations with some examples :

(i) **Alcohols and phenols.** In case of both alcohols and phenols, the free —OH groups give rise to strong absorption bands in the region  $3650\text{--}3600\text{ cm}^{-1}$ . On the other hand, hydrogen bonded OH group gives broad absorption band in the region  $3400\text{--}3200\text{ cm}^{-1}$ .

(ii) **Carboxylic acid.** Carboxylic acids generally exists as dimers having strong intermolecular hydrogen bonds.



Due to the large strengths of hydrogen bonds, there is large decrease in absorption frequency of C=O and O—H stretching frequencies in these dimers. Thus carboxylic acid dimers exhibit a very broad band due to O—H stretching at  $3000\text{--}2500\text{ cm}^{-1}$  (as compared to about  $3600\text{ cm}^{-1}$  for free O—H group). Similarly there is a downward shift for C = O stretching in acids from about  $1750\text{ cm}^{-1}$  (for free C = O) to about  $1700\text{ cm}^{-1}$  (for dimeric form).

(iii) **Amines.** Due to relatively weaker hydrogen bonding in amines, the downward shift in the absorption frequencies of N—H bond is only from about  $3500\text{ cm}^{-1}$  (in free form) to about  $3300\text{ cm}^{-1}$  (in hydrogen bonded form). This is much lesser than in case of O—H bond in alcohols and carboxylic acids.

## 2.8. INSTRUMENTATION : MECHANICS OF RECORDING THE IR SPECTRA

In an infrared spectrophotometer, the sample of the substance under investigation is placed in a beam of infrared radiation. The relative intensity of transmitted and, therefore, absorbed radiation is automatically measured and plotted on a graph showing intensity of transmission or absorption as a function of wavelength or frequency of infrared radiation.

A simplified diagram of the commonly used infrared spectrometer is shown in fig. 2.5. It consists of the following parts :

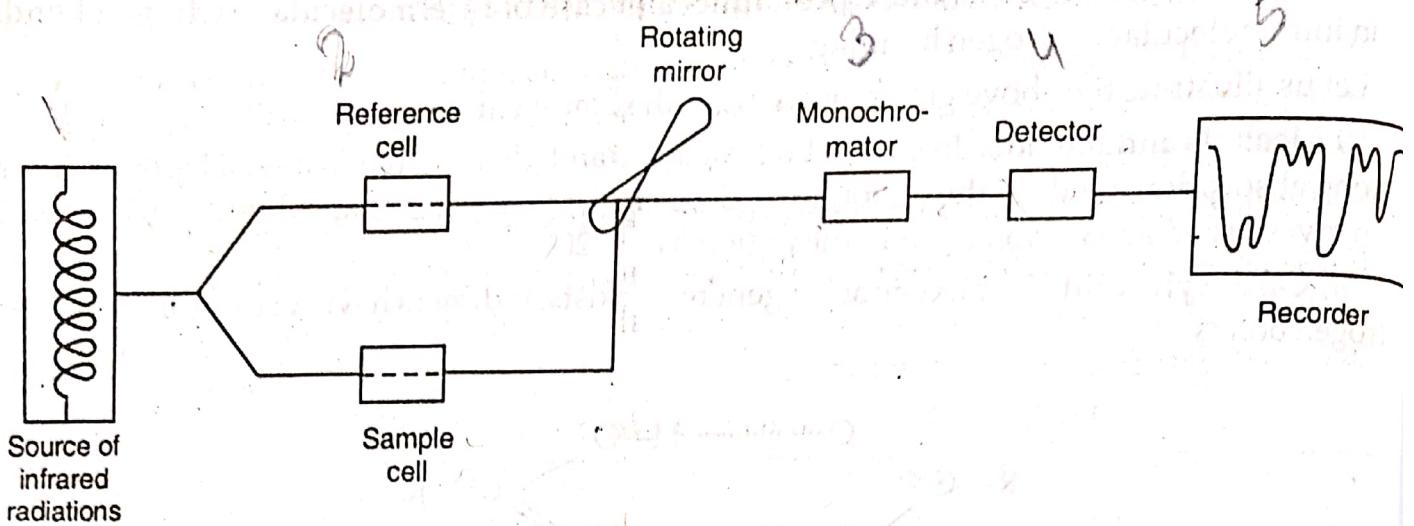
**1. Source of infrared radiations.** A common source for infrared radiation is the Nernst glower which consists of a mixture of zirconium oxide, yttrium oxide and erbium oxide heated electrically to about 1775 K. Infrared radiation can also be produced by heating a rod of silicon carbide (Globar) electrically.

The beam of infrared radiation is split into two beams. One beam passes through the sample cell while the other passes through the reference cell which contains only the solvent. The two beams are alternately allowed to enter the monochromator by means of a rotating mirror.

**2. Sample containers.** The sample under examination may be employed in the gaseous, liquid, solid or solution form. However, solids scatter the radiation too much if placed in the path of light directly. As such they are either dissolved in an organic solvent (such as  $\text{CCl}_4$ ,  $\text{CHCl}_3$  or  $\text{CS}_2$ ) or ground with 'nujol' (liquid paraffin) to form a mull or converted into a pellet with potassium bromide.

The sample containers (called cells) and the optical parts of the spectrometer are made of rock salt ( $\text{NaCl}$ ) or certain other alkali metal halides such as  $\text{CsI}$  since glass is opaque to infrared radiations.

ROH. R. 2014



**Fig. 2.5.** Infrared spectrometer

**3. Monochromator.** By means of prisms or diffraction gratings, the monochromator allows radiations of only one frequency to enter the detector at a time. The frequency of radiation gets automatically varied.

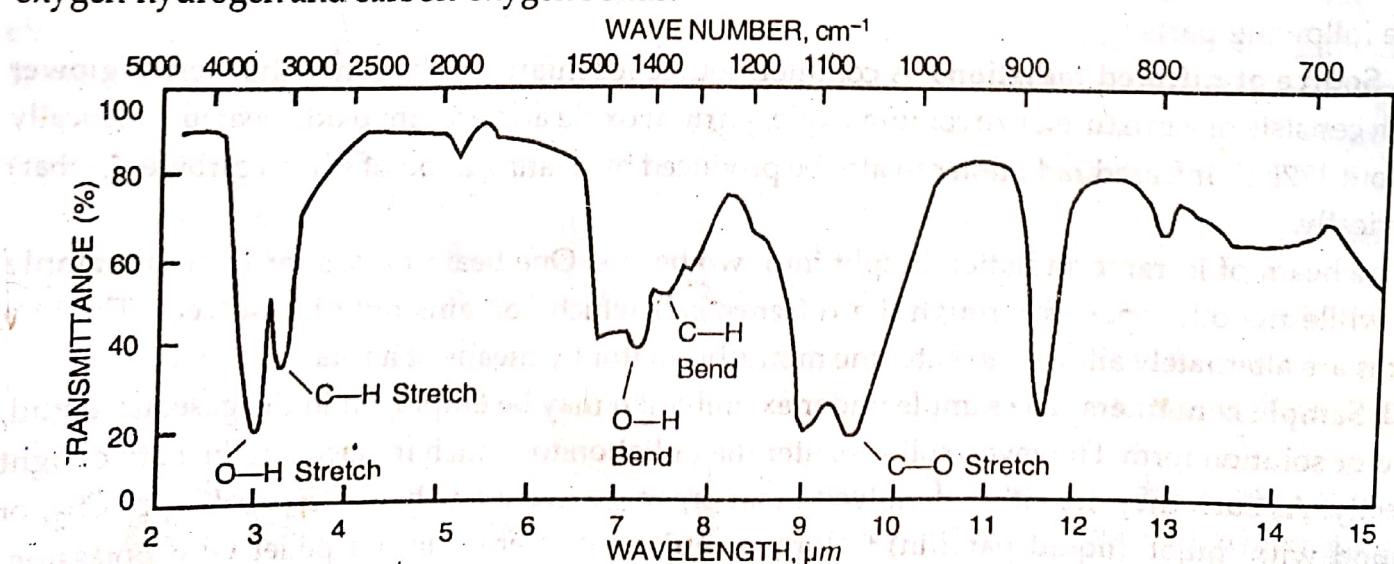
**4. Detector.** The detector scans the range of infrared frequencies received from the monochromator and transforms the energy of the radiation received into an electrical signal. This signal is proportional to the difference in the intensity of the radiation in the sample and reference beams.

