
UNIT 3 INFRA RED SPECTROMETRY

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3.1 INTRODUCTION

In the previous unit, you have studied about the UV-VIS spectrometry – an important analytical tool that involves the measurement of the consequence of interaction of electromagnetic radiation in the UV and/or visible regions with the molecules, ions or complexes. The spectra so obtained could be utilised to study the presence, nature and the amount of chromophores in a molecule.

In this unit, we take up the study of infra red (IR) spectrometry-another common spectroscopic technique used by organic and inorganic chemists for structure elucidation and compound identification. We shall begin by understanding the theory behind IR spectroscopy in terms of the origin of the spectrum, the types and number of vibration modes possible in a molecule and the characteristic features of an IR spectrum. It will be followed by a brief account of the essential components of an IR spectrometer and different types of IR spectrometers with their principles, advantages and disadvantages. Thereafter we shall discuss the applications of IR spectrometry in diverse areas. In the next unit, we shall take up the study of Raman spectrometry – another important spectroscopic method of analysis.

Objectives

After studying this unit, you should be able to:

- explain the origin of IR spectrum,
- calculate the vibrational degrees of freedom for different polyatomic molecules,
- describe different types of vibrational modes of molecules,
- identify the IR active and inactive modes of vibration for small molecules,
- explain the reasons for the complex nature of IR spectrum,
- describe briefly the components of IR instruments,

- explain the principles of different types of IR instruments,
- compare and contrast different types of instruments in terms of their principles and applications, and
- list and explain different applications of IR spectrometry.

3.2 THEORY OF INFRA RED SPECTROMETRY

You know that the bond between two atoms in a molecule is not rigid. It has elasticity and as a consequence the atoms in the molecule do not remain fixed in their positions. They are in a constant state of motion around their mean position. The molecule is said to be undergoing vibrational motion. The quantum mechanical treatment of the molecular vibrational motion shows that it is quantised. As the transitions between these quantised energy levels can be brought out by using EM radiation in the infra-red range it gives rise to an IR spectrum. As the excitation among the quantised vibrational energy levels of the molecules is involved, the IR spectroscopy is also known as **vibrational spectroscopy**. Let us learn about the vibration motion of the molecules and origin of IR spectrum. We begin with diatomic molecules.

3.2.1 Vibrations of Diatomic Molecules

A vibrating diatomic molecule, AB can be visualised as a **simple harmonic oscillator** in Fig. 3.1. The two atoms A and B (shown as balls) are assumed to be joined by a bond (shown as a spring) of length r_{eq} and molecule is oscillating around its mean position, r_{eq} .

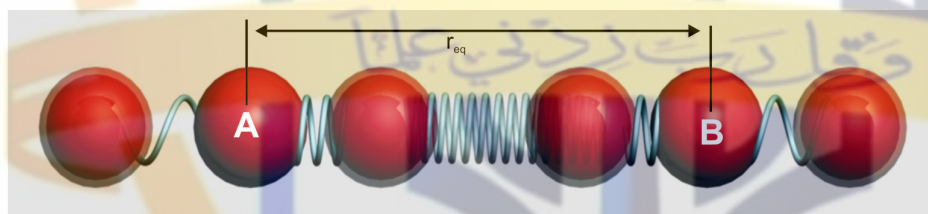


Fig. 3.1: Representation of a harmonic oscillator

The quantised energy levels obtained by the quantum mechanical treatment of the harmonic oscillator are given in Fig 3.2 (a). A higher energy corresponds to a larger amplitude of oscillation. The harmonic oscillator model of a diatomic molecule however, is oversimplified and has some limitations. For example, such a molecule would never dissociate no matter how much of the energy we provide. More and more energy would just increase the amplitude of vibration. This, as you know, is in contradiction with the actual situation as the real molecules do dissociate. The real molecules are not like harmonic oscillators; these have some element of **anharmonicity**. When we consider the anharmonic nature of the vibrating diatomic molecule, the energy levels get modified as shown in Fig. 3.2(b).

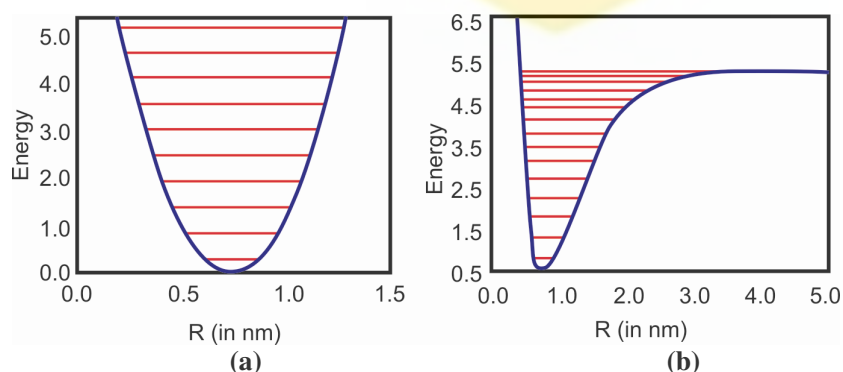


Fig. 3.2: The potential energy curves for a) harmonic and b) anharmonic oscillator

Necessary Condition for Observing IR Spectrum

The presence of quantised energy levels does not ensure transitions amongst them when the radiation of appropriate wavelength is made to fall on it. For the oscillating electrical field of the EM radiation to interact with the vibrating molecule, **it is essential that the molecule has a fluctuating or oscillating dipole moment**. In the absence of such a dipole moment the radiation cannot interact with the molecule and we say that the vibration in the molecule is IR inactive. For example, a homonuclear diatomic molecule like H_2 would not give an IR spectrum because it does not have a dipole moment and also it does not generate a fluctuating dipole moment. On the other hand, HBr gas has a dipole moment and it does absorb in the IR region.

Now, if a molecule has a fluctuating dipole moment, which transitions would we observe? For this we need to know about the selection rule.

Selection Rule for the Vibrational Spectroscopy

The selection rule for a spectroscopy refers to the condition that tells us about the transitions that are possible (or allowed) amongst the quantised energy levels. The selection rule for the vibrational spectroscopy is, $\Delta v = \pm 1, \pm 2, \pm 3 \dots$ etc.. This means that the molecule may go over from any vibrational level to any other level. This in turn means that the spectrum would be quite complex. However the actual IR spectrum for a diatomic molecule is not so complex. The pure vibration spectrum of a diatomic molecule consists of mainly three signals: an intense signal for the **fundamental vibration**, that arise from the transitions from ground state ($v = 0$) to the first ($v = 1$) excited vibrational level (Fig.3.3). The second is a weak signal for its **first overtone** that is observed at roughly double the frequency of the fundamental band; it is due to the transitions from ground state ($v = 0$) to the second ($v = 2$) excited vibrational level. The third and the weakest signal is observed at roughly triple the frequency of the fundamental band; it is due to the transitions from ground state ($v = 0$) to the third ($v = 3$) excited vibrational level. It is called the **second overtone**.

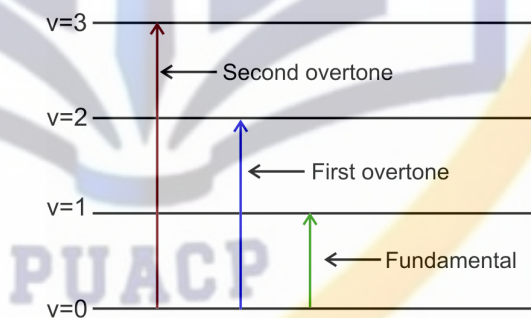


Fig. 3.3: The transitions for fundamental vibration and the overtones

What would be the nature of spectrum in a polyatomic molecule? Let us try to extend our understanding of the vibrational behaviour of a diatomic molecule to polyatomic molecules.

