UNIT 13

IR SPECTROSCOPY

Structure

13.1 INTRODUCTION

Scientists have done extensive research on utilizing infrared (IR) spectroscopy to characterize numerous compounds. Infrared spectroscopy is an analytical technique which is based on the vibrational transitions of a molecule. In this unit and in the next unit you are going to mainly learn how IR spectroscopy helps in the determination of the structure of simple organic molecules. In the next unit you are going to learn more about how to use IR spectroscopy to identify simple organic molecules for both known and unknown simple organic compounds. In this way, with the help of units 13 and 14 of this block, you will be able to understand how to use IR spectroscopy as a powerful tool to identify simple organic molecules.

Expected Learning Outcomes

After studying this unit, you should be able to:

- ❖ understand the range of IR Radiation as well as that of the Fingerprint Region;
- ❖ discuss the different types of molecular vibrations; and
- ❖ gain knowledge about the characteristic frequencies of functional groups.

13.2 RANGE OF IR RADIATION (FINGERPRINT REGION)

While identifying a simple organic molecule, it is very important to understand the following:

- How the atoms are connected together?
- Which bonds are single, double, or triple?
- What functional groups exist in the molecule?
- Do we have a specific stereoisomer?

The answers to these questions can be found to a large extent from IR spectroscopy of the compounds which we are going to discuss now.

Infrared spectroscopy

The IR spectroscopy involves in triggering molecular vibrations through irradiation with infrared light. Infrared radiation is largely thermal energy. It induces strong molecular vibrations in covalent bonds, which are almost the same as springs holding together two masses, or atoms as shown in Fig. 13.1 below.

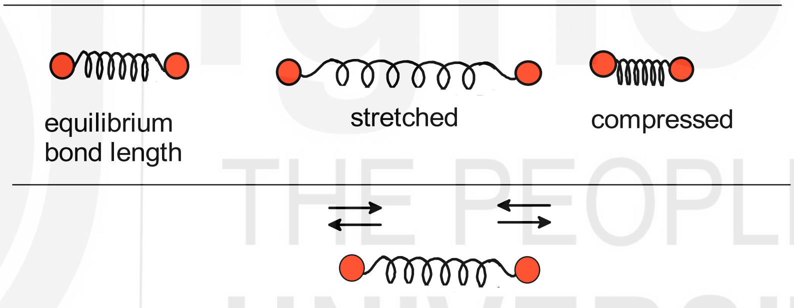


Fig. 13.1: Springs holding together two masses, or atoms.

IR spectroscopy provides mostly information about the presence or absence of certain functional groups. Specific bonds respond to (absorb) specific frequencies. Upon irradiation with infrared light, certain bonds respond by vibrating faster. This response can be detected and translated into a visual representation called a spectrum as shown in Fig. 13.2.

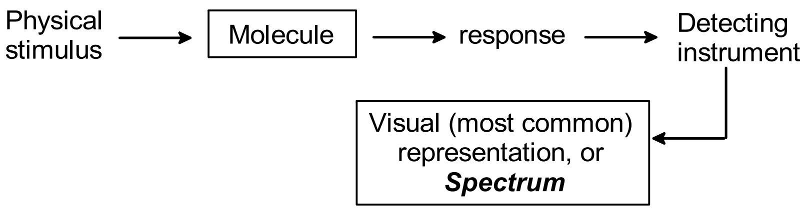


Fig.13.2: Spectral information as obtained from spectroscopy.

Spectroscopic techniques, including, infrared (IR) spectroscopy, involve the interaction of molecules with electromagnetic radiation. Thus, to understand the fundamentals of spectroscopy, you must recapitulate the fundamentals of electromagnetic radiation.

In previous Unit 11 of this course, you have recapitulated about electromagnetic radiation, and we will provide only a summary here. Gamma rays, X-rays, ultraviolet light, visible light, **infrared radiation**, microwaves and radio waves are all examples of **electromagnetic radiation** and part of the electromagnetic spectrum. Because electromagnetic radiation behaves as a wave travelling at the speed of light, it is described in terms of its wavelength and frequency. Fig. 13.3 shows the electromagnetic spectrum where the IR region has been highlighted.

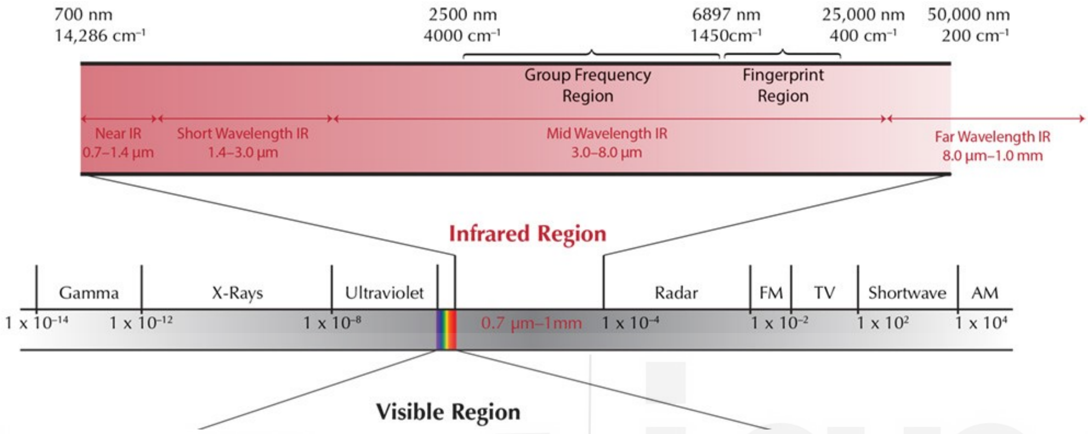


Fig. 13.3: The electromagnetic spectrum where the IR region has been highlighted.