**5. Recorder.** The detector signal is automatically recorded on a chart paper showing intensity of transmission (or absorption) as a function of wavelength or frequency of infrared radiation. In actual practice, it is the transmitted light (and not the absorbed light) from 0 – 100% which is plotted in the infrared spectra.

For recording the infrared spectrum, a very small amount of the sample (a few milligrams) is needed. But the sample used must be absolutely dry because water gives strong absorption near  $2.7\text{ }\mu\text{m}$  (or  $3710\text{ cm}^{-1}$ ) and near  $6.15\text{ }\mu\text{m}$  (or  $1630\text{ cm}^{-1}$ ). These absorptions may overlap absorptions due to the sample being analysed.

*More sophisticated and sensitive spectrometers are now available and are gradually replacing the instruments used earlier.* One such spectrometer is Fourier transform infrared (FT-IR) spectrometer which has a much better sensitivity and takes only 1-2 seconds for recording the spectrum.

The infrared spectrum of ethanol ( $\text{CH}_3 - \text{CH}_2\text{OH}$ ) is shown in Fig. 2.6. It depicts clearly the absorption bands which result from the stretching and bending vibrations of carbon-hydrogen, oxygen-hydrogen and carbon-oxygen bonds.



**Fig. 2.6.** Infrared spectrum of ethanol.

*It may be seen that in the infrared spectra the peaks are "upside down". This is due to the operational technique used in infrared spectrophotometer.*

## 2.9. CHARACTERISTIC ABSORPTION REGIONS OF VARIOUS BONDS

The characteristic infrared absorption regions of various types of bonds and functional groups are collected in the form of tables called **correlation tables**. Table 2.1. is the correlationship of the data on absorption patterns of some important bonds and functional groups. The letters *s*, *m*, *w* and *v* denote whether the intensity of absorption is **strong**, **moderate**, **weak** or **variable**.

It should be remembered, however, that the table gives only the approximate positions of absorption bands. But, as already stated, *the exact position of the absorption band of a particular bond depends upon its actual molecular environment.*

Table 2.1. Some characteristic infrared absorption regions

Bond	Type of compound	Wavelength (in $\mu\text{m}$ )	Frequency or wave number (in $\text{cm}^{-1}$ )	Intensity
$\begin{array}{c}   \\ -\text{C}-\text{H} \\   \end{array}$	Alkanes	3.38–3.51	2850–2960	<i>m–s</i>
$=\text{C}-\text{H}$	Alkenes	3.22–3.32	3010–3100	<i>m</i>
$\equiv\text{C}-\text{H}$	Alkynes	3.03	3300	<i>s</i>
$\text{C}-\text{H}$	Aromatic ring	3.22–3.33	3000–3100	<i>m</i>
$\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{H} \end{array}$	Aldehydes	3.47–3.77	2650–2880	<i>w</i> (often two bands)
$\begin{array}{c}   \\ -\text{C}-\text{C} \\   \end{array}$	Alkanes	6.66–16.66	600–1500	<i>w</i> (seldom useful for identification)
$>\text{C}=\text{C}<$	Alkenes	5.95–6.2	1620–1680	<i>v</i> ✓ 5, 6
$-\text{C}\equiv\text{C}-$	Alkynes	4.42 – 4.76	2100–2660	<i>v</i> ✓ 4
$-\text{C} \cdots \text{C}-$	Aromatic rings	6.25–6.66	1500–1600	<i>v</i>
$\begin{array}{c}   \\ -\text{C}-\text{O} \\   \end{array}$	Alcohols, ethers, carboxylic acids, esters	7.7–10	1000–1300	<i>s</i>
$>\text{C}=\text{O}$	Aldehydes, ketones, carboxylic acids, esters	5.68–5.95	1680–1760	<i>s</i>
$-\text{O}-\text{H}$	Monomeric alcohols and phenols	2.74–2.78	3600–3650	<i>v</i>
$-\text{O}-\text{H}$	Hydrogen bonded alcohols and phenols	2.94–3.11	3200–3400	<i>s</i> (broad)
	Hydrogen bonded acids	3.33–4	2500–3000	<i>v</i> (broad) ✓ 1, 3
$-\text{N}-\text{H}$	Amines	2.86–3.03	3300–3500	<i>m</i> ✓ 2
$\begin{array}{c}   \\ -\text{C}-\text{N} \\   \end{array}$	Amines	7.36–8.49	1180–1360	<i>v</i> ✓ 9
$-\text{C}\equiv\text{N}$	Nitriles	4.42–4.52	2210–2260	<i>v</i>
$-\text{NO}_2$	Nitro compounds	6.5–7.5	1330–1540	Pair of strong bands ✓ 7, 8,

## 2.10. SPECTRAL FEATURES OF SOME CLASSES OF COMPOUNDS

Having discussed the fundamental aspects of infrared spectroscopy in the previous section we now take up the spectral features of some classes of compounds.

### 2.10.1. Hydrocarbons

(1) Alkanes. Infrared spectra of alkanes are generally quite simple and not very informative because alkanes do not contain any functional groups. The most common peaks exhibited by alkanes are given below:

$-\text{CH}_3$ ,  $>\text{CH}_2$  and  $\geq\text{CH}$  groups present in alkanes give rise to C—H stretching absorption bands in the region 2960–2850 cm<sup>-1</sup>.

$-\text{CH}_3$  and  $>\text{CH}_2$  also exhibit bending or deformation bands in the region 1470–1430 cm<sup>-1</sup>. C—C bonds are less characteristic and they are responsible for weak bands in the region 1300–800 cm<sup>-1</sup>.

The main features of the spectra of alkanes are summed up in table 2.2.

Table 2.2. Alkanes

Group	Type of vibration	Position of band (cm <sup>-1</sup> ) and intensity
$-\text{CH}_3$ $>\text{CH}_2$ $\geq\text{CH}$	C—H stretching	2960–2850 (m-s) (Two or three bands usually) 2890–2880 (w)
$-\text{CH}_3$ $>\text{CH}_2$	C—H bending	1470–1430 (m)
C—C	C—C stretching	1300–800 (w) (Many weak bands)

(2) Alkenes. Infrared spectra of alkenes show many characteristic absorptions which can be very useful in structure determination. The most prominent peak is the vinylic (=C—H) stretching at slightly greater than 3000 cm<sup>-1</sup>; the actual position depending upon the extent of substitution in alkene.

C=C stretching vibrations give rise to bands of variable intensity at 1680–1620 cm<sup>-1</sup>. Conjugation shifts the position to lower frequency and increases the intensity of absorption.

The important absorption bands are summed up in table 2.3.

Table 2.3. Alkenes

Group	Type of vibration	Position of band (cm <sup>-1</sup> ) and intensity
$>\text{C}=\text{C}<\begin{matrix} \text{H} \\ \text{H} \end{matrix}$	C—H Stretching	3095–3075 (m)
$\text{CH}_2=\text{C}<\begin{matrix} \text{H} \end{matrix}$		3040–3010 (m)
RCH=CH <sub>2</sub> Monosubstituted		995–985 (s)
$\begin{matrix} \text{R} \\ \text{H} \end{matrix}>\text{C}=\text{C}<\begin{matrix} \text{H} \\ \text{R} \end{matrix}$ Disubstituted (trans)	C—H out of plane bending	970–960 (s)
$\begin{matrix} \text{R} \\ \text{H} \end{matrix}>\text{C}=\text{C}<\begin{matrix} \text{R} \\ \text{H} \end{matrix}$ Disubstituted (cis)		730–675 (m)
Non-conjugated C=C Conjugated C=C	C=C stretching	1680–1620 (m) 1660–1580 (w)

(3) **Alkynes.** They exhibit strong absorption band for  $\equiv \text{C}-\text{H}$  stretching near  $3300 \text{ cm}^{-1}$  and another intense bond  $\equiv \text{C}-\text{H}$  bending at  $650-610 \text{ cm}^{-1}$ . A weak  $\text{C}\equiv\text{C}$  stretching absorption band occurs at  $2100-2260 \text{ cm}^{-1}$ ; the band is more intense for terminal alkynes than non-terminal alkynes.

