

3.1 Introduction

Infra-red spectrum is an important record which gives sufficient information about the structure of a compound. Unlike ultraviolet spectrum which comprises of relatively few peaks, this technique provides a spectrum containing a large number of absorption bands from which a wealth of information can be derived about the structure of an organic compound. The absorption of Infra-red radiations (quantised) causes the various bands in a molecule to stretch and bend with respect to one another. The most important region for an organic chemist is 2.5μ to $15 \mu^*$ in which molecular vibrations can be detected and measured in an infra-red spectrum and in a Raman spectrum. The ordinary infra-red region extends from 2.5μ to 15μ . The region from 0.8μ to 2.5μ is called **Near infra-red** and that from 15μ to 200μ is called **Far IR Region**.

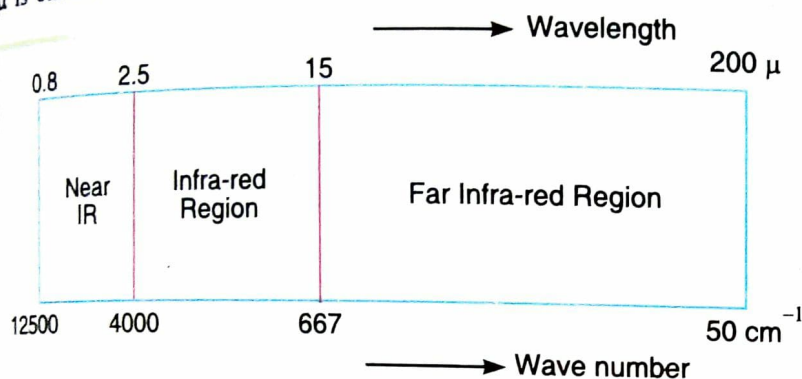


Fig. 3.1. Infra-red region.



Radiation.

The absorption of Infra-red radiations can be expressed either in terms of wavelength (λ) or in wave number ($\bar{\nu}$). Mostly infra-red spectra of organic compounds are plotted as percentage transmittance against wave number. The relationship between wavelength and wave number is as follows:

$$\text{Wave number} = \frac{1}{\text{wavelength in centimetres}}$$

If wavelength (λ) is $2.5 \mu = 2.5 \times 10^{-4} \text{ cm}$, then

$$\text{Wave number } (\bar{\nu}) = \frac{1}{2.5 \times 10^{-4} \text{ cm}}$$

$$= 4000 \text{ cm}^{-1} \quad \left[\bar{\nu} = \frac{1}{\lambda \text{ in cm}} \right]$$

The wavelength 15μ corresponds to wave number equal to 667 cm^{-1} . Thus, in terms of wave number, the ordinary infra-red region covers 4000 cm^{-1} to 667 cm^{-1} .

Band intensity is either expressed in terms of absorbance (A) or Transmittance (T).

$$A = \log_{10} (1/T)$$

This technique can be employed to establish the identity of two compounds or to determine the structure of a new compound. In revealing the structure of a new compound, it is quite useful

μ represents microns.

$$1 \mu = 10^{-4} \text{ cm}$$

$$\text{Wave number in } \text{cm}^{-1} = \frac{10000}{\text{wavelength in microns}}$$

to predict the presence of certain functional groups which absorb at definite frequencies. For example, the hydroxyl group in a compound absorbs at $3600\text{--}3200\text{ cm}^{-1}$; carbonyl group of ketones gives a strong band at 1710 cm^{-1} . The shift in the absorption position helps in predicting the factors which cause this shift. Some of the factors which shift the absorption band for a particular group from its characteristic frequency (or wave number) are inductive effect, conjugation, angle of strain, hydrogen bonding etc. It is, thus, a very reliable technique for disclosing the identity of a compound.