In Unit 11 you have also recapitulated about wavelength λ and it SI base unit of meters and its relation with the **frequency** ν in s^{-1} (also called **hertz, Hz**). Alternatively, the electromagnetic radiations in terms of particles have also been discussed there.

You have already studied that molecules are flexible structures with atoms and groups of atoms able to rotate around covalent single bonds. Covalent bonds stretch and bend just as if the atoms were joined by flexible springs as shown earlier in Fig. 13.1. We know from experimental observations and from theories of molecular structure that all energy changes within a molecule are quantized; that is, they are subdivided into small, but well-defined, increments. For example, vibrations of bonds within a molecule can undergo transitions only between allowed vibrational energy levels.

We can cause an atom or molecule to undergo a transition from energy state E_1 to a higher energy state E_2 by irradiating it with electromagnetic radiation corresponding to the energy difference between states E_1 and E_2 as illustrated schematically in Fig. 11.1 in Unit 11 of this block.

When the atom or molecule returns to the ground state from excited state, equivalent amount of energy is emitted. When a compound is irradiated with electromagnetic radiation of various wavelengths, it absorbs energy of particular wavelengths, while the wavelengths not absorbed simply pass through or are reflected from the sample unchanged. In infrared (IR) spectroscopy, when we irradiate a compound with infrared radiation, this radiation is absorbed when its energy (frequency) is exactly equal to the energy required to excite a molecule to a higher energy state. Because different functional groups have different bond strengths, the energy required to bring about these transitions varies from one functional group to another. Thus, in infrared spectroscopy, we can detect functional groups by the vibrations of their bonds.

The infrared region of the electromagnetic spectrum (Fig. 13.3) covers the range of wave lengths from 7.8 x 10^{-7} m (just longer than the visible region) to 2.0 x 10^{-3} m (just shorter than the microwave region). In chemistry, however, we routinely use only the portion that extends from 2.5 x 10^{-6} to 2.5 x 10^{5} m. This region is often called the **vibrational infrared** region and we commonly refer to radiation in this region by its **wavenumber** $(\bar{\nu})$, the number of waves per centimeter which you have already learnt in section 11.2 of Unit 11. For molecular vibrations, the frequency value is very large, so it is convenient to use wave number for IR spectroscopy.

$$\bar{\nu} = \frac{1}{\lambda}$$

So we can say,

$$\bar{\nu} = \frac{\nu}{c} \quad \text{(Frequency/Velocity of light)}$$

e.g., For ν = 3 x 10^{13} s^{-1}, the wave number is

$$\bar{\nu} = \frac{3\text{x}10^{13}\,\text{s}^{-1}}{3\text{x}10^{10}\,\text{cms}^{-1}}$$

$$\bar{\nu} = 1000 \text{ cm}^{-1}$$

Expressed in wavenumbers, the vibrational region of the infrared spectrum extends from 4000 to 400 cm^{-1} (the unit cm^{-1} is read 'reciprocal centimeter'). An advantage of using wavenumbers is that they are directly proportional to energy: the higher the wavenumber, the higher the energy of radiation.

Now, let us understand what is meant by absorption of IR light and what is meant by transmission? Well, when a chemical sample is exposed to the infrared light, some of the frequencies can be absorbed while the rest may be transmitted. Even some of the light may be reflected back to the source as shown in Fig. 13.4 below. The detector detects the transmitted frequencies, and by doing so also reveals the values of the absorbed frequencies.

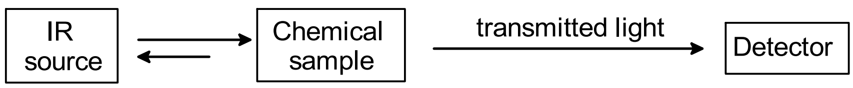


Fig. 13.4: Transmission and absorption of IR light by a chemical sample.

Next let us understand the situation when the we see the IR spectrum in the absorption mode. The absorption of radiation corresponds to trough or valley. Strange as it may seem, we commonly refer to infrared absorptions as peaks, even though they are actually troughs.

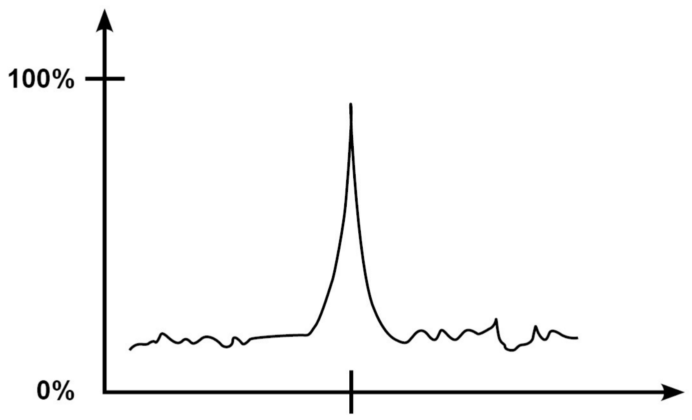


Fig. 13.5: An IR spectrum in the absorption mode.

The IR spectrum is actually the plot of transmitted (or absorbed) frequencies versus the intensity of the transmission (or absorption). Frequencies are given in units of inverse centimeters (wavenumbers) and is in the x-axis. The intensities are plotted in the y-axis in percentage units. The graph in Fig. 13.5 shows the IR spectrum in the absorption mode. The vertical axis measures transmittance, with 100% transmittance at the top and 0% transmittance at the bottom. Thus, the baseline for an infrared spectrum (100% transmittance of radiation through the sample = 0% absorption) is at the top of the chart.

