

<b>Subject</b>	<b>Chemistry</b>
<b>Paper No and Title</b>	<b>Paper 12: Organic Spectroscopy</b>
<b>Module No and Title</b>	<b>Module 4: Basic principles and Instrumentation for IR spectroscopy</b>
<b>Module Tag</b>	<b>CHE_P12_M4_e-Text</b>

<b>Principal Investigator</b>		<b>Co- Principal Investigator and Technical Coordinator</b>
<b>Prof A.K.Bakhshi</b> Sir Shankar Lal Professor, Department of Chemistry University of Delhi		<b>Dr Vimal Rarh</b> Deputy Director, Centre for e-Learning and Assistant Professor, Department of Chemistry, SGTB Khalsa College, University of Delhi  <i>Specialised in : e-Learning and Educational Technologies</i>
<b>Paper Coordinator</b>	<b>Content Writer</b>	<b>Reviewer</b>
<b>Prof Diwan S Rawat</b> Department of Chemistry University of Delhi	<b>Prof Diwan S Rawat</b> Department of Chemistry University of Delhi  <b>Dr. Deepak Kumar</b> Assistant Professor Department of Chemistry University of Delhi	<b>Prof MSM Rawat</b> Department of Chemistry Hemwati Nandan Bahuguna Garhwal University
<b>Anchor Institute : SGTB Khalsa College, University of Delhi</b>		

**CHEMISTRY**
**PAPER No. 12: ORGANIC SPECTROSCOPY**
**MODULE No. 4: Basic principles and  
Instrumentation for IR spectroscopy**

**TABLE OF CONTENTS**

1. Learning Outcomes
2. Introduction
3. Origin of Infra-red Spectroscopy
4. Molecular Vibrations
5. Selection Rule
6. Fundamental Vibrations
7. Sample preparation
8. IR-Spectrometer
9. Dispersive Infrared Spectrometer
10. Fourier-Transform Infrared Spectrometer
11. Hands-on Operation of an FTIR Spectrometer
12. Summary

 **Pathshala**  
पाठशाला  
A Gateway to All Post Graduate Courses

**CHEMISTRY****PAPER No. 12: ORGANIC SPECTROSCOPY****MODULE No. 4: Basic principles and  
Instrumentation for IR spectroscopy**

## 1. Learning Outcomes

After studying this module, you shall be able to

- To understand the concept of Infra-red spectroscopy
- To predict the number of fundamental modes of vibration of a molecule
- To know how to make samples for recording the spectra of different organic compounds
- To understand the working of IR-spectrophotometer
- Hands-on experience of recording the IR-spectrum

## 2. Introduction

The most frequent spectroscopic technique used by organic and inorganic chemists is Infrared (IR) spectroscopy. It deals with the absorption of radiation in the infrared region of the electromagnetic spectrum. IR spectrum gives sufficient information about the structure (identification of functional groups) of a compound and can also be used as analytical tool to assess the purity of a compound. The absorption of infrared radiation by a molecule causes changes in their vibrational and rotational energy levels and hence IR-spectroscopy is also known as vibrational-rotational spectroscopy. Unlike UV-spectroscopy which has very few peaks in their spectrum, IR spectroscopy provides spectrum with a large number of absorption bands and hence provide plenty of information about the structure of a compound. Different bonds present in the spectra correspond to various functional groups and bonds present in the molecule.

The infrared spectrum can be divided into three main regions: the far infrared ( $<400\text{ cm}^{-1}$ ), the mid-infrared ( $4000\text{--}400\text{ cm}^{-1}$ ) and the near-infrared ( $13000\text{--}4000\text{ cm}^{-1}$ ). The mid IR region is of greatest practical use to the organic chemist, but the near- and far-infrared regions also provide important information about certain materials.

**Mid IR region:** The mid-infrared spectrum extends from  $4000$  to  $400\text{ cm}^{-1}$  and results from vibrational and rotational transitions. This region is most useful for the organic chemist since most of the organic molecules absorb in this region. The mid-infrared can be divided into two regions viz functional group region ( $4000\text{--}1300$ ) and finger print region ( $1300\text{--}600$ ).