3.2 Principle of Infra-red Spectroscopy

The absorption of Infra-red radiations causes an excitation of molecule from a lower to the higher vibrational level. We know that each vibrational level is associated with a number of closely spaced rotational levels. Clearly, the Infra-red spectra is considered as **vibrational-rotational spectra**. All the bonds in a molecule are not capable of absorbing infra-red energy but only those bonds which are accompanied by a **change in dipole moment** will absorb in the infra-red region. Such vibrational transitions which are accompanied by a change in the dipole-moment of the molecule are called infra-red active transitions. Thus, these are responsible for absorption of energy in the Infra-red region. On the other hand, the vibrational transitions which are not accompanied by a change in dipole-moment of the molecule are not directly observed and these are Infra-red inactive. For example, vibrational transitions of $\text{C}=\text{O}$, $\text{N}-\text{H}$, $\text{O}-\text{H}$ etc. bands are accompanied by a change in dipole-moment and thus, absorb strongly in the Infra-red region. But transitions in Carbon-Carbon bonds in symmetrical alkenes and alkynes are not accompanied by the change in dipole-moment and hence do not absorb in the infra-red region. It is important to note that since the absorption in infra-red region is quantised, a molecule of the organic compound will show a number of peaks in the infra-red region.

3.3 Theory—Molecular Vibrations

Absorption in the infra-red region is due to the changes in the vibrational and rotational levels (see Fig. 3.2). When radiations with frequency range less than 100 cm^{-1} are absorbed, molecular rotation takes place in the substance. As this absorption is quantised, discrete lines are formed in the spectrum due to molecular rotation. Molecular vibrations are set in, when more energetic radiation in the region 10^4 to 10^2 cm^{-1} are passed through the sample of the substance. The absorption causing molecular vibration is also quantised. Clearly, a single vibrational energy change is accompanied by a large number of rotational energy changes. Thus, the vibrational spectra appear as vibrational-rotational bands. In the Infra-red spectroscopy (Region $2.5\text{ }\mu\text{--}15\text{ }\mu$), the absorbed energy brings about predominant changes in the vibrational energy which depends upon:

- (i) Masses of the atoms present in a molecule,
- (ii) Strength of the bonds, and
- (iii) The arrangement of atoms within the molecule.

It has been found that no two compounds except the enantiomers can have similar Infra-red spectra.

It may be noted that the atoms in a molecule are not held rigidly. The molecule may be visualised as consisting of balls of different sizes tied with springs of varying strengths. Here balls and springs correspond to atoms and chemical bonds respectively. When Infra-red light is passed through the sample, the vibrational and the rotational energies of the molecules are increased. Two kinds of fundamental vibrations are:

(a) **Stretching.** In this type of vibrations, the distance between the two atoms increases or decreases but the atoms remain in the same bond axis.



Fig. 3.2. Types of vibrations : (a) Stretching, (b) Bending.

(b) **Bending.** In this type of vibrations, the positions of the atoms change with respect to the original bond axis. We know that more energy is required to stretch a spring than that required to bend it. Thus, we can safely say that stretching absorptions of a bond appear at high frequencies (higher energy) as compared to the bending absorptions of the same bond.

The various stretching and bending vibrations of a bond occur at certain quantised frequencies. When Infra-red radiation is passed through the substance, energy is absorbed and the amplitude of that vibration is increased. From the excited state, the molecule returns to the ground state by the release of extra energy by rotational, collision or translational processes. As a result, the temperature of the sample under investigation increases.

Types of stretching vibrations. There are two types of stretching vibrations:

- Symmetric stretching.** In this type, the movement of the atoms with respect to a particular atom in a molecule is in the same direction.
- Asymmetric stretching.** In these vibrations, one atom approaches the central atom while the other departs from it.



Symmetric stretching



Asymmetric stretching

Fig. 3.3. Types of stretching vibrations.

Types of bending vibrations. (Deformations). Bending vibrations are of four types:

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



Scissoring

Rocking

Wagging

Twisting

Fig. 3.4. Types of bending vibrations. (a) Scissoring, (b) Rocking, (c) Wagging, (d) Twisting

Note. Bending vibrations require lesser energy and hence occur at higher wavelengths (lower numbers than stretching vibrations).