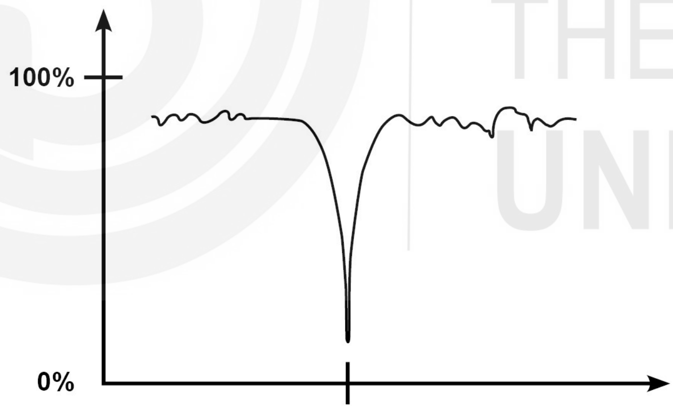


Fig. 13.6 An IR spectrum in the transmittance mode.

The graph in Fig.13.6 shows the IR spectrum in the transmittance mode (this transmittance mode graph). You will find in most chemistry and spectroscopy books and is widely used. Henceforth we will use this transmittance mode representation only.

You must also know that the IR bands may be classified as strong(s), medium (m), or weak (w), depending on their relative intensities in the infrared spectrum. Almost the whole of y-axis is covered by a strong band whereas, at about half of the y-axis falls the medium band. At almost one-third or less of the y-axis falls the weak band. Fig.13.7 shows the relative intensities in the IR spectrum of weak, medium and strong bands.

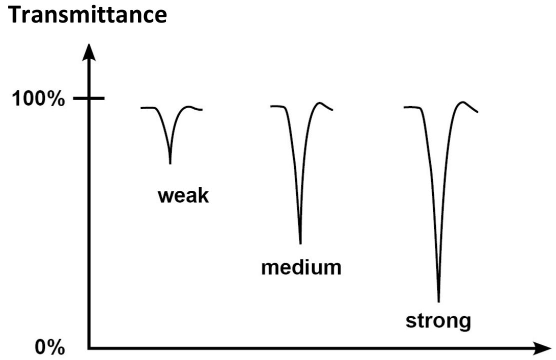


Fig. 13.7: Relative intensities in the IR spectrum of weak, medium and strong bands.

The IR region falls between wavenumbers 4000 cm^{-1} and 600 cm^{-1}. But here you must note specially the **1500 - 600 cm^{-1} region**. Above 1500 cm^{-1}, it is the diagnostic region and all the functional groups may be detected in this region. It is also easy to assign the bands above 1500 cm^{-1} to a particular group. But below 1500 cm^{-1}, it will not be easy to assign the bands. Especially in the region 1450-900 cm^{-1}, even structurally similar molecules give different absorption patterns. This is the reason for referring to this region as **fingerprint region**.

Below in Fig. 13.8 is given a sample IR spectrum where the diagnostic part and the fingerprint regions are labelled. It is clear that you must focus your analysis on the left marked part which is the diagnostic part and not bother about the complicated fingerprint region on the right side of the spectrum.

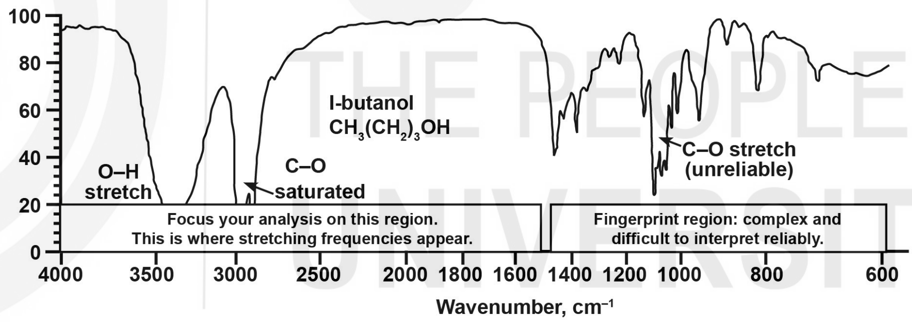
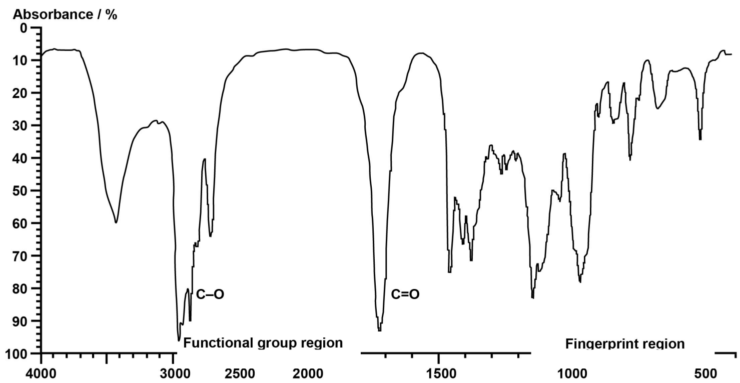


Fig. 13.8: The diagnostic and the fingerprint region of a sample IR spectrum.

SAQ 1

Based on the IR spectrum given below, what interpretations you can derive? Label the functional group region and the fingerprint region in it.



13.3 TYPES OF MOLECULAR VIBRATIONS

(Total degrees of freedom)-(translational degrees of freedom+rotational degrees of freedom)= Vibrational degrees of freedom.