**Functional group region ( $4000\text{--}1300$ ):** Most of the functional groups present in organic molecules exhibits absorption bands in the region  $4000\text{--}1300\text{ cm}^{-1}$ , hence this is known as functional group region. In this region each band can be assigned to a particular deformation of the molecule, the movement of a group of atoms, or the bending or stretching of a particular bond.

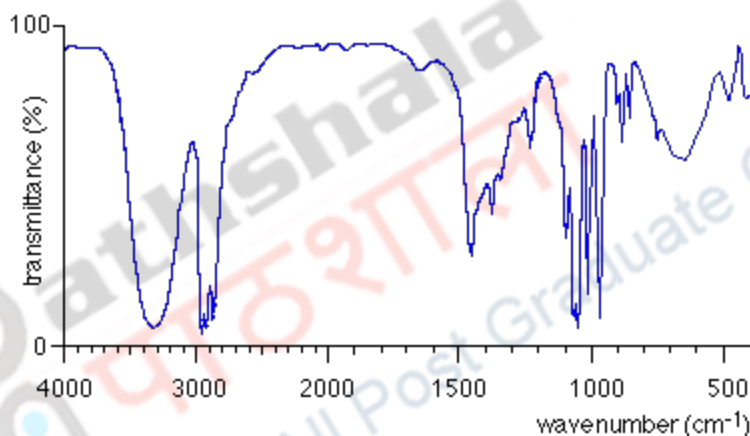
**Finger print region ( $1300\text{--}600$ ):** The region from  $1300\text{ cm}^{-1}$  to  $600\text{ cm}^{-1}$  usually contains a very complicated series of absorptions. These are mainly due to molecular vibrations, usually bending motions that are characteristic of the entire molecule or large fragments of the molecule. Except enantiomers, any two different compounds cannot have precisely the same absorption pattern in this region. Thus absorption patterns in this region are unique for any particular compound that is why this is known as finger print region.

It is very difficult to assign individual bands in this region. Two molecules having the same functional group may show similar spectra in the functional group region but their spectra differ in the finger print region. Therefore both the regions are very useful for confirming the identity of

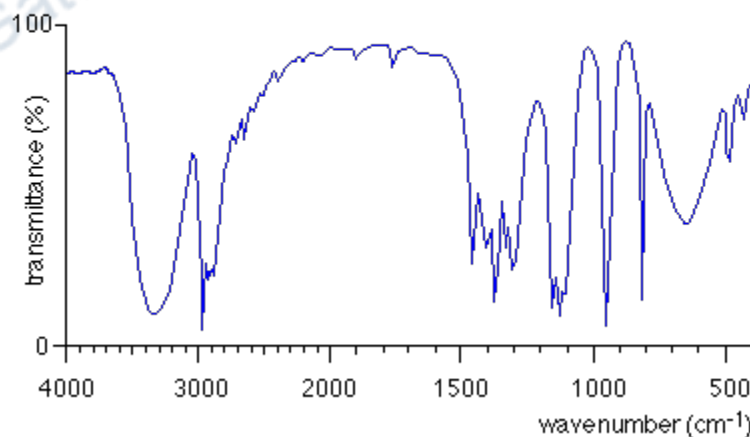
a chemical substance. This is generally accomplished by comparing the spectrum of an authentic sample. When two compounds show a good match between the IR spectra in all frequency To understand the importance of finger print region to identify a compound, we can take the example of propan-1-ol and propan-2-ol.

Both the compounds are alcohols and contain exactly the same bonds. Now if you compare the infra-red spectra of these compounds, the functional group region is very similar for both the compounds but the fingerprint region is totally different. Therefore fingerprint region could be crucial to identify the compound.

infra-red spectrum of propan-1-ol,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$



infra-red spectrum of propan-2-ol,  $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$



**Near-infrared region (13000–4000  $\text{cm}^{-1}$ ):** The absorptions observed in the near-infrared region (13000–4000  $\text{cm}^{-1}$ ) are overtones or combinations of the fundamental stretching bands. Bands in the near infrared are usually weak in intensity. They are often overlapped and hence are less useful than the bands in mid-infrared region.