Table 2.4. Alkynes

Group	Type of vibration	Position of band ( $\text{cm}^{-1}$ ) and intensity
$\equiv \text{C}-\text{H}$	C—H stretching	$\sim 3300 (\text{s})$
	C—H bending	$650-610 (\text{s})$
$\text{R}-\text{C}\equiv\text{CH}$	$\text{C}\equiv\text{C}$ stretching	$2140-2100 (\text{w})$
$\text{R}'-\text{C}\equiv\text{C}-\text{R}''$		$2260-2190 (\text{w})$

(4) **Cycloalkanes.** Cycloalkanes exhibit mainly C—H stretching absorption bands. The region of absorption moves to higher values with the increase in angle strain. For example, C—H stretching for cyclopropane is at  $\sim 3050 \text{ cm}^{-1}$  while that for cyclohexane is at  $2990 \text{ cm}^{-1}$ .

(5) **Aromatic hydrocarbons.** These compounds exhibit C—H stretching absorption at  $3050-3000 \text{ cm}^{-1}$  and C—C stretching absorption at  $1600-1450 \text{ cm}^{-1}$ . There are four prominent C—C stretching bands at  $\sim 1600 \text{ cm}^{-1}$ ,  $1580 \text{ cm}^{-1}$ ,  $1500 \text{ cm}^{-1}$  and  $1450 \text{ cm}^{-1}$ ; absence of these bands means that the compound is not aromatic.

There are also a number of C—H bending bands at  $900-700 \text{ cm}^{-1}$ ; the actual number and position of these bands depends upon the extent and position of substitution of the aromatic ring.

Table 2.5. Aromatic hydrocarbons

Group	Type of vibration	Position of band ( $\text{cm}^{-1}$ ) and intensity
Aryl —H	C—H stretching	$3040-3010 (\text{v})$
	C—H bending	$900-700 (\text{m})$
C—C (Aromatic rings)	C—C stretching	$\sim 1600 (\text{v})$ $\sim 1580 (\text{v})$ $\sim 1500 (\text{v})$ $\sim 1450 (\text{v})$
Monosubstituted benzenes  <i>o</i> -Disubstituted <i>m</i> -Disubstituted  <i>p</i> -Disubstituted	C—H bending	$710-680 (\text{s})$
	C—H bending	$770-730 (\text{s})$
	C—H bending	$770-735 (\text{v})$
	C—H bending	$710-690 (\text{m})$
	C—H bending	$800-750 (\text{m})$
		$840-800 (\text{m})$

## 2.10.2. Hydroxy Compounds

(1) **Alcohols.** The O—H functional group of alcohols gives a characteristic O—H stretching absorption band in the infrared spectrum. But, as we might expect, this absorption is significantly influenced by hydrogen bonding. If there is no hydrogen bonding (which is possible if a dilute solution of alcohol in a non-polar solvent is used), an alcohol gives a sharp variable band at  $3640-3610 \text{ cm}^{-1}$ . In the associated state involving intermolecular hydrogen bonding, a strong broad band appears at  $3400-3200 \text{ cm}^{-1}$ .

In case of intramolecular hydrogen bonding, the O—H stretching band appears at 3570–3450 cm<sup>-1</sup> and is of variable intensity.

In addition alcohols also exhibit a strong and broad band in the range 1200–1000 cm<sup>-1</sup> due to C—O stretching. The exact location of the band depends upon whether the alcohol is primary; secondary or tertiary. Therefore, it can be used to determine the class of alcohol.

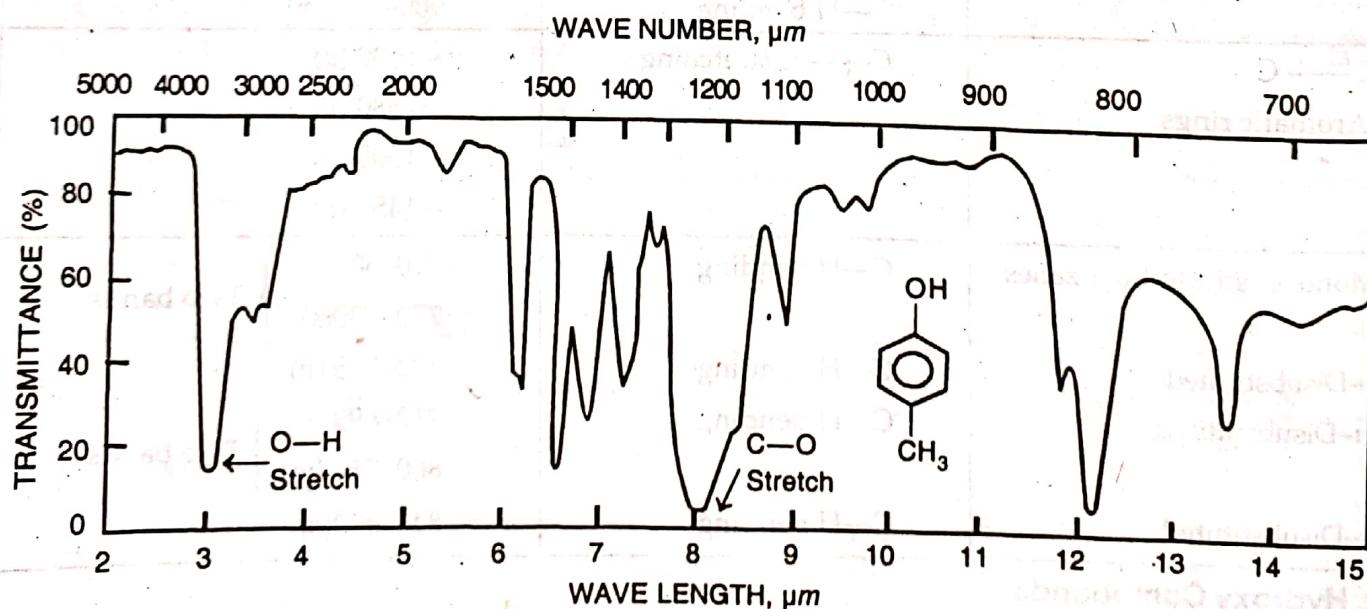
**Table 2.6. Alcohols**

Group	Type of vibration and its intensity	Position of band ( $\text{cm}^{-1}$ )
O—H (Free)	O—H stretching	3640–3610 (v)
O—H (intermolecular hydrogen bonding)	O—H stretching	3400–3200 (s)
O—H (intramolecular hydrogen bonded)	O—H stretching	3570–3450 (v)
C—O (1° alcohol)	C—O stretching	~ 1050 (s)
(2° alcohol)	C—O stretching	~ 1100 (s)
(3° alcohol)	C—O stretching	~ 1150 (s)

The complete spectrum of alcohols, of course, exhibits other absorption bands as well due to the presence of other structural units such as C—C and C—H bonds. This is quite evident from the IR spectrum of ethyl alcohol shown in Fig. 2.6 (given earlier).

(2) **Phenols.** As in case of alcohols, phenols exhibit a strong band due to O—H stretching in the range  $3600\text{--}3200\text{ cm}^{-1}$ . However, the C—O stretching band in phenols appears in a higher region (about  $1230\text{ cm}^{-1}$ ) as compared with alcohols ( $1200\text{--}1000\text{ cm}^{-1}$ ).

Infrared spectrum of *p*-cresol is shown in Fig. 2.7.



**Fig. 2.7.** Infrared spectrum of *p*-cresol.

### 2.10.3. Ethers

**2.10.3. Ethers** The infrared spectra of ethers are characterised by strong absorption bands in the region 1300 to  $1000\text{ cm}^{-1}$  due to C—H stretching vibrations. Alkyl ethers show a single absorption in the region 1150–1060  $\text{cm}^{-1}$ . Aryl and vinyl ethers exhibit a strong band in the region 1275–1200  $\text{cm}^{-1}$  and a weaker band in the region 1200–1075  $\text{cm}^{-1}$ .

The C—O stretching absorption bands of ethers are similar to those of alcohols, carboxylic acids and esters. However ethers can be distinguished from alcohols by the absence of O—H stretching at 3600–3200 cm<sup>-1</sup>. Similarly ethers can be distinguished from carboxylic acids and esters by the absence of C=O stretching absorption at 1770–1680 cm<sup>-1</sup>.

#### 2.10.4. Aldehydes and Ketones

The infrared spectra of aldehydes and ketones are extremely useful in detecting the presence of these compounds. The carbonyl group in these classes of compounds shows a strong C=O stretching band around 1700 cm<sup>-1</sup>; the actual position the band depending upon the nature of groups attached to the carbonyl group.