3.2.2 Vibrations of Polyatomic Molecules

You would agree that the vibration spectrum of a polyatomic molecule with a number of bonds is expected to be quite complex. Indeed, the IR spectrum for a molecule of a reasonable size is quite complex and it is almost impossible (and mostly not desirable) to interpret all the signals obtained. However, with a little understanding of the possible vibration modes, their IR activity (or otherwise) and the concept of characteristic group frequencies we can make enough leads into deciphering the structural complexities of the molecules. Let us try to make an attempt to have that understanding.

A diatomic molecule has only one possible way of executing vibrational motion because there is only one bond and the molecule is linear. A molecule containing more than two atoms has more than one bond and also these bonds may be at angle with respect to each other. For example, water is a triatomic molecule having two O – H bonds at an angle of about 104.5° . Such a molecule can vibrate in more than one possible way, like both the bonds of the molecule may vibrate symmetrically i.e., in unison or they may be showing an asymmetric vibration or the vibration may involve a change in the bond angle (Fig 3.5). How do we ascertain the possible number of such modes of vibration for a larger molecule? The discussion that follows will help to give an answer.

For a molecule containing N atoms we need to specify $3N$ coordinates (three for each atom) so as to completely describe the molecule. This fixes all the bond lengths and angles for the molecule. We may say that the molecule has $3N$ degrees of freedom. You are aware that the molecule shows translational, rotational and vibrational motions. Since the molecule can move around anywhere in the three dimensional space, the position of the molecule can be specified in terms of the three coordinates of the centre of mass of the molecule. That is, we need three degrees of freedom to account for or to describe the translation motion. So, we are left with $(3N - 3)$ degrees of freedom for rotational and vibrational motion.

The translation motion of the molecule refers to the simultaneous movement of all the atoms of the molecule in the same direction.

The number of rotational modes depends on the geometry of the molecule. A linear molecule can rotate around only two of the three axes. If the molecule lies along the "x" axis, then it can rotate only around the "y" or "z" axis. If we try to rotate the molecule around the "x" axis, then the positions of the atoms do not change. We therefore say that a linear molecule can have only two rotational degrees of freedom along with its three translational modes. However, a non-linear molecule may rotate around each of the three axes i.e., it has three rotational degrees of freedom. So we are left with $(3N - 5)$ degrees of freedom for a linear molecule and $(3N - 6)$ degrees of freedom for a non-linear molecule. These are the vibrational modes of the molecule. Thus, the linear CO_2 molecule will have $3(3) - 5 = 9 - 5 = 4$ vibrational modes whereas, water – a non linear triatomic molecule – would have only $3(3) - 6 = 9 - 6 = 3$ vibrational modes.

For a linear molecule containing N atoms, the total vibrational modes are $3N - 5$ and for a non-linear molecule of the same size, the total number of vibrational modes is $3N - 6$.

SAQ 1

What is the basis of IR spectrum?

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Normal Modes of Vibrations

A molecule can vibrate only in certain modes, known as **normal modes**. In the course of normal mode of vibration each atom is displaced in such a way 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 i.e., there is no translational motion of the molecule as a result of vibration.

Each normal mode corresponds to a vibrational degree of freedom. Alternatively, we can visualise a normal mode refers to an independent simultaneous motion of atoms or group of atoms that may be excited without leading to the excitation of any other

The linear and nonlinear molecules have $(N - 1)$ stretching vibrations.

This concept of normal mode helps in understanding of the concept of group frequencies discussed later.

normal mode. There are two types of the normal modes of vibration for a polyatomic molecule. These are **stretching vibrations** and **bending vibrations**. Let us try to understand about these.

- i) **Stretching vibrations:** In stretching vibrations, the atoms move along the bond axis so that the bond length increases or decreases at regular intervals. The stretching vibrations again are of two types- **symmetric** and **antisymmetric stretching**. In symmetric stretching of a triatomic molecule, both the bonds connected to a common atom either elongate or contract simultaneously. In case of antisymmetric stretching, if one bond is lengthened, the other bond is shortened or vice-versa. The stretching vibrations along with the bending vibrations (discussed below) are shown in Fig. 3.4 and Fig. 3.5, respectively for linear and angular molecules of the AB_2 type. The arrows attached to each atom show the direction of its motion during half of the vibration; it reverses in the other half.

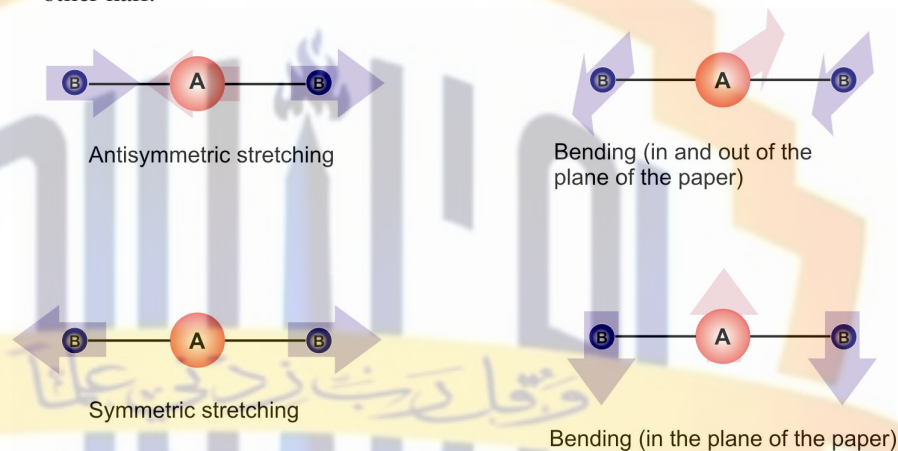


Fig. 3.4: Normal modes of vibrations of a linear triatomic molecule, AB_2

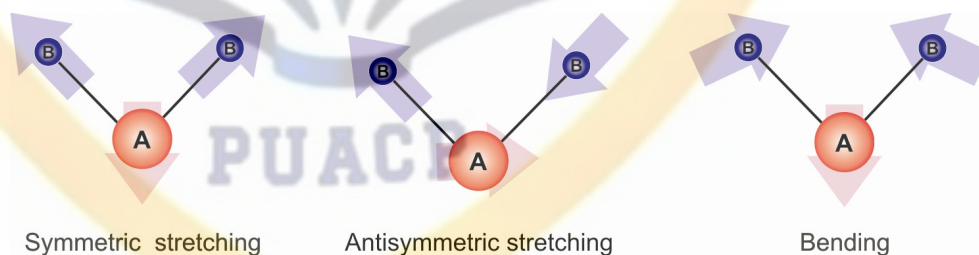


Fig. 3.5: Normal modes of vibrations of an angular triatomic molecule, AB_2

In general there are $(2N - 4)$ and $(2N - 5)$ bending vibrations for linear and nonlinear molecules respectively.

- ii) **Bending vibrations:** The bending vibrations are said to occur when there is a change in the 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 bending vibrations for a polyatomic molecule. A linear triatomic molecule has two bending vibrations as shown in Fig.3.4, while a nonlinear triatomic molecule has only one bending vibration (Fig.3.5). The bending modes also are of different types. These are called **scissoring**, **rocking**, **wagging** and **twisting**. For methylene ($-\text{CH}_2$) group, the possible bending modes of vibrations are shown in Fig. 3.6. The $3N - 6$ rule does not apply here because $-\text{CH}_2$ group is not a molecule but only a portion of it.