For a molecule to absorb infrared radiation, the bond undergoing vibration must be polar, and its vibration must cause a periodic change in the bond dipole. The greater the polarity of the bond, the is the cause a periodic change in the bond dipole; the greater the polarity of the bond, the more intense is the absorption. Any vibration that meets these criteria is said to be infrared active. Covalent bonds in homonuclear diatomic molecules, such as H_2 and Br_2, and some carbon-carbon double or triple bonds in symmetrical alkenes and alkynes do not absorb infrared radiation because they are not polar bonds. The multiple bonds in the following two molecules, for example, do not have a dipole moment so are not infrared active. For a molecule as simple as ethanol, CH_3CH_2OH, there are 21 fundamental vibrations, and for hexanoic acid, $CH_3(CH_2)_4COOH$, there are 54. Thus, even for relatively simple molecules, a large number of vibrational energy levels exist, and the patterns of energy absorption for these and larger molecules are quite complex.

Looking at a diatomic molecule you can say that it has only one fundamental vibration or one vibrational coordinate. This arises due to the stretching and compression of the bond connecting two atoms just like a spring (see Fig. 13.1). Let us calculate the vibrational degrees of freedom of a polyatomic molecule. First let us assume that each atom is free to move in three perpendicular directions (along *x, y* and *z* axes) and thus has three **degrees of freedom.** The degrees of freedom are the number of directions in which an atom can move freely independent of other atoms in the molecule. Hence, for a molecule containing *N* atoms, the total degrees of freedom in 3*N*.

We know that a molecule has translational, rotational and vibrational motions. A molecule can have only three degrees of translational motion since centre of mass of the molecule can move only along three axial directions. That is, the whole molecule can move along the three axes. In addition, when the molecule is nonlinear, there are three degrees of freedom due to rotational motions about the three axes. Therefore there remains $3N - (3+3) = (3N-6)$ coordinates which account for vibrational degrees of freedom for nonlinear polyatomic molecules.

For a linear molecule, there are two rotational degrees of freedom as the rotations about two axes perpendicular to internuclear bond axis only are allowed. The rotation about the internuclear axis is not possible since the moment of inertia along the internuclear axis is zero. Therefore a linear molecule possesses $3N - (3+2) = (3N-5)$ vibrational degrees of freedom. The details of the number of degrees of freedom for linear and nonlinear molecules are presented in Table 13.1.

Table 13.1: Degrees of Freedom for Polyatomic Molecules

Degrees of Freedom	Linear	Nonlinear
Total	3*N*	3*N*
Translational	3	3
Rotational	2	3
Vibrational	(3*N*-5)	(3*N*-6)

Using Table 13.1, can you state the vibrational degrees of freedom of CO_2, H_2O and NH_3 molecules? It is worth recollecting that CO_2 is linear, H_2O is angular and NH_3 is pyramidal. CO_2 molecule has (3 x 3 – 5) = 4 vibrational degrees of freedom; H_2O molecule has (3 x 3 – 6) = 3 vibrational degrees of freedom and NH_3 molecule has (3 x 4 – 6) = 6 vibrational degrees of freedom.

> The displacement of each atom during each normal mode of vibration is such that all atoms move with the same frequency and in phase but with different amplitude.
>
> The amplitudes of vibrations of atoms are such that the centre of mass does not move. In other words, there is no translational motion of the molecule as a result of vibration and also there is no rotational motion of the molecule.
>
> The normal mode concept can facilitate the understanding of the vibrational excitation of a particular group depending on the frequency of incident radiations; this radiation has no effect on the other part of the molecule.

Normal Modes Vibrations

A molecule can vibrate only in certain modes, known as normal modes. Each normal mode corresponds to a vibrational degree of freedom. A normal mode is an independent simultaneous motion of atoms or group of atoms that may be excited without leading to the excitation of any other normal mode. **In general, a normal vibration is one in which all atoms in a molecule vibrate at the same frequency and in phase with each other.**

For a polyatomic molecule, the normal modes of vibration are of two types:

(i) stretching vibrations (ii) bending vibrations

The linear and nonlinear molecules have (N-1) stretching vibrations. The bending vibrations for linear and nonlinear molecules are (2N - 4) and (2N - 5), respectively.

In **stretching vibrations,** the atoms move along the bond axis so that the bond length increases or decrerases at regular intervals. The stretching vibrations again are of two types. They are symmetric and antisymmetric stretching. In symmetric stretching of a triatomic molecule, both the bonds connected to a common atom can simultaneously either elongate or contract. In the case of antisymmetric stretching, if one bond is lengthened, the other bond is shortened or vice versa. These stretching are shown in Figs. 13.9a and b and Figs. 13.10a and b for linear and angular molecules of the type AB_2.

The arrows attached to each atom show the direction of its motion during half of the vibration. In Figs. 13.9 and 13.10, we indicate the type of each vibration mode as parallel (II) or perpendicular ($\perp$) . In a parallel vibration, the dipole change takes place along the line of the principal axis of symmetry. In a perpendicular vibration, the dipole change takes place perpendicular to the line of the principal axis of symmetry.

> Vibrations are classified as parallel (II) or perpendicular($\perp$) vibrations depending on whether the dipole moment change is parallel or perpendicular to the principal axis of the molecule.