(1) **Aldehydes.** The position of C=O stretching absorption band in aldehydes varies slightly according as the aldehyde is a saturated aliphatic aldehyde or aromatic aldehyde or  $\alpha$ ,  $\beta$ -unsaturated value while the electron-releasing groups (+ I effect) shifts the absorption to lower value while the electron-attracting groups (-I effect) shifts the absorption to higher value.

In addition to C=O stretching bands, aldehydes show characteristic C—H stretching bands near 2820 cm<sup>-1</sup> and 2720 cm<sup>-1</sup>. Generally, the band near 2720 cm<sup>-1</sup> is seen and it is very useful in distinguishing aldehydes from ketones.

Table 2.7. Aldehydes

Compound	Type of vibration	Position of band (cm <sup>-1</sup> ) and intensity
Saturated aldehydes, $\begin{array}{c} \text{H} \\   \\ \text{R}-\text{C}=\text{O} \end{array}$	C=O stretching	1740–1720 (s)
Aromatic aldehydes, $\begin{array}{c} \text{H} \\   \\ \text{Ar}-\text{C}=\text{O} \end{array}$	C=O stretching	1710–1690 (s)
$\alpha$ , $\beta$ -unsaturated aldehydes, $-\text{C}=\text{C}-\text{C}=\text{O}$	C=O stretching	1705–1680 (s)
All aldehydes	C—H stretching	$\sim 2820 \text{ cm}^{-1}$ $\sim 2720 \text{ cm}^{-1}$

Infrared spectrum for *n*-butyraldehyde is shown in fig. 2.8.

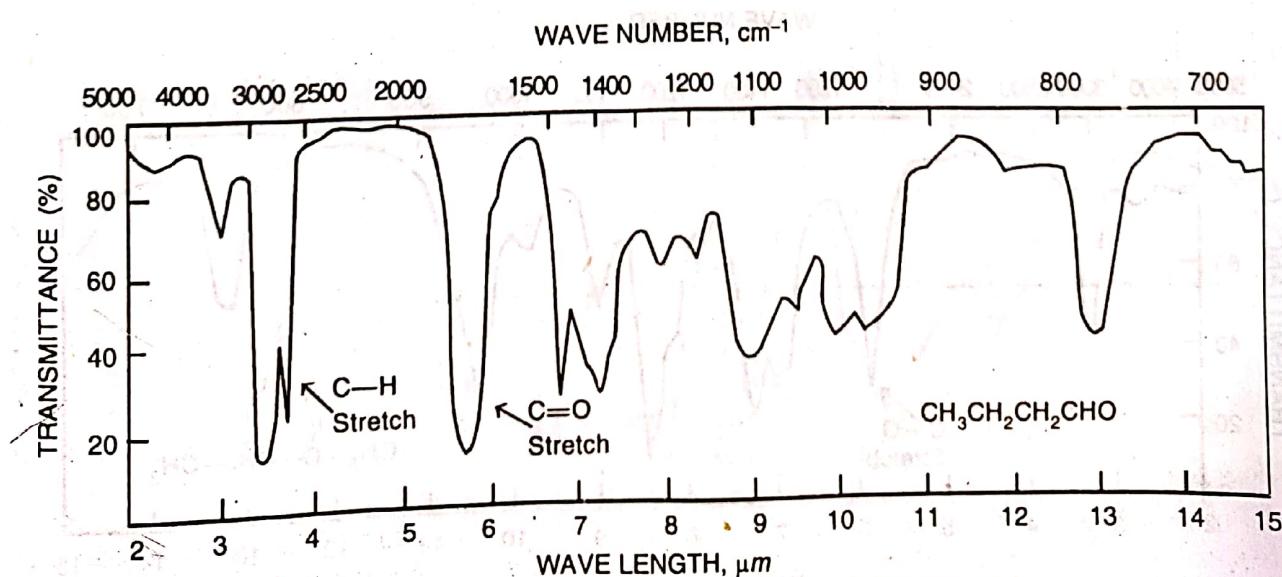


Fig. 2.8. IR spectrum of *n*-butyraldehyde,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CHO}$

(2) **Ketones.** The C = O stretching band in ketones appears at lower frequency or wave number as compared to aldehydes due to the large + I effect operating in ketones. The C = O stretching absorption takes place at still lower value for aromatic ketones and  $\alpha$ ,  $\beta$ -unsaturated ketones.

In case of cycloalkanones, the position of the C = O stretching band depends upon the size of the ring. As the size of the ring decreases, the absorption shifts to higher value due to increase in angle strain.

Table 2.8. Ketones

Compound	Type of vibration	Position of band ( $\text{cm}^{-1}$ ) and intensity
Dialkyl ketones, $\text{RCOR}'$		1725–1705 (s)
Alkyl aryl ketones, $\text{ArCOR}$		1690–1680 (s)
Diaryl ketones, $\text{ArCOAr}$		1670–1660 (s)
$\alpha$ , $\beta$ -unsaturated ketones		1690–1675 (s)
Cyclopropanone	C = O stretching	~1815 (s)
Cyclobutanone		~1780 (s)
Cyclopentanone		~1750 (s)
Cyclohexanone		~1725 (s)
		1725–1710 $\text{cm}^{-1}$ (s)
		1680–1665 (s) 1670–1660 (s)

Infrared spectrum of ethyl methyl ketone is shown in fig. 2.9 for the sake of illustration.

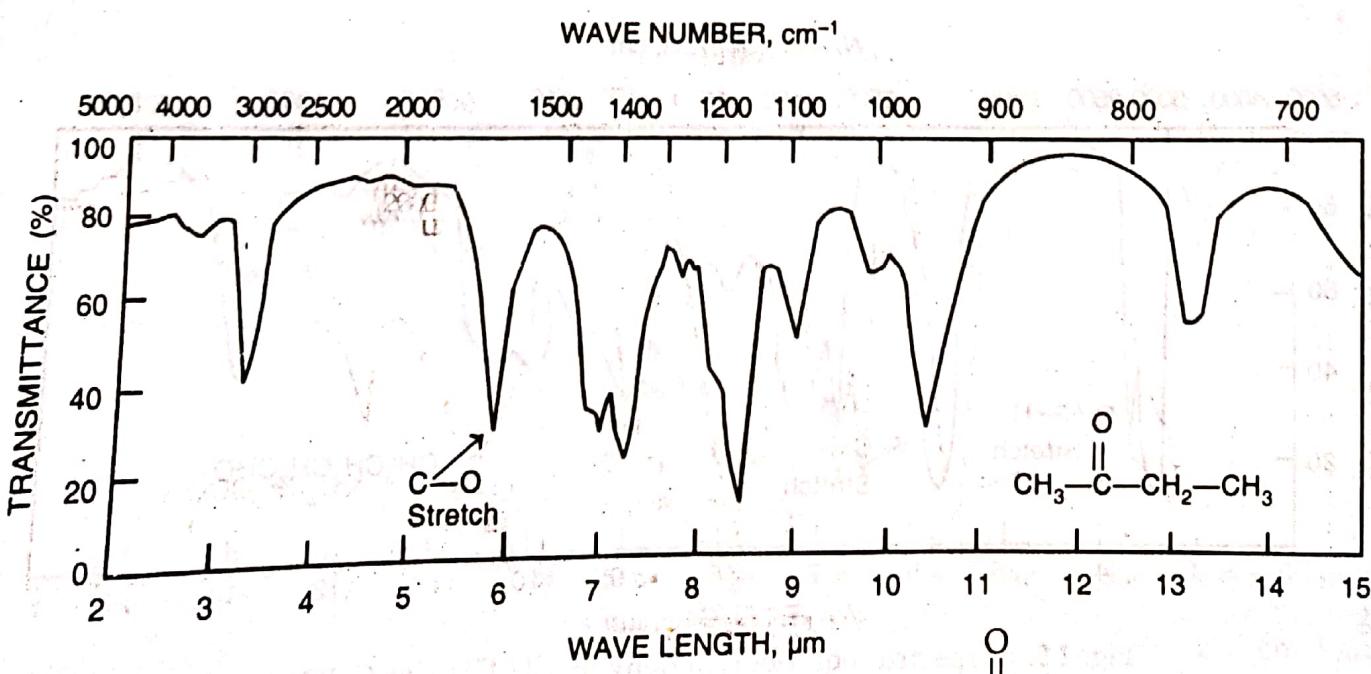


Fig. 2.9. IR spectrum of ethyl methyl ketone,  $\text{CH}_3-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{CH}_2\text{CH}_3$ .