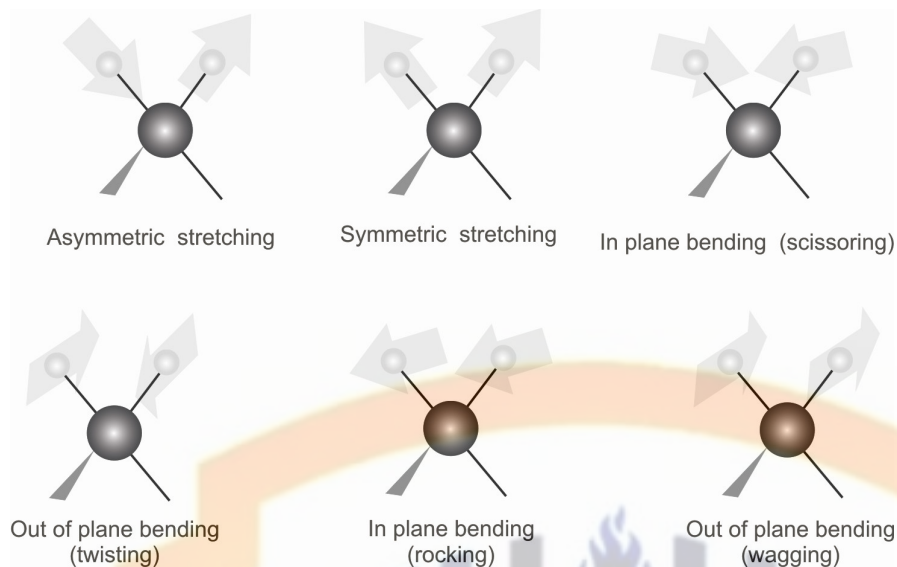


Fig. 3.6: Vibrational modes of methylene ($-\text{CH}_2$) group

3.2.3 Complexity of the IR Spectra of Polyatomic Molecules

In the light of the discussion above we can say that the infrared spectrum of a polyatomic molecule would consist of an absorption band at each of the $(3N - 6)$ or $(3N - 5)$ fundamental frequencies for nonlinear and linear molecules, respectively along with the corresponding overtones. However, in addition, we may also have weak bands due to combination of two fundamentals vibrations called **combination bands** or difference of two fundamentals called **difference bands**. More so, when sometimes a fundamental and an overtone have frequencies very close to each other, these may resonate leading to the appearance of signals at frequencies higher and lower relative to the original. This phenomenon is called **Fermi resonance**.

The infrared spectrum of a compound consists of strong fundamental absorptions and weak overtones, combination band and Fermi resonance bands.

As the number of atoms in a molecule increases, the spectrum becomes quite complex. Let us take example of a larger molecule say n-decane, $\text{C}_{10}\text{H}_{22}$, having 32 atoms. The number of fundamental vibrational modes would be $3(32) - 6 = 96 - 6 = 90$. Along with the corresponding overtones and combination bands the spectrum is expected to have a few hundred signals. However, the actual spectrum has much fewer of them. This is so because all the vibrations may not be IR active. You would recall that for a vibration mode to be IR active it must be associated with a change in the dipole moment. Other reasons for not observing so many signals could be that either they are too weak or are outside the range of the instrument.

3.2.4 Characteristics of IR Spectrum

We are sure that on the basis of the discussion above you would have created some picture of the IR spectrum in your mind and must be anxious to know how the IR spectrum actually looks like. A typical IR spectrum is given in Fig. 3.7.

As you can see the ordinate (Y-axis) represents percent transmittance whereas the abscissa (X-axis) is either wavenumber or wavelength. It means that is the positions of IR absorption signals are presented as either wavenumbers (ν) or wavelengths (λ). The wavenumber unit (in cm^{-1} , reciprocal centimetre or centimetre inverse) however is preferred over wavelength (in μm , micrometers), because an increase in it corresponds to an increase in energy (and frequency) whereas the wavelength is related inversely to the energy. Also, though abscissa is marked in cm^{-1} it is commonly (though incorrectly) referred to as the frequency. The frequency by itself is normally not used

Molecular Spectroscopic Methods-I

Recall from sec 1.2 that Wavenumber is the inverse of wavelength.

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

Generally it is expressed in terms of cm^{-1} and obtained by taking the inverse of the wavelength in cm.

$$\bar{\nu} \text{ (in cm}^{-1}\text{)} = \frac{1}{\lambda \text{ (in } \mu\text{m)}} \times 10^4$$

due to its inconvenient size. You must also take note of the change in the scale of abscissa at 2000 cm^{-1} ; it is more compact at higher values.

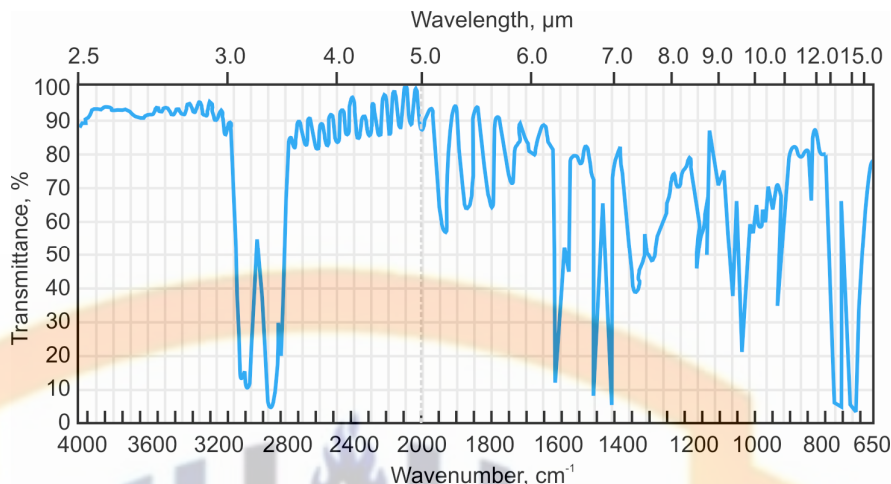


Fig. 3.7: A representative IR spectrum

$$\text{Transmittance, } T = \frac{P}{P_o}$$

$$\% T = \frac{P}{P_o} \times 100\%$$

You have learnt in the previous unit on UV-VIS spectrometry that the transmittance, T , is the ratio of radiant power transmitted by the sample (P) to the radiant power incident on the sample (P_o). It ranges from 0 to 100% T .

Having learnt about the origin and the characteristics of IR spectrum let us now learn about the components of the instruments used for recording the IR spectrum. However, before going ahead why don't you answer the following SAQs.

SAQ 2

Calculate the number of vibrational degrees of freedom for methane, CH_4 . How many of these would be bending modes?

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SAQ 3

Why is the IR spectrum preferably shown in wavenumber units?

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3.3 BASIC COMPONENTS OF IR INSTRUMENTS

As IR spectrometry is also based on absorption spectroscopy like UV-VIS spectrometry, the basic components of IR instruments are also similar to that of the UV-VIS spectrometers, as discussed in the previous unit. The essential components of an IR instrument are as follows.

- A **stable and powerful** source of radiation

- Sampling device transparent to the radiation
- Monochromator or frequency modulator
- Transducers or detectors,
- Signal processing and output device

Let us learn about these components in brief.

3.3.1 Sources of IR Radiation

The commonly employed IR source is generally an electrically heated inert solid that emits a continuum of radiation like a black body. The best sources available and commonly employed in the IR spectrophotometers are

- Nernst or Glower filament lamp
- Globar
- Ni-Cr (Nichrome) wire
- Carbon dioxide LASER

Nernst Glower: It is a cylindrical rod made up of a mixture of **zirconium, yttrium and erbium oxides** (diameter of 1–2 mm and length of about 20 mm). It is electrically connected through platinum wire and heated by the passage of an electrical current to a temperature of about 1200 to 2200 K.

Globar: It is a **silicon carbide rod** (diameter of 5 mm and length of about 50 mm) which is electrically heated to about 1500 K. The electrical contacts have a risk of arcing therefore water cooling of the contacts is used. The spectral output is comparable with the Nernst glower, except at short wavelengths (less than 5 μm) where its output becomes larger.