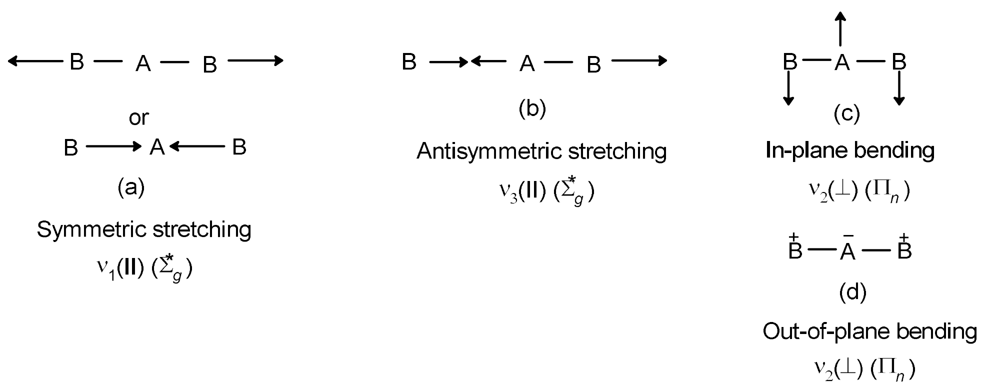


Fig. 13.9: Normal modes of a triatomic linear molecule, AB_2 (e.g., CO_2). (a) symmetric stretching (ν_1) (b) antisymmetric stretching (ν_3) (c) in-plane bending and (d) out of plane bending; both (c) and (d) are degenerate and hence these two give rise to only one band (ν_2); (+) sign shows that the atom is going above the plane while (-) sign indicates that the atom is going below the molecular plane. The ν_1 and ν_3 vibrations are

parallel (II) vibrations whereas the degenerate vibration ν_2 is a perpendicular ($\perp$) vibration.

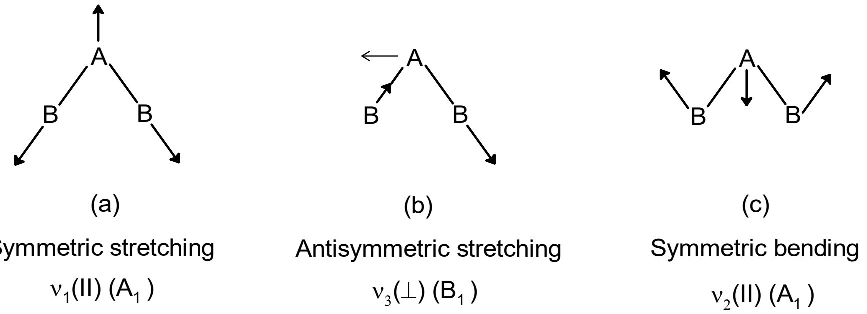


Fig. 13.10: Normal modes of vibrations of a triatomic angular molecule, AB_2 (e.g., H_2O). (a) symmetric stretching (ν_1) (b) antisymmetric stretching (ν_3) (c) symmetric bending (ν_2). ν_1 and ν_2 are parallel vibrations whereas ν_3 is a perpendicular vibration.

Degeneracy of a vibrational mode is the number of normal modes which have same energy. For instance, the degeneracy of ν_2 mode of CO_2 is two since the two bending modes (in-plane and out-of-plane) have same energy.

The **bending vibrations** occur when there is a change in bond angle between bonds connected to a common atom. In some cases, the movement of a group of atoms with respect to the remaining atoms in the molecule also causes vibrations for a polyatomic molecule. A linear triatomic molecule has two bending vibrations (Fig. 13.9c and d) while a nonlinear triatomic molecule has only bending vibration (13.10 c). Thus for a linear triatomic molecule (e.g., CO_2), we could expect four vibrational modes, two stretching and two bending. Both these bending vibrations are identical in all respects except the direction. Such vibrations have same frequency (and energy) and, are said to be degenerate. For instance, the two bending vibrations of CO_2 are degenerate. As a result of this, only three absorption bands are found for CO_2, two corresponding to the stretching vibrations and one to the bending vibration. A nonlinear angular triatomic molecule (e.g. H_2O) also has three vibrational modes, two being due to the stretching modes and one due to the bending mode. The difference between the linear and nonlinear triatomic molecules lies in the degeneracy of the bending mode of the former.

Using the materials in this section, answer the following SAQ.

SAQ 2

State the number of stretching and bending modes of C_2H_2.

13.4 CHARACTERISTIC FREQUENCIES OF FUNCTIONAL GROUPS

The normal modes of vibration can be divided into two types, namely, skeletal vibrations and the characteristic group vibrations. The skeletal vibrations involve displacements of all atoms to the same extent. The skeletal vibrations usually fall in the range 1400 – 700 cm^{-1}. The ether linkage, saturated hydrocarbon chains, aromatic rings etc. give rise to skeletal vibraton bands. A complex pattern of bands may occur in the IR spectrum of a compound which could be identified as due to a particular skeletal structure. We shall discuss this later in the next unit.

The second type of normal modes which are the characteristic group vibrations, involve the displacement of only a small portion of the molecule independent of the rest of the molecule. The absorption bands which arise due to the characteristic group vibrations are called **group frequencies.** The group frequencies are in general indepdndent of the structure of the molecule as a whole. A few instances of the perturbation of group frequencies are discussed in the next unit.

Many commonly occurring functional groups such as $-CH_3$, $>C{=}O$, $-NH_2$ etc. have characteristic group frequencies when they are present in a molecule. For example, all compounds containing a $-CH_3$ group possess absorption bands in the region of 2950 cm^{-1} (stretching) and 1400 cm^{-1} (bending). Such group frequencies are listed in Table 13.2 which is also known as chart of group frequencies.