# INFRARED ABSORPTION SPECTROSCOPY

It must be emphasised that  $\text{C}=\text{O}$  stretching band is also given by carboxylic acids and their derivatives. However, these compounds also show certain other bands which help to distinguish them from aldehydes and ketones. For example, carboxylic acids also show a broad O—H band in the region 3000–2500  $\text{cm}^{-1}$  in addition to the carbonyl band.

## 2.10.5. Carboxylic Acids

The infrared absorption spectra of carboxylic acids exhibit a number of absorption bands which



are very helpful in the detection of  $\text{C}-\text{OH}$  function group. There is a very broad and intense band in 3000–2500  $\text{cm}^{-1}$  range due to O—H stretching. This is clearly indicative of stronger hydrogen bonding than in alcohols where the O—H stretching band is in the region 3600–3200  $\text{cm}^{-1}$ . Another strong band appears around 1700  $\text{cm}^{-1}$  (1700–1680  $\text{cm}^{-1}$  for aromatic acids and 1725–1700  $\text{cm}^{-1}$  aliphatic acids) due to  $\text{C}=\text{O}$  stretching.

In addition, carboxylic acids also show a C—O stretching band at about 1250  $\text{cm}^{-1}$  and a bending band for O—H near 1400  $\text{cm}^{-1}$  and 920  $\text{cm}^{-1}$  (broad).

**Table 2.9. Carboxylic acids**

Compound	Type of vibration	Position of band ( $\text{cm}^{-1}$ ) and intensity
All carboxylic acids	O—H stretching	3000–2500 (s)
Saturated carboxylic acids, $\text{R}-\text{C}(=\text{O})-\text{OH}$	$\text{C}=\text{O}$ stretching	1725–1700 (s)
Aromatic carboxylic acids, $(\text{Ar}-\text{C}(=\text{O})-\text{OH})$ and $\alpha, \beta$ -unsaturated acids, $(-\text{C}=\text{C}-\text{C}(=\text{O})-\text{OH})$	$\text{C}=\text{O}$ stretching	1700–1680 (s)
All carboxylic acids	C—O stretching~	1250 (m)
All carboxylic acids	O—H bending	$\sim 1400 \text{ cm}^{-1}$ $\sim 920 \text{ cm}^{-1}$ } Two bands

Fig. 2.10 depicts the infrared spectrum of propionic acid.

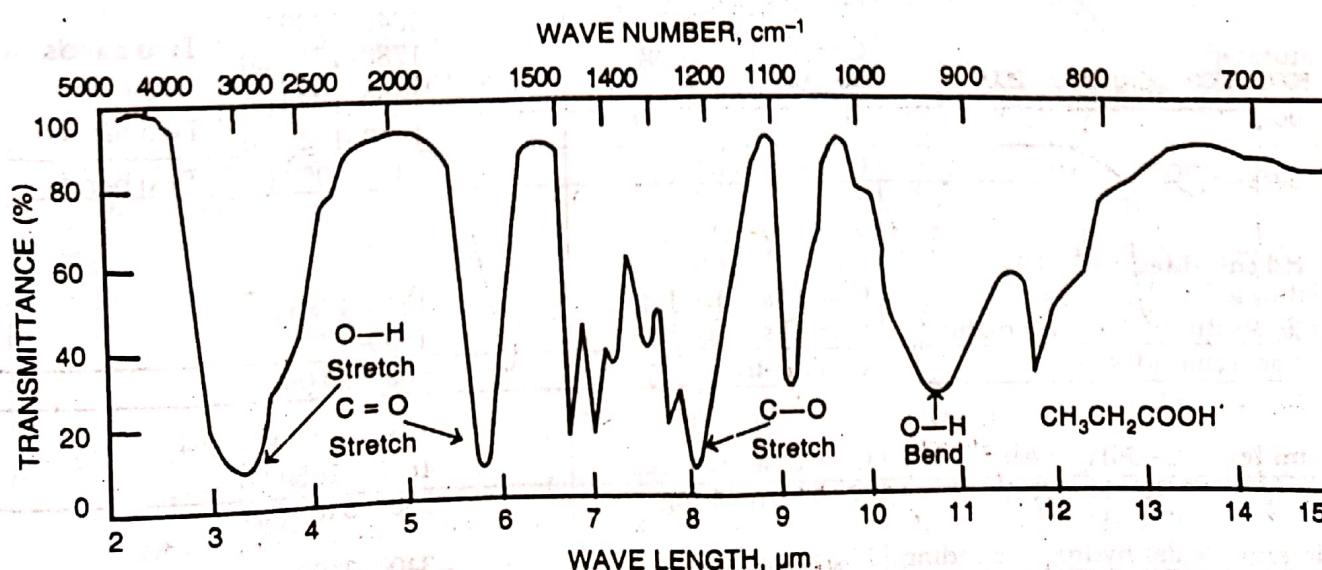


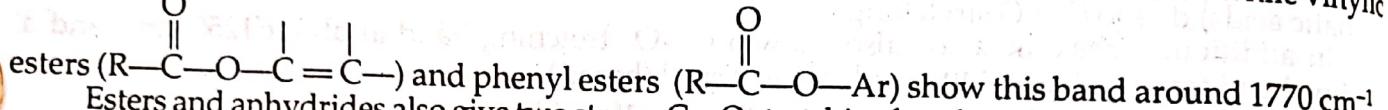
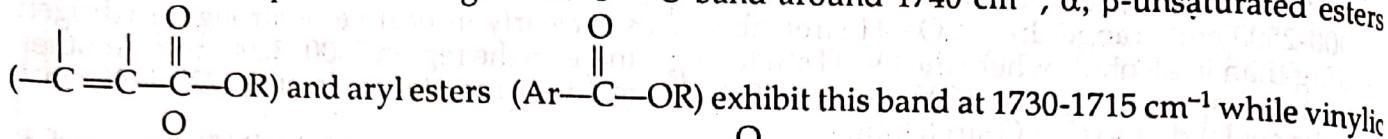
Fig. 2.10. Infrared absorption spectrum of propionic acid,  $\text{CH}_3\text{CH}_2\text{COOH}$ .

### 2.10.6. Carboxylic Acid Derivatives

As expected, the infrared spectra of acid derivatives (*i.e.* acid chlorides, anhydrides, esters and amides) are characterised by the presence of strong C=O stretching bands; the exact frequency of the band depending upon the nature of the compound. Thus acid chlorides show a strong band at 1815–1785 cm<sup>-1</sup> while acid anhydrides exhibit two strong bands at 1840–1800 cm<sup>-1</sup> and 1780–1740 cm<sup>-1</sup>. However, in conjugated acid chlorides and anhydrides, these bands occur at 15–20 cm<sup>-1</sup> lower frequencies.

Amides show C=O stretching bands at 1690–1650 cm<sup>-1</sup>.

Saturated aliphatic esters give the C=O band around 1740 cm<sup>-1</sup>;  $\alpha$ ,  $\beta$ -unsaturated esters



Esters and anhydrides also give two strong C=O stretching bands in the region 1350–1050 cm<sup>-1</sup>; this serves to distinguish them from ketones.

Acid chlorides show C–Cl stretching bands in the 800–650 cm<sup>-1</sup> range.

Amides show N–H stretching bands at 3500–3100 cm<sup>-1</sup> and also N–H bending bands around 1600 cm<sup>-1</sup>.

Unlike carboxylic acids, acid derivatives do not give any broad O–H stretching bands.

The main features of the spectra of acid derivatives are summed up in table 2.10.