Incandescent nichrome wire: It is a tightly wound coil of **nichrome (Ni-Cr)** wire, electrically heated to 1100 K. It produces a lower intensity of radiation than the Nernst or Globar sources, but has a longer working life.

Alternatively, a rhodium wire heater sealed in a ceramic cylinder may be used as an incandescent wire source.

Carbon dioxide lasers: The tuneable carbon dioxide lasers produce closely spaced discrete lines in a limited range of IR radiation (900 to 1100 cm^{-1}). Though the tuneable laser has limited range but it provides a much larger intensity of all the lines in the range. The laser can be tuned to any of these lines and can be used for the quantitative determination of different species like, ammonia, benzene and nitrogen dioxide etc.

Carbon dioxide lasers find application as a source in selective monitoring of atmospheric pollutants.

In addition, some IR sources like, **mercury arc and tungsten** filament lamp are also used.

3.3.2 Sampling Devices

The handling of sample for the measurement of IR spectra is not simple. Firstly because unlike UV-VIS spectrometry, glass or quartz cannot be used as a material for making **cuvettes** to be used in the infrared region. It is so because glass absorbs strongly at most of the frequencies in this region. Secondly, analysing an analyte as a solution is also not easy because most of the solvents of the organic compounds themselves absorb in many regions of the IR spectrum. **In fact there is no solvent that is transparent in the whole range.**

The surfaces of the IR windows get fogged by absorbing moisture and need to be polished with buffing powder to regain transparency

In the absence of glass, the salts like NaCl and KBr which are transparent in the IR region are used for the construction of the cuvettes. **These cuvettes are called IR windows.** The **NaCl windows** are most commonly used for routine work in the region

4000-650 cm^{-1} as these are cheaper than **KBr windows**. However, for measurements below 650 cm^{-1} , the KBr cells are the right choice because NaCl starts absorbing in this region.

The sampling techniques depend upon the phase (solid, liquid or gas) of the sample being analysed. Let us discuss the sample preparation procedures of samples in different physical states:

- i) **Sampling of Gases:** The gaseous samples are taken in approximately 10 cm long cuvettes having sodium chloride windows at either end as shown in Fig. 3.8(a). The cuvette is kept across the path of infrared beam. The path length of the cells can be easily varied over a long range. In these specially designed cuvettes the internal surfaces are made reflective whereby the radiation can be made to travel through the sample many a times before coming out of it.

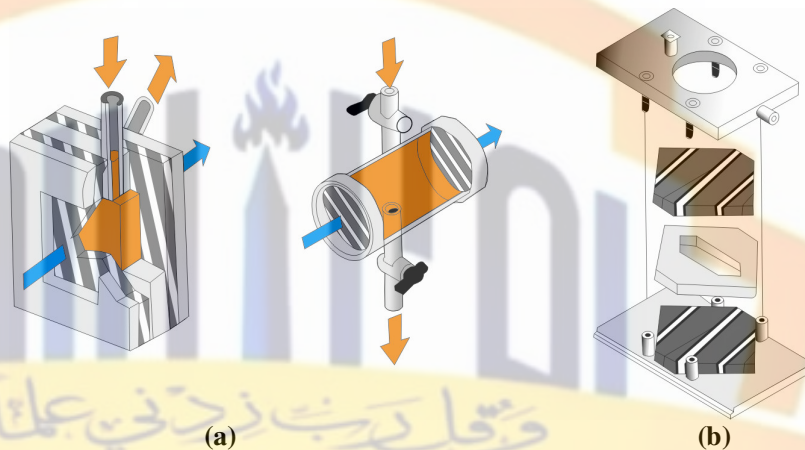


Fig. 3.8: Sampling cuvettes for a) gaseous and b) liquid samples

- ii) **Sampling of Liquids:** For liquid samples, cuvettes with fixed path lengths as well as of variable path lengths are commercially available. The cuvettes of less than 0.01 mm thickness are made of sodium chloride or potassium bromide rectangular plates sealed by gaskets and clamped together as depicted in Fig.3.8 (b). A drop of liquid is squeezed between the NaCl/KBr plates which are put in a cuvettes holder and scanned.
- iii) **Sampling of Solids:** As most of the organic compounds absorb extensively in the mid IR region, it becomes difficult to find a suitable solvent whose signals would not interfere with those of the sample. In such case it becomes almost essential to analyse the solid itself. There are two techniques for handling a solid sample. These are as follows:
- Mull technique
 - Pelleting with KBr

Mull technique: In this technique called **Nujol mull** technique, the sample is finely ground to a paste in a small amount of **mineral oil hexachlorobutadiene (nujol)**. It forms a fine suspension or mull of the sample in the oil. The mull is pressed between two NaCl or KBr plates to give a thin film of the sample. The two plates are then clamped in a holder with open windows on both sides and the assembly is kept in the path of the infrared beam.

KBr Pelleting : in this technique, a small amount of sample (~ 1 –2 mg) is mixed and **ground with about hundred times its mass of potassium bromide**. The mixture is transferred to an evacuable die (Fig. 3.9), to remove the moisture

This technique is useful when the amount of the liquid sample is small or when a suitable solvent is not available

In addition to these two methods, the solid samples may be analysed by using attenuated total reflectance spectrometry or with the help of photoacoustic IR spectrometry.

and then a high pressure is applied to yield a transparent pellet. It is put in a suitable holder and the whole assembly is placed in the line of the infrared beam.



Fig. 3.9: Die assembly for making KBr pellets

Thin films: The IR spectrum of a thin film can be obtained by placing a sample of the film in a suitable holder, such as a card with a slot for the sample window. This method is quite useful in the calibration of the instrument with a standard like polystyrene for which the bands are accurately known.

SAQ 4

Why is it difficult to take IR spectra in solution phase?

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SAQ 5

Why can't we use glass cell holders for IR spectrometry?

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3.3.3 Monochromators and Frequency Modulators

In the previous unit you have learnt about rotating prisms and diffraction gratings as **monochromators** which disperse the radiations from the source falling on it and can be used to allow the radiations of different wavelengths to come out of the exit slit. These are then passed through the sample and the interaction is monitored. In **dispersive IR spectrometers (discussed in subsection 3.4.1)** we use similar components, the only difference being that the monochromator is placed after the sample. You would recall that the monochromator is placed before the sample in UV-VIS spectrometry.

A monochromator is an optical device that transmits a selectable narrow band of wavelengths of radiation chosen from a wider range of wavelengths available at the input.

In FT-IR instruments (subsec. 3.4.2), used quite extensively now a days, the radiations are not dispersed before or after passing through the sample. Instead, the response of the sample to all the wavelengths in the range is measured simultaneously and the signal so obtained is modulated and collected in time domain. This is then Fourier transformed to get the desirable frequency domain signal.

The modulation of the signal is achieved by **Michelson interferometer**. It modulates the frequency of the IR radiation into the audio frequency range. The fluctuations of

the radiation power in the audio frequency range are then followed by suitable transducers. This results into a modulated time domain signal which contains all the information about the spectrum. This is then be Fourier transformed to retrieve the information in the frequency domain.

3.3.4 Transducers or Detectors

There are three categories of transducers employed for detecting IR radiation. These are as follows:

- Thermal transducers : Thermocouples and Bolometers
- Pyroelectric transducers
- Photoconducting transducers

Let us learn about these in brief.

Thermal Transducers: These are the ones whose response depends, as the name suggests, on the thermal effects. There are two types of thermal transducers-the thermocouples and bolometers.

The **thermocouples** consist of a pair of junctions of different metals; for example, two pieces of bismuth fused to either end of a piece of antimony. The infrared radiations are made to fall at one junction called **hot junction**, the other junction called **cold junction** is kept at a constant temperature. The difference in temperature causes an electrical potential difference between the two joints and its value would depend on the difference in temperature between the junctions. The potential difference, thus, would depend on the amount of radiation falling on the hot junction and therefore is a measure of the radiation.