Table 13.2: Group Frequencies

Group	Intensity	Range/cm^{-1}
A. Hydrocarbon chromophore		
1. C-H STRETCHING		
a. Alkane	(m-s)	2962-2853
b. Alkene	(m)	3100-3000
c. Alkyne	(s)	3300
d. Aromatic	(v)	3030
2. C-H BENDING		
a. Alkane, C-H	(w)	1340
Alkane, CH_2	(m)	1485-1445
Alkane, CH_3	(m)	1470-1430 and
	(s)	1380-1370
Alkane, gem-dimethyl	(s)	1385-1380 and
(doublet)	(s)	1370-1365
Alkane, tert-butyl	(m)	1395-1385 and
(doublet)	(s)	~ 1365
b. Alkene, monosubstituted	(s)	995-985
(vinyl)	(s)	915-905 and
	(s)	1420-1410
Alkene, disubstituted, *cis*	(s)	690
Alkene, disubstituted, *trans*	(s)	970-960 and
	(m)	1310-1295
Alkene, disubstituted, *gem*	(s)	895-885 and
	(s)	1420-1410
Alkene, trisubstituted	(s)	840-790
c. Alkyne	(s)	630
d. Aromatic substitution type:		
Five adjacent hydrogen atoms	(v,s)	750 and
(monosubstituted)	(v,s)	700

Three adjacent hydrogen atoms (1,2,3-trisubstituted)	(v,m)	780
Two adjacent hydrogen atoms (1,2,3,4-tetrasubstituted)	(v,m)	830
One hydrogen atom (pentasubstituted)	(v,w)	880
3. **C-C MULTIPLE BOND STRETCHING**		
a. Alkene, nonconjugated	(v)	1680-1620
Alkene, monosubstituted (vinyl)	(m)	1645
Alkene, disubstituted, *cis*	(m)	1656
Alkene, disubstituted, *trans*	(m)	1675
Alkene, disubsituted, *gem*	(m)	1653
Alkene trisubstituted	(m)	1669
Alkene tetrasubstituted	(w)	1669
b. Alkyne, monosubstituted	(m)	2140-2100
Alkyne, disubstituted	(v,w)	2260-2190
c. Aromatic	(v)	1600
	(v)	1580
	(m)	1500 and
	(m)	1450
B. Carbonyl chromophore		
1. KETONES		
a. saturated	(s)	1725-1705
b. α, β-Unsaturated	(s)	1685-1665
c. Aryl	(s)	1700-1680
2. ALDEHYDES		
a. Carbonyl stretching		
Saturated, aliphatic,	(s)	1740-1720
α, β-Unsaturated, aliphatic	(s)	1705-1680
Aryl	(s)	1715-1695
b. C-H stretching	(w)	2900-2920 and
(two bands)	(w)	2775-2700
3. ESTERS		
a. Carbonyl stretching		
Saturated, acyclic	(s)	1750-1735
Saturated, cyclic:		
δ-lactones (and larger rings)	(s)	1750-1735
γ-lactones	(s)	1780-1760
β-lactones	(s)	1820
Unsaturated:		

Vinyl ester type	(s)	1800-1770
α,β-unsaturated and aryl	(s)	1730-1717
α-ketoesters	(s)	1755-1740
β-ketoesters(enolic)	(s)	1650
b. C-O stretching		
All types of esters stated above; one or two bands		1300-1050
4. CARBOXYLIC ACIDS		
a. Carbonyl stretching:		
Saturated aliphatic	(s)	1725-1700
α,β-unsaturated aliphatic	(s)	1715-1690
Aryl	(s)	1700-1680
b. Hydroxyl stretching	(w)	2700-2500
(bonded), several bands		
c. Carboxylate anion stretching	(s)	1610-1550 and 1400-1300
5. AMIDES		
a. Carbonyl stretching		
Primary, solid and concentrated	(s)	1650
Solution		
Primary, dilute solution	(s)	1690
Secondary, solid and concentrated solution	(s)	1680-1630
Secondary, dilute solution	(s)	1700-1670
Tertiary, solid and all solutions	(s)	1670-1630
b. N-H stretching		
Primary, free: two bands	(m) (m)	3500 and 3400
Primary, bonded: two bands	(m) (m)	3350 and 3180
Secondary, free: one band	(m)	3430
Secondary, bonded: one band	(m)	3320-3140
c. N-H bending		
Primary amides, dilute solution	(s)	1620-1590
Secondary amides, dilute solution	(s)	1550-1510
C. Miscellaneous chromophoric groups		
1. **ALCOHOLS AND PHENOLS**		
a. O-H stretching		
Free O-H	(v, sh)	3700-3600
Intermolecularly hydrogen		
bonded (changes on dilution)		

Single bridge compounds	(v, sh)	3550-3450
Polymeric association	(s,b)	3400-3300
Intramolecularly hydrogen		
Bonded (no change on dilution)		
Single bridge compounds	(v, sh)	3570-3450
Chelate compounds	(w,b)	3200-2500
b. O-H bending and C-O		
Stretching		
Primary alcohols	(s)	1050 and
	(s)	1350-1260
Secondary alcohols	(s)	1100 and
	(s)	1350-1260
Tertiary alcohols	(s)	1150 and
	(s)	1410-1310
Phenols	(s)	1200 and
	(s)	1410-1310
2. Ethers		
C-O stretching		
Dialkyl ethers	(s)	1150-1070
Alkyl vinyl ethers or	(s)	1275-1200
Alkyl phenyl ethers	(s)	1075-1020
3. AMINES		
a. N-H stretching		
Primary, free; two bands	(m)	3500 and
	(m)	3400
Secondary, free; one band	(m)	3500-3310
Imines (=N-H); one band	(m)	3400-3300
b. N-H bending		
Primary	(s-m)	1650-1590
Secondary	(w)	1650-1550
c. C-N stretching		
Aromatic, primary	(s)	1340-1250
Aromatic, secondary	(s)	1350-1280
Aromatic, tertiary	(s)	1360-1310
Aliphatic	(w)	1220-1020 and
	(w)	1410
4. UNSATURATED NITROGEN COMPOUNDS		
a. C≡N stretching		
Alkyl nitriles	(m)	2260-2240
α,β-unsaturated alkyl nitriles	(m)	2235-2215
Aryl nitriles	(m)	2240-2220
b. C=N stretching		
(imines, oximes)		
Alkyl compounds	(v)	1690-1640
α,β-unsaturated compounds	(v)	1660-1630

c. C-NO_2, Nitro compounds		
aromatic	(s)	1570-1500 and
	(s)	1370-1300
Aliphatic	(s)	1570-1550 and
	(s)	1380-1370
5. HALOGEN COMPOUNDS		
a. C-F	(s)	1400-1000
b. C-Cl	(s)	800-600
C. C-Br	(s)	600-500
d. C-I	(s)	500
6. SULFUR COMPOUNDS		
a. S-H stretching	(w)	2600-2550
b. C=S stretching	(s)	1200-1050
c. S=O stretching		
Sulfonamides	(s)	1180-1140 and
	(s)	1350-1300
Sulfonic acids	(s)	1210-1150
	(s)	1060-1030 and
		650

Abbreviations: s = strong, m = medium, w = weak, v = variable, b = broad, sh = sharp.