Table 2.10. Carboxylic acid derivatives

Compound and functional group	Type of vibration	Position of bands (cm <sup>-1</sup> ) and intensity
1. Ester, $-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{OR}$		
Saturated esters	C=O stretching	~ 1740 (s)
$\alpha$ , $\beta$ -unsaturated esters and aryl esters	C=O stretching	1730–1715 (s)
Vinylic esters and phenyl esters	C=O stretching	~ 1770 (s)
All esters	C–O stretching	1350–1050 (s) ] Two bands
2. Acid anhydrides, $\begin{array}{c} \text{O} \\    \\ -\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{O}-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{O}- \end{array}$		
Saturated	C=O stretching	1840–1800 (s)
$\alpha$ , $\beta$ -unsaturated and aromatic	C=O stretching	1780–1740 (s) } Two bands
		1800–1770 (s) } Two bands
		1760–1720 (s) } Two bands
All anhydrides	C–O stretching	1350–1050 (s) ] Two bands
3. Acid chlorides, $-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{Cl}$		
Saturated	C=O stretching	1815–1785 (s)
$\alpha$ , $\beta$ -unsaturated and aromatic	C=O stretching	1800–1770 (s)
All acid chlorides	C–Cl stretching	800–650 (m)
4. Amides, $-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{NH}_2$ ; All amides		
N–H (Free)	N–H stretching	3500–3400 (m)
N–H (intermolecular hydrogen bonding)	N–H stretching	3400–3100 (m)
All amides	N–H bending	~ 1600 (s)

Fig. 2.11 shows the infrared spectrum of ethyl acetate.

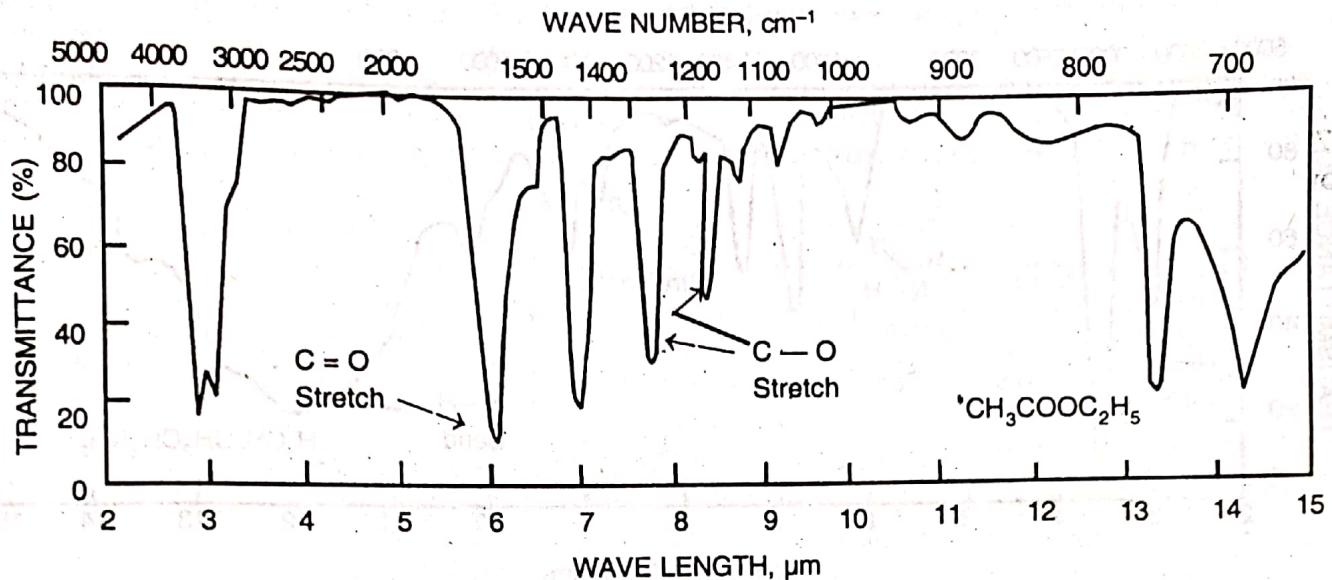


Fig. 2.11. Infrared spectrum of ethyl acetate,  $\text{CH}_3\text{COOC}_2\text{H}_5$ .

### 2.10.7. Amines

The infrared spectra of amines show characteristic absorption bands due to N—H stretching, N—H bending and C—N stretching; the number and position of bands depends upon the class to which the amine belongs.

Primary and secondary amines exhibit moderately weak absorption at 3500–3200  $\text{cm}^{-1}$  due to N—H stretching vibrations. However, primary amines have two such bands in this region while secondary amines show only one band. Tertiary amines do not have any N—H bands in their molecules and, therefore, they do not exhibit such bands. Hydrogen bonding tends to shift the N—H bands to lower frequencies but the shift is not as much as in case of hydroxy compounds. This is because the hydrogen bonding in amines is weaker than that in hydroxy compounds.

Primary amines exhibit moderately strong N—H bending bands at 1650–1560  $\text{cm}^{-1}$  and 900–650  $\text{cm}^{-1}$  while secondary amines show weak bands of this type around 1600–1500  $\text{cm}^{-1}$ .

The C—N stretching bands of aliphatic amines appear in the region 1230–1030  $\text{cm}^{-1}$  (tertiary amines generally show two bands); the intensity of absorption being weak. On the other hand, aromatic amines exhibit two strong bands at 1360–1180  $\text{cm}^{-1}$  due to C—N stretching. These bands may be used to distinguish between aliphatic and aromatic amines.

The salts of amines such as hydrochlorides show a broad band in the 3000–2200  $\text{cm}^{-1}$  region, which is typical of ammonium ion.

The main features of infrared spectra of amines are given in table 2.11.

Table 2.11. Amines

Compound	Type of vibration	Position of band ( $\text{cm}^{-1}$ ) and intensity
Primary and secondary amines	N—H stretching	3500–3200 (m)
Primary amines	N—H bending	1650–1560 (m) 900–650 (m)
Secondary amines	N—H bending C—N stretching	1600–1500 (w) 1230–1030 (w)
Aliphatic amines	C—N stretching	1360–1180 (s)
Aromatic amines	C—N stretching	Two bands

Infrared spectrum of *n*-butylamine is shown in Fig. 2.12.

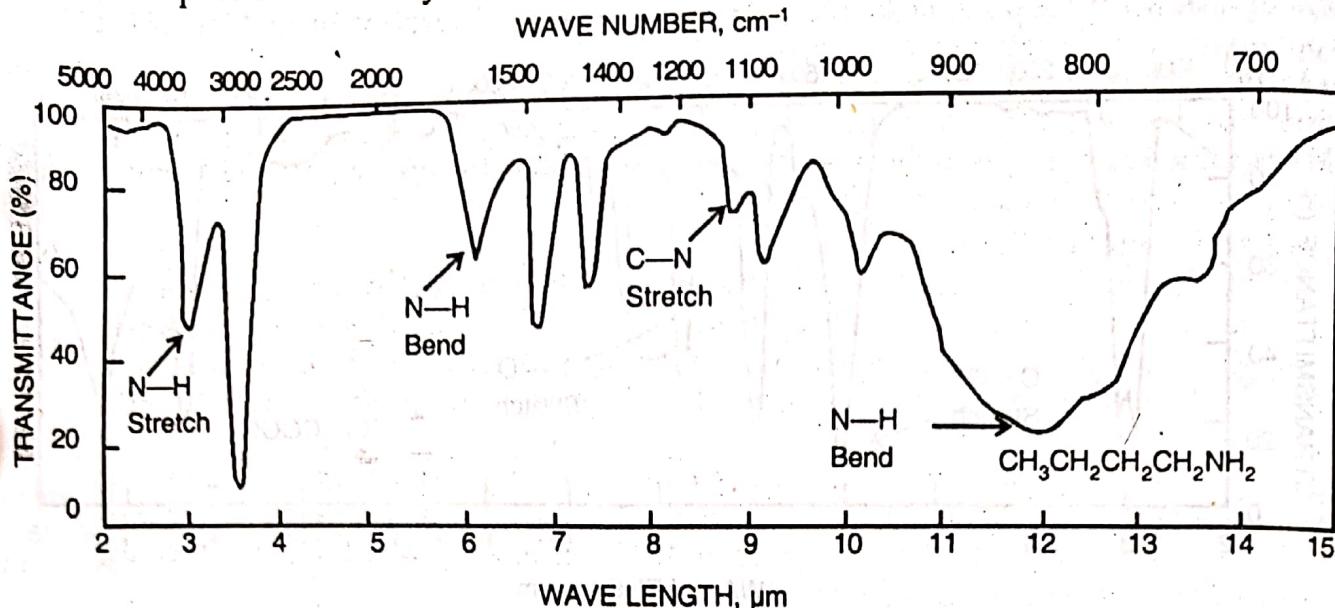


Fig. 2.12. Infrared spectrum of *n*-butylamine.

### 2.10.8. Nitriles

The infrared spectra of nitriles are characterised by the presence of C≡N stretching absorption band at 2260–2220 cm<sup>-1</sup> of variable intensity.