Some bolometers are prepared from semiconductors and are called **thermistors**.

The **bolometers** on the other hand are a kind of **resistance thermometer**. These are prepared using thin strips of **platinum or nickel**. You know that in general the **resistance of a metallic conductor changes with temperature**; these materials show quite a large changes in the resistance on changing the temperature. When infrared radiations falls on a bolometer, its temperature changes and causes a corresponding change in its resistance. The resistance so measured indicates the amount of the radiation falling on the bolometer.

The pyroelectric material undergo electric polarisation when an electric field is applied across it. The polarization persists even on removing the field and the degree of polarisation depends on the temperature.

Pyroelectric Detectors: these are temperature dependant capacitors made from a single crystalline wafer of a pyroelectric material, such as triglycerine sulphate. The heating effect of incident IR radiation causes a change in the capacitance of the capacitor which in turn can be measured in the external circuit as current. Pyroelectric detectors have a quick response time to be able to respond to the signal from the interferometer. Therefore they are used in most of the commercially available FT-IR instruments.

Photoelectric Transducers: these are like the mercury cadmium telluride transducers and comprise of a film of semiconducting material deposited on a glass surface which is sealed in an evacuated envelope. This is similar to the photomultiplier tube provided with dynodes in UV-VIS spectrophotometry. Absorption of IR radiation by them causes the electrical resistance of the semiconductor to decrease which can be measured. These transducers have better response characteristics than pyroelectric transducers, and also find use in FT-IR hyphenated instruments especially GC - FT-IR etc.

3.3.5 Signal Processing and Output Devices

The electrical signal from the transducer is suitably amplified or processed before it is sent to the recorder to give an output. In dispersive IR instruments, as discussed later, an **optical null system** is employed to achieve the equal intensities of the sample and

reference beams. The mechanism of processing the signal to give the recorder output is given in section 3.4.1. On the other hand in FT-IR instruments, the interferogram obtained in the time domain is mathematically processed by the computer to generate its Fourier transform i.e., the signal in frequency domain. This is then further processed to get the recorder output.

We are sure that having read about different components of IR instruments and their importance, you are equipped to learn about the IR spectrometers. It would be worthwhile to make an assessment of the understanding. Try to attempt the following SAQ before proceeding.

SAQ 6

In which type of IR spectrometers the tunable laser sources are useful?

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3.4 INSTRUMENTS FOR IR SPECTROMETRY

Infrared region of the electromagnetic spectrum spreads from the wavelengths of 0.8 to 1000 μm or wave numbers from roughly 12,500 to 10 cm^{-1} . It is bound by the red end of the visible region at lower wavelength end and the microwave region at higher wavelength end. It is further divided into three regions called **near IR**, **mid IR** and **far IR regions** (Fig. 3.10). The far infrared region (200 cm^{-1} to 10 cm^{-1}) is useful for molecules containing heavy atoms such as inorganic compounds and the near IR region (12000 cm^{-1} to 4000 cm^{-1}) concerns routine quantitative determinations of the simple molecules like water, CO_2 etc. of industrial and agricultural importance. **It is the mid infrared region (4,000 cm^{-1} to 200 cm^{-1}) that is of interest for general chemical analysis purposes.**

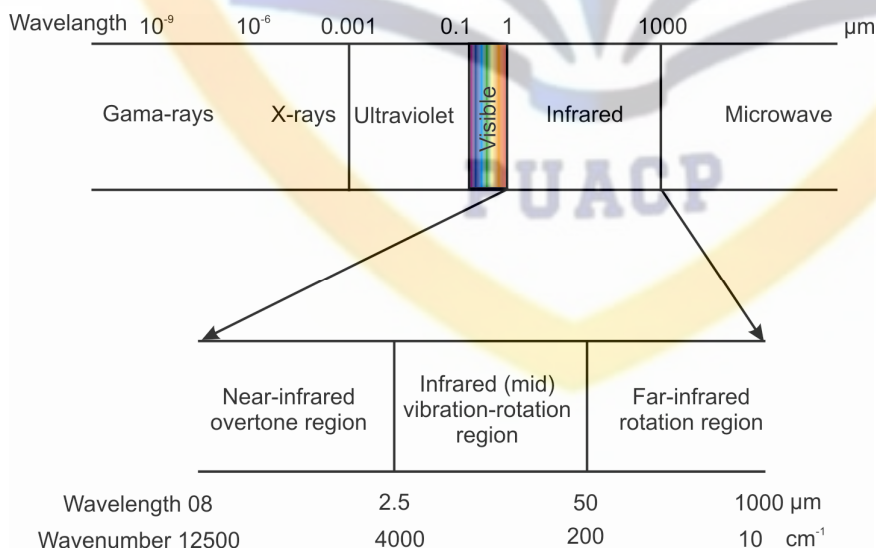


Fig. 3.10: Location of IR region in the electromagnetic spectrum

Since it is the mid IR region, which is commonly employed we would like to confine ourselves with the instrumentation of mid IR spectrometers only. Further, we do not intend to take up the detailed working and the construction of an IR spectrometer. We would be contented if you get an impression of the basic principles that lie behind an IR spectrometer. **There are three types of IR instruments.** These are,

- Dispersive infrared spectrometers
- Fourier-transform infrared spectrometers
- Non-dispersive infrared spectrometers

We would briefly discuss about the first two of these only as the third one is similar to the filter photometers discussed in Unit 2.

3.4.1 Dispersive Infra Red Spectrometers

As these instruments employ dispersion of radiation, these are called dispersive IR spectrometers.

These instruments though slightly outdated but are still employed, for qualitative work, due to economic reasons. The general set up of a dispersive IR instrument is similar to that of the double beam UV - Visible instrument. However there are two differences. Firstly, the radiation emerging out of the sample cell is dispersed with the help of a suitable grating and not by diffraction grating as in UV-VIS spectrometers. And secondly, in IR, the sample is located between the source and the monochromator. This arrangement helps in getting rid of the scattered radiation from the cell compartment. A schematic diagram of the double beam dispersive instrument is given in Fig. 3.11.

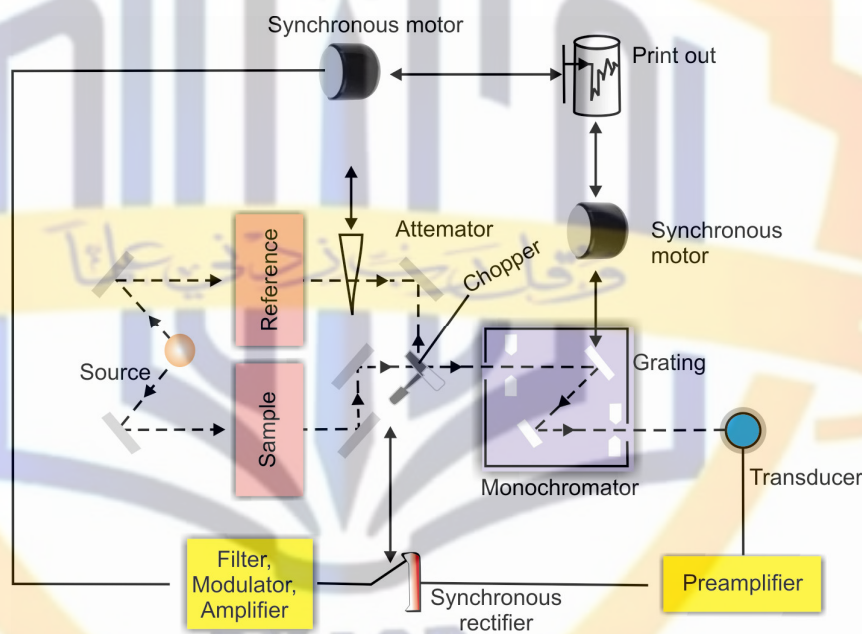


Fig. 3.11: A schematic diagram showing different components and the optic path of a dispersive IR spectrometer

The radiation produced from an IR source is made to fall on a beam splitter which splits the beam into two equivalent half beams. These beams are focused by separate concave mirror systems on the sample and the reference (normally the solvent) cells. The beam emerging from the reference cell is made to fall on the chopper through an attenuator while the radiation from the sample is sent directly on to the chopper. The chopper alternately allows the reference beam or the sample beam to enter the monochromator. These beams after dispersion by the monochromator are made to fall on the detector. The signals originating from the detector are then suitably processed and send to the recorder for an output.