3.4 Vibrational Frequency

The value of the stretching vibrational frequency of a bond can be calculated fairly accurately by the application of **Hooke's law** which may be represented as:

$$\begin{aligned}\frac{\nu}{c} &= \bar{\nu} = \frac{1}{2\pi c} \left[\frac{k}{m_1 m_2} \right]^{1/2} \\ &= \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}\end{aligned}$$

where μ is the reduced mass.

m_1 and m_2 are the masses of the atoms concerned in grams in a particular bond.

k = Force constant of the bond and relates to the strength of the bond. For a single bond is approximately $5 \times 10^5 \text{ gm sec}^{-2}$. It becomes double and triple for the double and triple bonds respectively.

c = Velocity of the radiation = $2.998 \times 10^{10} \text{ cm sec}^{-1}$

Thus, the value of vibrational frequency or wave number depends upon:

- (i) Bond strength, and (ii) Reduced mass.

Clearly, if the bond strength increases or the reduced mass decreases, the value of the vibrational frequency increases.

Let us calculate the approximate frequency of C—H stretching vibration from the following data:

$$k = 5 \times 10^5 \text{ gm sec}^{-2}$$

$$\text{Mass of carbon atom } (m_1) = 20 \times 10^{-24} \text{ gm}$$

$$\text{Mass of hydrogen atom } (m_2) = 1.6 \times 10^{-24} \text{ gm}$$

$$\begin{aligned}\bar{\nu} &= \frac{1}{2\pi c} \sqrt{\frac{k}{m_1 m_2}} \\ &= \frac{7}{2 \times 22} \left(\frac{5 \times 10^5 \text{ gm sec}^{-2}}{\frac{20 \times 10^{-24} \text{ gm} \times 1.6 \times 10^{-24} \text{ gm}}{(20 + 1.6) 10^{-24} \text{ gm}}} \right)^{1/2} \\ &= 9.3 \times 10^{13} \text{ sec}^{-1}\end{aligned}$$

This value of frequency can be converted into wave number as follows:

$$\bar{\nu} = \frac{\nu}{c} = \frac{9.3 \times 10^{13} \text{ sec}^{-1}}{3.0 \times 10^8 \text{ m sec}^{-1}} = 3.1 \times 10^5 \text{ m}^{-1} = 3100 \text{ cm}^{-1}$$

C = C stretching is expected to absorb at higher frequency than C—C stretching. It is due to the higher bond strength (value of k) of the double bond compared to the single bond. Similarly, O—H stretching absorbs at higher frequency compared to C—C bond. It can be explained on the basis of the smaller value of reduced mass for O—H compared with C—C bond. We can expect O—H to absorb at higher frequency as compared to F—H. But this is not true. Actually, F—H absorbs at the higher frequency. This can be explained due to the higher electronegativity of fluorine compared to that of oxygen.



Hooke's Law

EXAMPLE 1. Calculate the wave number of stretching vibration of a carbon-carbon double bond. Give force constant ($k = 10 \times 10^5 \text{ dynes cm}^{-1}$)

SOLUTION. Atomic mass of carbon = 12 amu

Reduced mass

$$(\mu) = \frac{m_1 m_2}{m_1 + m_2} = \frac{12 \times 12}{12 + 12} = 6 \text{ amu}$$

$$= \frac{6}{6.02 \times 10^{23}} \text{ gm} = 9.97 \times 10^{-24} \text{ gm}$$

Wave number

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

$$\bar{\nu} = \frac{1}{2 \times 3.142 \times 3 \times 10^{10} \text{ cm s}^{-1}} \sqrt{\frac{10 \times 10^5 \text{ gm sec}^{-2}}{\frac{6 \text{ gm}}{6.02 \times 10^{23}}}}$$

$$= \frac{1}{18.852 \times 10^{10} \text{ cm s}^{-1}} \times \sqrt{10.03 \times 10^{28}} = 0.1680 \times 10^4 \text{ cm}^{-1}$$

$$= 1680 \text{ cm}^{-1}.$$

3.5 Number of Fundamental Vibrations

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