### 2.10.9. Nitro compounds

The infrared spectra of nitro compounds show two strong bands at about 1560 cm<sup>-1</sup> and 1350 cm<sup>-1</sup> due to symmetrical and asymmetrical stretching of N=O bonds. Primary nitro compounds ( $\text{RCH}_2\text{NO}_2$ ) absorb at higher frequency as compared to secondary ( $\text{R}_2\text{CHNO}_2$ ) while tertiary compounds ( $\text{R}_3\text{CNO}_2$ ) absorb at even lower frequency.

Aromatic nitro compounds exhibit strong bands at about 1550 and 1350 cm<sup>-1</sup> due to symmetrical and asymmetrical N=O stretching.

## 2.11. INTERPRETATION OF IR SPECTRA

Having studied the characteristic absorption positions of various functional groups, we give below a few useful tips for remembering the specific absorption regions and interpreting the infrared spectra.

### 2.11.1. Remembering the specific absorption regions

For this purpose, the infrared range from 4000 to 700 cm<sup>-1</sup> may be broadly treated as consisting of four parts:

(1) The region from 4000 to 2500 cm<sup>-1</sup> is the absorption region of C—H, O—H and N—H single bond stretching vibrations. N—H and O—H bonds absorb in the region 3300 – 3600 cm<sup>-1</sup> while C—H bond absorption occurs around 3000 cm<sup>-1</sup>.

(2) The region from 2500 to 2000 cm<sup>-1</sup> corresponds to C≡C and C≡N triple bond stretching absorptions.

(3) The region from 2000 to 1500 cm<sup>-1</sup> deals with C=C, C=O and C≡N double bond stretching vibrations. Carbonyl group generally absorbs between 1670 to 1780 cm<sup>-1</sup> while ethylenic double bond absorption generally takes place from 1640 to 1680 cm<sup>-1</sup>.

(4) The region below 1500 cm<sup>-1</sup> constitutes the finger print region where a number of complex absorption bands appear due to different kinds of C—C, C—O, C—N and C—halogen single bond vibrations.

### 2.11.2. Interpreting the infrared spectrum

The following points should prove very helpful in the interpretation of infrared spectrum.

(1) Always start with the high frequency end of the spectrum. The absorption bands due to most of the stretching vibrations appear in the region above 1500 cm<sup>-1</sup>.

(2) The region below  $1500\text{ cm}^{-1}$  is used only for the confirmation of the identity of the compound.

(3) It is neither necessary nor possible to interpret each and every absorption band. Most of the information is obtained from a relatively few bands.

(4) The negative evidence is always more reliable. What this statement means is that the absence of a characteristic absorption band of a bond or group is sure guarantee of the absence of that particular bond or group. For example, if there is no absorption band in the region ( $1600$ – $1800\text{ cm}^{-1}$ ), carbonyl group must be absent in the compound.

### 1.3. Overtones and Coupling Peaks

Before concluding this discussion, it may be pointed out that the actual appearance of IR spectrum becomes rather complicated due to the appearance of certain absorption bands *in addition* to the bands due to the fundamental vibrational modes of the various bonds. Such additional bands are called *overtones* and *coupling peaks*. *But these additional bands are much less intense than fundamental bands.*

**Overtones.** These are high frequency bands which may occur at or near integral multiples (*i.e.* two times, three times etc) of the fundamental band frequency. For example, in the spectra of carbonyl compounds, such overtones are present in the range of  $3200$ – $3550\text{ cm}^{-1}$  which is two times the characteristic absorption frequency of  $\text{C}=\text{O}$  stretching vibration.

**Coupling peaks.** These are additional bands which result from the combination of two fundamental vibration frequencies by their **addition** or **subtraction**. For two fundamental frequencies  $a$  and  $b$ , combination bands can appear at  $(a+b)$  or  $(a-b)\text{ cm}^{-1}$ . But only certain combinations of coupling vibrations are allowed by consideration of quantum mechanics.

## 2. IR SPECTRA OF SOME SIMPLE MOLECULES

As practical illustration of the interpretation of IR spectra, let us now identify the significant absorption bands in the spectra of some simple molecules.

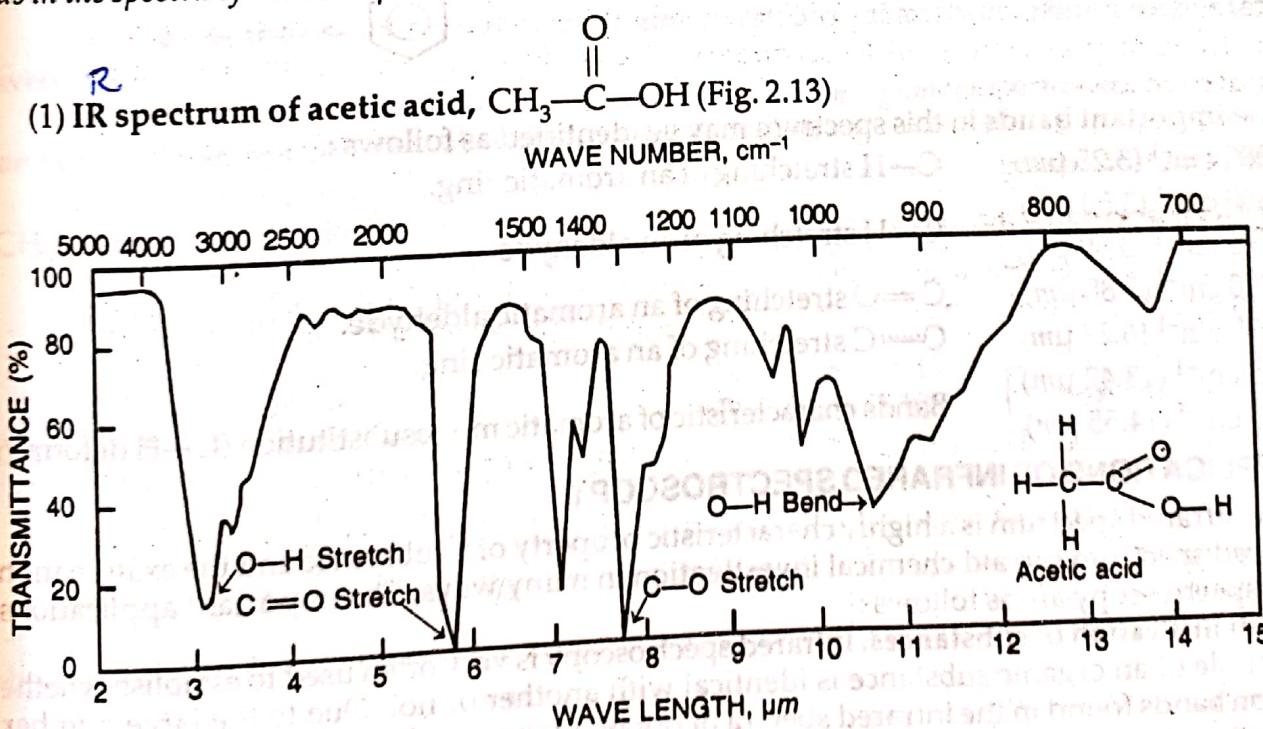


Fig. 2.13. IR spectrum of acetic acid,  $\text{CH}_3\text{—C}\text{—OH}$ .

The important bands in the above spectrum are as follows :

$3030\text{ cm}^{-1}$  ( $3.3\text{ }\mu\text{m}$ ) ; a broad band of hydrogen bonded  $\text{O}\text{—H}$  stretching of a carboxylic acid.

$1710\text{ cm}^{-1}$  ( $5.85\text{ }\mu\text{m}$ ) ;  $\text{C}=\text{O}$  stretching of a saturated chain carboxylic acid.

$1280\text{ cm}^{-1}$  ( $7.8\text{ }\mu\text{m}$ ) ;  $\text{C}\text{—O}$  stretching of a carboxylic acid.

$945\text{ cm}^{-1}$  ( $10.6\text{ }\mu\text{m}$ ) ;  $\text{O}\text{—H}$  bending of a carboxylic acid.