Michelson interferometer is employed for the modulation of the signal; the output from the interferometer is an interferogram.

3.4.2 Fourier Transform Infra Red Spectrometers

In contrast to the dispersive IR spectrometers, where the signal from the sample is dispersed and the response at each wavelength (or wave number) is measured individually, the FT instruments collect the response at all the wavelengths simultaneously. In these multiplex instruments the monochromator is replaced by an

interferometer and the response of the sample to the whole range of IR radiation is suitably modulated and collected in the time domain. These are then decoded using the **Fourier transformation**. Therefore it is named the Fourier transform infra red spectrometer (FT-IR).

The basic instrument design for an FT-IR instrument is quite simple. A schematic diagram showing different components is given in Fig. 3.12. **The IR radiation from the source is first directed into an interferometer from where it is passed through the sample compartment and then it reaches to the detector.**

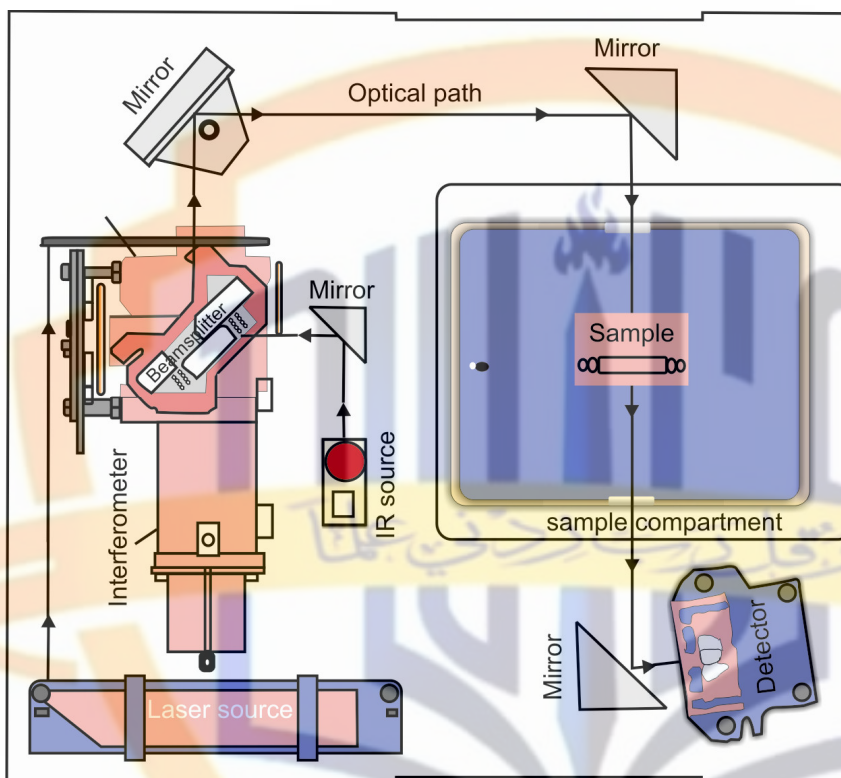


Fig. 3.12: A Schematic diagram showing different components and the optic path of a FT-IR spectrometer

In FT-IR spectrometers two types of detectors are commonly used. These are **deuterated triglycine sulfate (DTGS)** and **mercury cadmium telluride (MCT)** detectors. While, the DTGS detector is a **pyroelectric detector** that measures the changes in **temperature**, **MCT detector is a photon detector** that depends on the quantum of radiation generating electricity. Both of these detectors deliver rapid responses. Further while the DTGS detectors operate at room temperature, MCT detectors need to be maintained at liquid nitrogen temperature (77 °K) to be effective.

An important aspect of FT-IR is that most bench top FT-IR spectrometers are single-beam instruments and do not obtain transmittance or absorbance IR spectra in real time. A typical operating procedure is as follows:

Steps in getting an FT-IR spectrum of the sample with interferometer

1. In the first step, an interferogram is recorded without any sample in the beam and saved in computer memory. This interferogram is characteristic of the experimental set up and consists of the response of the spectrometer in terms of the performance of source, interferometer, and the detector. **This so called background spectrum also includes the contribution from any ambient water and carbon dioxide present in the optical bench.**

2. The interferogram is recorded again; this time with a sample introduced into the beam and also stored in computer memory. It contains signals from the sample and the background air or solvent.
3. The first interferogram is subtracted from the second with the help of a computer.
4. The resulting difference interferogram is then Fourier transformed to give the spectrum.

In the process of taking the difference between the two interferograms the absorption due to atmospheric gases is also removed.

Advantages of FT-IR Spectrometers

To minimise the strong background absorption from water and carbon dioxide in the atmosphere, the optical bench is generally purged with an inert gas or with dry air from which carbon dioxide has been removed.

- As the absorption at all wavelengths is recorded at the same time, this saves lot of experiment time. This is called the **multiplex or Fellgett advantage**. This leads to a spectrum with a better **signal to noise (S/N)** ratio in the same time as compared to a dispersive instrument.
- These are much faster and a given spectrum can be taken in less than a second. This provides for taking multiple scans for low concentration samples and then averaging them.
- FT-IR spectrometers give better frequency resolution and reproducibility.
- As there are no narrow slits in an FT-IR spectrometer, the energy output is much greater than in a dispersive instrument. This is referred to as the **Jacquinot advantage**. This also leads to a higher signal to noise ratio (S/N ratio) than the dispersive infrared spectrometers.
- In some FT-IR spectrometers a **helium neon laser** is used as an internal reference. This provides an **automatic calibration** with an accuracy of better than 0.01 cm^{-1} and eliminates the need for external calibrations. This internal laser reference is called **Connes advantage**.
- These can be easily adapted for remote use. For example, the beam may be **diverted to pass through an external cell and detector, as in GC- FT-IR**
- Due to its simple mechanical design with only one moving part (the moving mirror in interferometer), there **is less wearing out of** the components and hence **better reliability of** the spectrometer.
- Even though the spectra of many samples can be easily run on either FT-IR or dispersive instruments; the FT-IR spectrometers are the preferred choice for **samples because of higher sensitivity.**

GC-FT-IR uses a gas chromatograph to separate the components of sample mixtures and an FT-IR spectrometer to provide identification or structural information on these components.

Although GC-FT-IR spectroscopy is not as sensitive as GC-MS, it offers a major advantage in that it has the ability to identify structural isomers.

SAQ 7

Outline the steps involved in taking a FT-IR spectrum.

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3.5 APPLICATIONS OF INFRA RED SPECTROMETRY

IR spectroscopy is widely used in both research and industry as a simple and reliable technique for measurement, quality control and monitoring of dynamic processes. The intensity and position of the signals in infra-red spectrum allow the identification of structural elements like typical functional groups, hydrogen bonding, etc. It can also

help in the determination of conformations and even in monitoring the progress of chemical reactions. IR spectrometry finds applications in quite diverse areas like drugs and pharmaceuticals, chemical industry, polymer industry, forensic determinations, air pollution monitoring, agriculture, semiconductor microelectronics, clinical and biomedical determinations etc. Let us discuss some of these applications. We would broadly put them into three categories viz. qualitative, quantitative and other applications.