Now we will study the characteristic regions of IR absorption using which it is possible to identify the functional groups in detail. We know that IR region falls between wavenumbers 4000 cm^{-1} and 600 cm^{-1}. The whole region can be divided into **four distinct regions** to facilitate easy identification of functional groups in a polyatomic organic molecule. The four distinct regions of absorption are given below:

4000 – 2500 cm^{-1}

2500 – 2000 cm^{-1}

2000 – 1500 cm^{-1}

1500 – 600 cm^{-1}

4000 – 2500 cm^{-1} region

The absorption occurring due to stretching of X-H bond (X=O, N and C) falls in this region. For organic compounds, the stretching vibrations noticed in this region invariably point out the presence of O-H, N-H, or C-H. This region extends upto 2500 cm^{-1}.

The O-H stretching band occurs at 3700 - 3600 cm^{-1} when not involved in hydrogen bonding. It is a relatively broad band. The O-H group of alcohols and phenols gives absorption in this region. Regarding the O-H stretching frequency of carboxylic acids, we shall discuss shortly under hydrogen bonding effect in the next unit 14. The N-H stretching can be noticed between 3500 and 3100 cm^{-1}. The amines and amides give absorption in this region. The primary amines (having - NH_2 group) show a doublet structure (two sharp bands), while secondary amines, (having > N-H group) give only one sharp band. The tertiary amines understandably do not show absorption as these do not have N-H bond.

The C-H stretching from aliphatic compounds also occur in the range of 3300-2850 cm^{-1}. They are moderately broad. A little care has to be exercised while identifying C–H stretching, because C–H stretching of aromatic compounds occur as shoulder above 3000 cm^{-1}. To be precise, the shoulder of aromatic hydrogen atoms can be noticed around 3030 cm^{-1}. The antisymmetric and symmetric stretchings of methylene ($>CH_2$) and methyl ($-CH_3$) groups can be seen between 2965 and 2880 cm^{-1}. The C–H stretching vibrations of alkenes occur between 3100 and 3000 cm^{-1} while those of akynes occur around 3300 cm^{-1}.

2500 - 2000 cm^{-1} region

The compounds conlaining triple bond absorb in this region. The triple bond corresponds to bond order three. The strength of the bond and hence the force constant is high. Since the vibrational frequency is directly proportional to the square root of force constant, the triple bonds absorb at higher frequency as compared to double and single bonds The carbon-carbon triple bond ($-C\equiv C-$) absorbs between 2300 and 2100 cm^{-1}. The band is normally of weak intensity. The nitrile group absorbs between 2300-2200 cm^{-1}. Further the band due to nitrile group is of medium intensity. Only by the intensities of the bands, these two groups can be distinguished. The change involved in dipole moment is greater for $-C\equiv N$ group than for $-C\equiv C-$ group. This is the reason for greater intensity of band for $-C\equiv N$ than for $-C\equiv C-$ group.

2000 - 1500 cm^{-1} region

All compounds having double bond show absorption in this region. The groups which exhibit significant absorption in this region are $>C=C<$ and $>C=O$. Among these two, the C = O stretching is easy to recognise in the IR spectra. It is an intense band observed between 1830 and 1650 cm^{-1} . This absorption helps in identifying carbonyl group in organic compounds.The C = C stretch is much weaker in character and can be noticed around 1650 cm^{-1}.

1500 - 600 cm^{-1} region

We have so far dealt with the groups which absorb above 1500 cm^{-1} because it is also easy to assign the bands above 1500 cm^{-1} to a particular group. But below 1500 cm^{-1}, it will not be easy to assign the bands. Especially in the region 1450-900 cm^{-1}, even structurally similar molecules give different absorption patterns. This is the reason for referring to this region as fingerprint region.

In this region, many of the single bonds such as C-C, C-N, C-O absorb, apart from absorptions due to **skeletal vibrations** mentioned at the beginning of this section. Further, there will also be coupling of vibrational bands. For example,

C - C stretching frequencies can couple with C - H bending vibrations. Much useful information can be derived from the finger print region. We shall now see briefly the characteristic absorption in this region.

i) The C - H stretching is between 1400-1000 cm^{-1} and it is an intense band.

ii) The aromatic rings and alkenes in general give rise to out-of-plane C – H bending vibrations and can be seen between 1000-700 cm^{-1}.

iii) In substituted benzenes, the spectral pattern in this region give information whether it is monosubstituted or 1,2-,1,3- or 1,4-disubstituted. This is because C-H bonds adjacent to these substituted positions appear distinctively in 850-690 cm^{-1} region. The position of absorption band varies with respect to substitution pattern as shown below:

Monosubstituted	750 cm^{-1} and 700 cm^{-1}
o-disubstituted	750 cm^{-1}
m-disubstituted	780 cm^{-1}
p-disubstituted	830 cm^{-1}

iv) The compound containing gem-dimethyl groups (> $C(CH_3)_2$) has a doublet band at about 1375 cm^{-l}.

v) The compound containing a chain of at least four methylene groups shows band at 720 cm^{-1} .