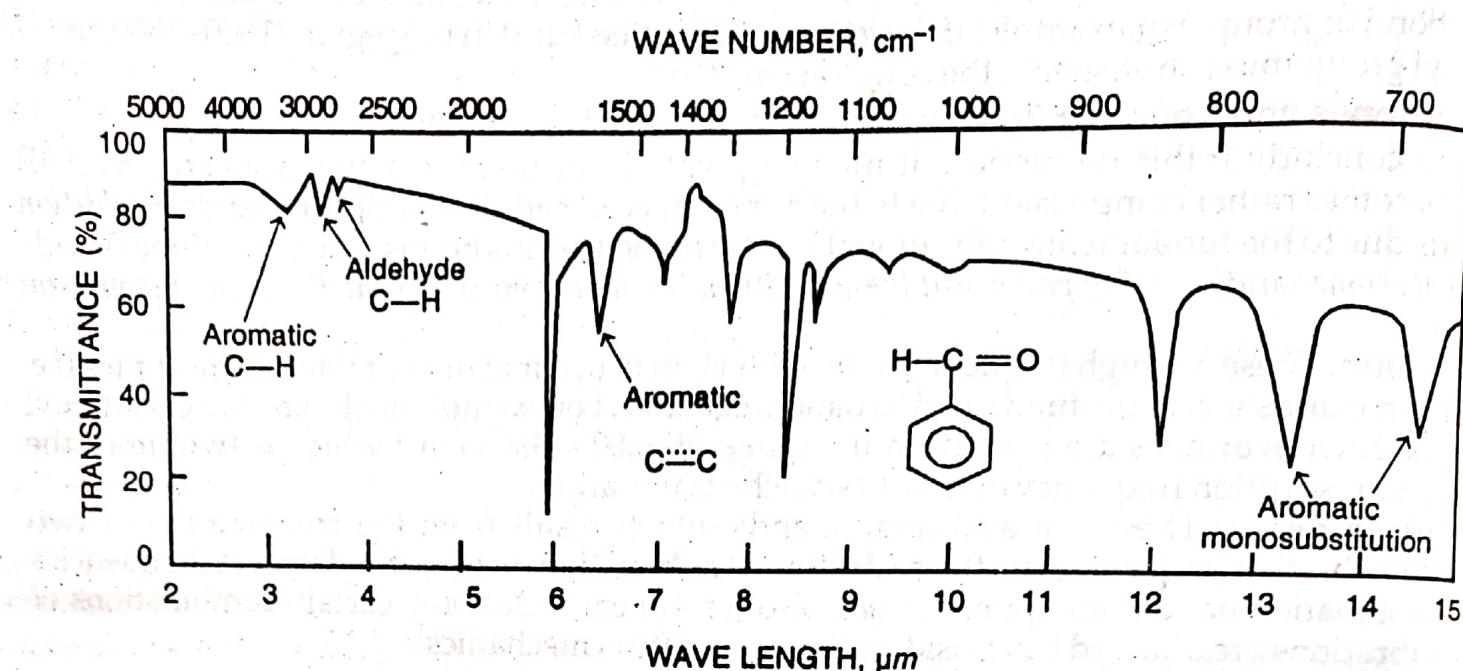


Fig. 2.14. IR spectrum of benzaldehyde,  $\text{H}-\text{C}=\text{O}$ .



The important bands in this spectrum may be identified as follows :

$3080 \text{ cm}^{-1}$  ( $3.25 \mu\text{m}$ )

$2860 \text{ cm}^{-1}$  ( $3.50 \mu\text{m}$ )

$2775 \text{ cm}^{-1}$  ( $3.60 \mu\text{m}$ )

$1700 \text{ cm}^{-1}$  ( $5.88 \mu\text{m}$ )

$1595 \text{ cm}^{-1}$  ( $6.27 \mu\text{m}$ )

$745 \text{ cm}^{-1}$  ( $13.42 \mu\text{m}$ )

$685 \text{ cm}^{-1}$  ( $14.55 \mu\text{m}$ )

C—H stretching of an aromatic ring.

C—H stretching of an aldehyde.

C=O stretching of an aromatic aldehyde.

C=C stretching of an aromatic ring.

Bands characteristic of aromatic monosubstitution (C—H deformation).

## 2.13. APPLICATIONS OF INFRARED SPECTROSCOPY

The infrared spectrum is a highly characteristic property of a substance and the examination of the infrared spectrum can aid chemical investigation in many ways. The important applications of infrared spectroscopy are as follows :

(i) **Identification of substances.** Infrared spectroscopy is very often used to establish whether a given sample of an organic substance is identical with another or not. Due to the large number of absorption bands found in the infrared spectra of organic compounds, the probability that any two different compounds will produce identical spectra is practically zero. This means that if two samples of different substances give identical spectra under similar conditions of measurement they must be samples of the same substance. However, the conditions of recording the spectra such as physical states of the samples, solvents used and concentrations of solutions must be the same because a substance may produce appreciable different spectra under different sets of conditions.

It may be noted that the infrared spectra of two enantiomeric compounds taken under the same conditions are exactly identical. In other words, *infrared spectroscopy fails to distinguish between enantiomers.*

(ii) **Determination of functional group and molecular structure.** Infrared spectroscopy is very helpful in determining the molecular structures of unknown substances. From an examination of the positions of absorption bands in the spectrum, it is often possible to establish the nature of the groups present in the molecule. For example, if a spectrum contains a strong band at  $5.82 \mu\text{m}$  ( $1717 \text{ cm}^{-1}$ ), the compound concerned must contain a carbonyl group. This information in conjunction with the study of other bands may tell a great deal about the structure of the compound. It is obvious that if a spectrum does not contain an absorption band typical of a particular functional group, the substance does not contain that group.

(iii) **Studying the progress of reactions.** Progress of a chemical reaction can be readily followed by examining spectra of small portions of reaction mixture withdrawn from time to time. The rate of disappearance of a characteristic absorption band of a reactant group or the rate of increasing absorption bands due to the formation of some product helps in studying the progress of the reaction. For example, the gradual disappearance of the hydroxyl stretching frequency at  $2.74\text{--}2.78 \mu\text{m}$  ( $3600\text{--}3650 \text{ cm}^{-1}$ ) and the consequent appearance of the carbonyl stretching frequency at  $5.68\text{--}5.95 \mu\text{m}$  ( $1680\text{--}1760 \text{ cm}^{-1}$ ) can be used to study the oxidation of an alcohol to a carbonyl compound.

Similarly the systematic interpretation of IR spectrum can be very useful in determining whether a reaction has occurred to give the expected product or not.

(iv) **Detection of impurities.** It is possible to determine whether a given sample of a compound is pure or not provided the reference spectrum of the pure compound is available. In contrast with the spectrum of the pure compound, the spectrum of an impure sample is blurred and not so sharp and contains many extra bands. For example, the presence of a ketone as an impurity in an alcohol leads to a rather poor spectrum having additional absorption bands due to the carbonyl group.

## 2.14. SOME EXAMPLES OF INFRARED SPECTROSCOPY

To illustrate the use of infrared spectroscopy in structural analysis, a few simple examples are given below :

**Example 2.2.** Indicate the expected important absorption regions in the IR spectra of the following compounds : Isopropyl alcohol, dimethyl ether and toluene.

**Solution.** (i) The important absorption bands expected in the IR spectrum of isopropyl alcohol,  $(\text{CH}_3)_2\text{CHOH}$ , are as follows :

$3200\text{--}3400 \text{ cm}^{-1}$  A strong and broad band due to hydrogen bonded O—H stretching.

$2850\text{--}2950 \text{ cm}^{-1}$  Due to C—H stretching.

$1000\text{--}1300 \text{ cm}^{-1}$  Due to C—O stretching.

(ii) The important absorption bands expected in the IR spectrum of dimethyl ether,  $\text{CH}_3\text{—O—CH}_3$ , are as follows :

$1060\text{--}1150 \text{ cm}^{-1}$  Due to C—O stretching.

$2850\text{--}2950 \text{ cm}^{-1}$  Due to C—H stretching of methyl groups.

(iii) The IR spectrum of toluene, — $\text{CH}_3$  would be expected to have the following important absorption bands.

$2850\text{--}2950 \text{ cm}^{-1}$  Due to C—H stretching of methyl group.

$3000\text{--}3100 \text{ cm}^{-1}$  Due to C—H stretching of aromatic ring.

$1500\text{--}1600 \text{ cm}^{-1}$  Due to C=C stretching of aromatic ring.

**Example 2.3.** Give the approximate positions of characteristic absorption bands of the carbonyl group in the IR spectra of the following compounds :