3.5.1 Qualitative Applications

The most important qualitative application of the **mid-IR spectrometry** is in the determination of the structures of organic and biochemical species. It is achieved in an empirical method wherein the signals in the IR spectra are identified with the help of correlation tables (briefly discussed below). Besides structure determination, we shall discuss how the IR spectra can be used in establishing the identity of a molecule? And also, how does it help in monitoring the progress of a reaction?

Structure Elucidation of Organic Molecules by IR Spectra

For structure determination of organic molecules, the infrared spectrum can be broadly divided into two regions. The region spanning from 3600 to 1200 cm^{-1} is called the **functional group region** and the region that includes all frequencies below 1200 cm^{-1} is called the **fingerprint region**. The two regions put together are important in the determination of the identity of a molecule. It is almost impossible to assign all the possible frequencies observed in the IR spectrum. However, identification of the characteristic features in the functional group region that includes stretching vibrations, of typical functional groups found in organic molecules, is quite important.

The fingerprint region involves molecular vibrations, characteristic of the entire molecule or large fragments of the molecule.

It may not be possible to conclusively assign a signal to the functional group because a number of functional groups may have absorptions in a given frequency range. However as the functional groups often give rise to a number of characteristic signals; we **must** look into other regions as well. Thus, the spectral interpretations should not be confined to one or two bands; the whole spectrum should be thoroughly examined. The characteristic frequencies of some important functional groups are summarised in a correlation chart given in Table 3.1. This would be quite useful to you when you attempt to interpret an unknown spectrum.

Though assigning the IR bands does not 'identify' the molecule, it does provide quite useful information about the nature of the molecule. The presence or absences of these bands in the spectrum provide crucial structural leads.

You can find a detailed account of how to use IR spectroscopy in the structure determination of organic compounds in Expt.4 of the MCHL-3 course. You would also learn how the IR spectrum can be used along with other spectroscopic tools in elucidating the structures of organic molecules in Unit 14 of the course.

Checking the Authenticity of a Compound

A common application of IR spectra is the comparative analysis of the spectra of an unknown compound with the spectra of the likely compounds. For this purpose the IR spectra may be considered analogous to a fingerprint of an individual. Like, there are no two individuals with the same set of fingerprints there are no two molecules with identical IR spectra, more so in the fingerprint region. Now a days we can subscribe to voluminous sets of catalogues containing IR, UV, NMR and mass spectra which are updated periodically. To decipher the true identity of a molecule we need to run co-IR. Here, the IR traces of the test molecule and the corresponding authentic sample or its spectrum from the available catalogues on the same chart are seen and matched. If the two compounds are identical then the signals in their IR spectra would match in terms of their positions and the relative intensities.

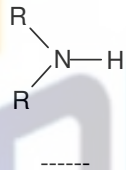
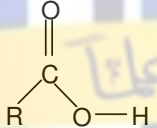

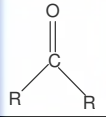
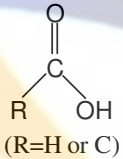
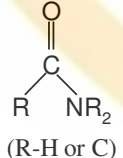
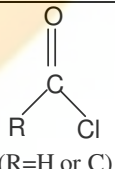
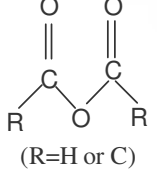
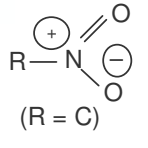
Besides the frequencies of the signals their shape and intensity also provide useful information about the nature of a compound being studied.

Monitoring the Progress of a Reaction

Another useful application of IR spectrometry is to monitor the progress of a reaction by monitoring the disappearance or appearance of a characteristic IR absorption

signal. For example, the oxidation of a secondary alcohol to a ketone can be monitored in terms of the disappearance of the O-H signal in the IR spectrum of the reaction mixture or by the appearance of the carbonyl signal of the ketone being produced. The rate of such reactions can also be measured by taking the time dependant spectra and using the Beer-Lambert Law.

Table 3.1: Characteristic IR frequencies of some functional groups

Functional group name	Structure (IR absorbing bond in bold)	IR frequency range (cm^{-1})	Functional group name	Structure (IR absorbing bond in bold)	IR frequency range (cm^{-1})
Alkane (C-H)	$\text{R}_3\text{C-H}$ (R= H or C)	3000-2800	Alkyne ($\text{C}\equiv\text{C}$)	$\text{RC}\equiv\text{CR}$ (R=H or C)	2260-2100
Alcohol (O-H)	RO-H	3600-3200 (broad band)	Nitrile ($\text{C}\equiv\text{N}$)	$\text{RC}\equiv\text{N}$ (R=C)	2260-2200
Amines, Amide (N-H)	 -----	3500-3300 (One band) 3500-3300 (two bands), 1650-1560 (bending)	Alkene ($\text{C}=\text{C}$)	$\text{R}_2\text{C}=\text{CR}_2$ (R=H or C)	1600-1680
Carboxylic acid (O-H)		3200-2500 (broad band)	Benzene ring ($\text{C}=\text{C}$)	 ($\text{C}=\text{C}$ ring "breathing")	1450-1600 2 to 3 bands
Aldehydes or Ketones ($\text{C}=\text{O}$)		1750-1705	Alcohol or Ether (C-O)	---	1300-1000 (R=H or C)
Carboxylic acid ($\text{C}=\text{O}$)	 (R=H or C)	1790-1680	Alkyne (C-H)	$\text{RC}\equiv\text{C-H}$ (R=C)	3300
Amide ($\text{C}=\text{O}$)	 (R-H or C)	1850-1800 and 1790-1730	Acid chloride ($\text{C}=\text{O}$)	 (R=H or C)	1815-1790
Acid anhydride ($\text{C}=\text{O}$)	 (R=H or C)	1850-1800 and 1790-1740 (two bands)	Nitro Compound (NO_2)	 (R = C)	1660-1500 (asymmetric stretch) 1390-1260 (symmetric stretch)

3.5.2 Quantitative Applications

In the previous unit you have learnt that how UV-VIS spectrometry can be used for quantitative determinations. In case of IR spectrometry the quantitative use is subject to a number of practical and instrumental problems. Some of these are as follows:

- Narrowness of the IR bands

- Low intensity of the source and low sensitivity of the transducer
- Non availability of the matched cells for the sample and reference
- Interference by solvents and IR absorbing air contaminants

In the light of these factors the quantitative application of IR requires a thorough planning of the experiment and a skilled execution of the procedure to obtain the spectrum. However in case of FT-IR, the results are much better. In addition, the technique of simultaneous determination discussed in Unit 2 can also be used for quantitative analysis using IR spectrometry.

A number of simple, portable and yet dependable IR spectrometers are available that may be used to quantitatively analyse a mixture of gaseous pollutants in a short time. These instruments are IR filter photometers and give good results but not as good as are possible with UV-VIS spectrophotometers.

3.5.3 Clinical and Biomedical Applications

IR spectroscopy has been employed for the analysis of several analytes in different biofluids and solid biological samples. This has applications in the analysis of pathological samples, for diagnostic purposes and also for non-invasive *in vivo* monitoring. For example, mid-IR spectroscopy has been used for analysing the faecal fat content or for the determination of the composition of urinary and gall stones. IR spectroscopic methods have also been used for the simultaneous quantification of serum concentrations of total protein, albumin, triglycerides, cholesterol, glucose urea, creatinine and uric acid etc. The serum samples are spread as a thin film onto an IR-transparent material and measured in the mid IR region after drying of the serum film. Combinations of visible microscopy and IR spectroscopy (FT-IR-MC) have been used in the development of methods for the diagnosis and identification of cancer cells.

SAQ 8

What do you understand by the finger print region of an IR spectrum? What is its significance?

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SAQ 9

What is meant by functional group region of an IR spectrum? How is it useful in deciphering the structure of an organic molecule?