We shall discuss the applications of IR spectra in structure determination in Unit 14.

SAQ 3

Give the reason for greater intensity of band for –C≡N than for –C≡C– group in the 2500 – 2000 cm^{-1} region of the IR spectrum.

13.5 SUMMARY

In this unit you have been introduced to the spectroscopic tool IR spectroscopy and how it helps in the determination of the structure of simple organic molecules. You have learnt about the range of IR radiation as well as that of the Fingerprint Region. Also the different types of molecular vibrations possible in small molecules have been discussed in detail. Lastly, the characteristic frequencies of functional groups have been given in a tabular form and introductory discussions in detail have been done on the different regions of the IR spectrum. In the next unit you are going to learn more about how to use IR spectroscopy to identify simple organic molecules in more details with the help of problems.

13.6 TERMINAL QUESTION

1. What information is obtained from the functional group region of a IR spectrum? What is its difference from the fingerprint region of the spectrum?

2. What are the normal modes if vibrations? Explain diagrammatically with a suitable example.

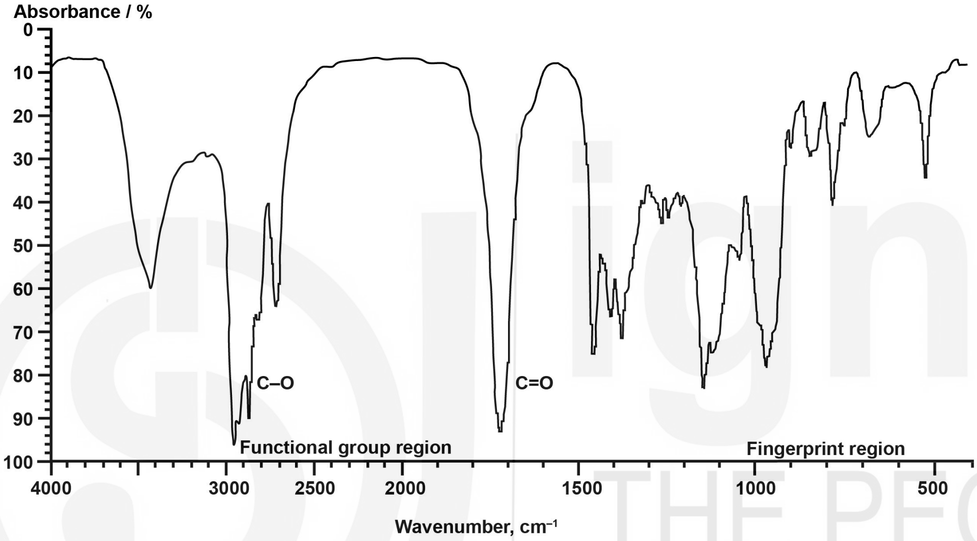
3. What are the requirements for a compound to absorb IR radiation?

4. Refer to Table 13.2 and give the stretching frequencies observed in alkyl and aryl nitriles. What is the strength of the bands?

13.7 ANSWERS

Self Assessment Questions

1. The given IR spectrum shows the x-axis as wavenumbers and the IR region falls between wavenumbers 4000 cm^{-1} and 600 cm^{-1}. The graph is in the transmittance mode which is commonly shown in most textbooks.



2. A linear molecule has (N - 1)stretching and (2N - 4)bending vibrations. Since N is four for C_2H_2, there are three stretching and four bending vibrations.

3. In the 2500 - 2000 cm^{-1} region the compounds conlaining triple bond absorb whose strength and hence the force constant is high. The carbon-carbon triple bond ($-C\equiv C-$) absorbs between 2300 and 2100 cm^{-1} and is of weak intensity. The nitrile group absorbs between 2300-2200 $cm^{-1}$and is of medium intensity. The change involved in dipole moment is greater for $-C\equiv N$ group than for $-C\equiv C-$ group. This is the reason for greater intensity of band for $-C\equiv N$ than for $-C\equiv C-$ group.

Terminal Questions

1. Most of the information that is used to interpret an IR spectrum is obtained from the functional group region. In practice, it is the polar covalent bonds than are IR "active" and whose excitation can be observed in an IR spectrum. In organic molecules these polar covalent bonds represent the functional groups. Hence, the most useful information obtained from an IR spectrum is what functional groups are present within the molecule. In the fingerprint region, the spectra tend to be more complex and much harder to assign.

2. A molecule can vibrate only in certain modes, known as normal modes. Each normal mode corresponds to a vibrational degree of freedom. A normal mode is an independent simultaneous motion of atoms or group of atoms that may be excited without leading to the excitation of any other normal mode. **In general, a normal vibration is one in which all atoms in a molecule vibrate at the same frequency and in phase with each other.** For a polyatomic molecule, the normal modes of vibration are of two types: (i) stretching vibrations (ii) bending vibrations

   The linear and nonlinear molecules have (N-1) stretching vibrations. The bending vibrations for linear and nonlinear molecules are (2N - 4) and (2N - 5), respectively.

3. The following are the requirements for a compound to absorb IR radiation:

   i) Correct wavelength of radiation - A molecule absorbs radiation when the frequency of vibrations of some part of a molecule is the same as the frequency of incident radiation.

   ii) Change in dipole moment - A molecule can only absorb IR radiations when its absorption causes a change in its electric dipole. A polar bond is usually IR active whereas non polar bond in a symmetrical molecule will absorb weakly or not at all

4. C=N stretching

Alkyl nitriles	(m)	2260-2240
α,β-unsaturated alkyl nitriles	(m)	2235-2215
Aryl nitriles	(m)	2240-2220

The bands are all medium in strength.