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3.6 SUMMARY

Infra red spectrometry is one of the most common spectroscopic techniques used for structural elucidation and compound identification. The IR spectrum is a consequence of excitation among the quantised vibrational energy levels of the molecules and is characterised by three major parameters, namely the number of bands in the spectrum, the positions of the bands and the intensities of the bands. It is essential that the

molecule has a fluctuating or oscillating dipole moment in the course of a vibration for it to absorb IR radiation.

The IR spectrum for a molecule of a reasonable size is quite complex and it is not desirable to interpret all the signals obtained.

The basic components of an IR instrument include a stable source of radiation, a suitable sampling device, a monochromator or frequency modulator, a transducer and signal processing and output device.

In IR spectrometry, glass or quartz cannot be used as a material for making cuvettes as it strongly absorbs the IR radiation. Therefore IR windows made from the salts like NaCl and KBr which are transparent in the IR region are used for the purpose. Since most of the common solvents absorb in many regions of the IR spectrum, it becomes difficult to run spectra of the solutions.

There are three types of IR instruments. These are dispersive, FT and non dispersive types. The dispersive IR instruments are somewhat outdated but can be used for qualitative work as these are quite inexpensive. These instruments use reflection grating for dispersing the radiation emerging out of the sample cell.

In contrast to the dispersive IR spectrometers, the FT instruments collect the response at all the wavelengths simultaneously. In these instruments the monochromator is replaced by an interferometer and response of the sample is suitably modulated and collected in time domain which is then decoded using the Fourier transformation.

The FT spectrometers have certain advantages over dispersive instruments like it saves time and gives a better signal to noise (S/N) ratio, better frequency resolution reproducibility and a higher sensitivity, etc.

IR spectroscopy finds applications in quite diverse areas like drugs and pharmaceuticals, chemical industry, polymer industry, forensic determinations, air pollution monitoring, agriculture, semiconductor microelectronics, clinical and biomedical determinations etc.

3.7 TERMINAL QUESTIONS

1. List the different regions of infrared spectrum. Which is the most commonly used region?
2. What is the prerequisite for a molecule to show IR spectrum? Will the asymmetric stretching mode of H₂O molecule be IR active?
3. Compute the number of normal modes of vibration for benzene.
4. Draw the vibrational modes of CO₂ molecule using Fig.3.4 and comment on their IR activity.
5. What are the reasons for the complex nature of IR spectra for polyatomic molecules.
6. Briefly describe the sampling techniques for solid samples.
7. What are transducers? Give an example of the pyroelectric transducer and the type of IR spectrometers where it is used.
8. List the essential components of an FT-IR spectrometer. What is the role of interferometer?
9. Enumerate the advantages of FT-IR spectrometer over its dispersive counterpart.
10. Give three clinical and biomedical applications of IR spectrometry.

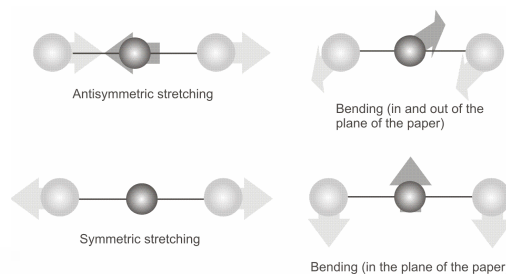
Self Assessment Questions

1. The excitation among the quantised vibrational energy levels of the molecules by absorption of electromagnetic radiation in the infra red region is the basis for IR spectrum.
2. For methane, $N = 5$, As the molecule is non linear the total vibrational degrees of freedom would be $3N - 6 = (3 \times 5) - 6 = 9$. Similarly, the number of bending modes would be, $2N - 5 = (2 \times 5) - 5 = 5$.
3. The wavenumber unit is preferred for the IR spectrum because an increase in it corresponds to an increase in energy.
4. It is difficult to take the IR spectrum of an analyte in a solution because most of the solvents of the organic compounds themselves absorb in many regions of the IR spectrum and therefore interfere in the spectrum of the compound.
5. Glass or quartz cannot be used as a material for making cells for taking IR spectra because it strongly absorbs at most of the frequencies in the IR region.
6. The tunable laser sources are useful in non dispersive IR spectrometers.
7. The FT-IR spectrum is recorded in the following four steps.
 - a) An interferogram is recorded without any sample in the beam and saved in computer memory.
 - b) The interferogram is recorded again with a sample introduced into the beam and also stored in computer memory.
 - c) The first interferogram is subtracted from the second with the help of a computer
 - d) The resulting difference interferogram is then Fourier transformed to give the spectrum
8. The fingerprint region in an IR spectrum refers to all the frequencies below 1200 cm^{-1} . The signals in this region arise from molecular vibrations characteristic of the entire molecule or large fragments of the molecule. There are no two molecules with identical IR spectra, more so in the fingerprint region. It can be used to check the authenticity of a compound. If the two compounds are identical then the signals in their IR spectra would match in terms of their positions and the relative intensities.
9. The region spanning from 3600 to 1200 cm^{-1} is called the functional group region. It arises from stretching vibrations of typical functional groups found in organic molecules. Assigning the bands in this region help in identifying the functional groups present in the molecule; these in turn help in deciphering the structure of the organic molecule.

Terminal Questions

1. Infrared region of the electromagnetic spectrum divided into the following three regions
 - Near IR,
 - Mid IR and
 - Far IRIt is the mid-IR region that is most commonly used.
2. The prerequisite for a molecule to show IR spectrum is that the vibrations within it must cause a net change in the dipole moment of the molecule. YES, the asymmetric stretching mode of H_2O molecule will be IR active.
3. Since benzene is not a linear molecule and has twelve atoms in it, the number of vibrational modes will be $[(3 \times 12) - 5 = 31]$.

4. The vibration modes of carbon dioxide can be drawn as follows:



Out of these all the modes other than the symmetric stretching mode will be IR active.

5. The IR spectra of polyatomic molecules are complex because of a number of reasons. First of all the infrared spectrum of a polyatomic molecule would consist of an absorption band at each of the $(3N-6)$ or $(3N-5)$ fundamental frequencies for nonlinear and linear molecules, respectively. In addition the overtones, the combination bands and the difference bands of these fundamental modes are also observed.
6. The sampling of the solids is done by preparing a dispersion of the solid in a liquid or a solid matrix. Accordingly there are two methods. In the *Nujol mull* technique, the sample is finely ground to a paste in a small amount of mineral oil (nujol) the mull is then pressed between two NaCl/KBr plates to give a thin film of the sample. In *KBr pelleting*, a small amount of sample (~ 1-2 mg) is mixed and ground with about hundred times its mass of potassium bromide and is transferred to an evacuable die to remove the moisture and then a high pressure is applied to yield a transparent pellet. The film or the pellet is then placed in the path of IR radiation.
7. Transducers are the specialized materials that respond to the IR radiation in terms of a temperature change or development of current or voltage. Deuterated triglycine sulfate (DTGS) is an example of pyroelectric transducer and is used in FT-IR spectrometers.
8. The essential components of a FT-IR spectrometer are
- Source
 - Interferometer
 - Sample assembly
 - Transducer or detector
 - Signal processing and output device
- The function of the interferometer is to modulate the signal.
9. Some of the advantages of the FT-IR instruments over the dispersive instruments are as follows:
- It is much faster because the absorption at all wavelengths is recorded at the same time and a given spectrum can be taken in less than a second.
 - These give better frequency resolution and reproducibility.
 - The energy output is much greater which leads to a higher S/N ratio.
 - FT-IR spectrometers do not need external calibration.
 - These have simple mechanical design which makes it more reliable.
10. Three clinical/biomedical applications of IR spectrometry are as follows.
- Determination of the composition of urinary and gall stones
 - Diagnosis and identification of cancer cells
 - Quantitative determination of serum constituents