NIR shows some similarities to UV-visible spectrophotometry and some to mid-IR spectrometry. Indeed the spectrometers used in this region are often combined UV-visible-NIR ones.

Usually Hydrogen-stretching vibrations that occur in the region 3 to 6  $\mu\text{m}$ , are the absorption bands due to overtones (or combination) of fundamental bands

NIR is generally used for quantitative organic functional-group analysis. The NIR region has also been used for qualitative analyses and studies of hydrogen bonding, solute-solvent interactions, organometallic compounds, and inorganic compounds

**Far-infrared region (600-100  $\text{cm}^{-1}$ ):** The far-infrared spectrum extends from 600 to 100  $\text{cm}^{-1}$ . Organometallic and inorganic molecules contain heavy atoms and have weak bonds, therefore the fundamental vibrations of these molecules fall in this region. Lattice vibrations of crystalline materials occur in this region.

### 3. Origin of Infra-red Spectroscopy

IR-spectroscopy gives the information about molecular vibrations or more precisely on transitions between vibrational and rotational energy levels. Since the absorption of infrared radiation leads to transition between vibrational and rotational energy levels, it is also vibrational-rotational spectroscopy.

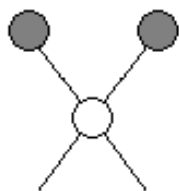
When a molecule absorb IR-radiation below 100  $\text{cm}^{-1}$ , transitions between rotational energy levels takes place. Since these energy levels are quantized, a rotational spectrum consists of discrete lines. If a molecule absorbs radiation in the range 100-10,000  $\text{cm}^{-1}$ , it causes transitions between vibrational energy levels. These energy levels are also quantised but vibrational spectra appear as bands rather than discrete lines. Each vibrational energy level is associated with a large number of closely spaced rotational energy levels or we can say that the energy difference between various rotational energy levels is very short than the energy difference between various vibrational energy levels. Therefore the vibrational spectra appear s vibrational-rotational bands instead of discrete lines. Organic chemists are mainly concerned with these transitions especially with those occur in the range 4000-667  $\text{cm}^{-1}$ .

### 4. Molecular Vibrations

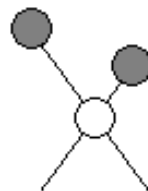
The atoms in a molecule do not remain fixed at certain positions. The two nuclei can vibrate backwards and forwards or towards and away from each other around an average position. There are two types of fundamental molecular vibrations viz stretching (change in bond length) and bending (change in bond angle).

**Stretching vibrations:** It involves a rhythmic movement along a bond axis with a subsequent increase and decrease in bond length. Stretching vibrations are of two types viz Symmetrical Stretching and asymmetrical stretching.

### Stretching vibrations



Symmetric

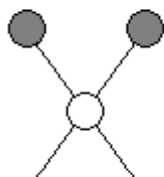


Asymmetric

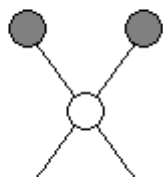
**Bending vibrations:** It involves a change in bond angle or movement of a group of atoms with respect to the rest of the molecule. Bending vibrations are of four types.

- i) Rocking
- ii) Scissoring
- iii) Wagging
- iv) Twisting

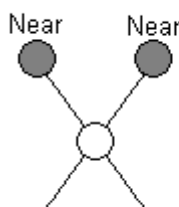
### Bending vibrations



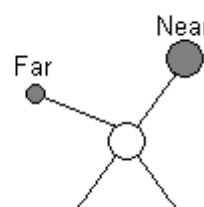
In-plane rocking



In-plane scissoring



Out-of-plane wagging



Out-of-plane twisting

All the bonds in a molecule are not capable of absorbing infrared radiation but only those bonds which are accompanied by a change in the dipole moment will absorb in the infra-red region. Thus, vibrations which are associated with the change in the dipole moment of the molecule are called infra-red active transitions otherwise the vibration is said to be IR-inactive and do not show any absorption band in the IR-spectrum. Generally, larger the change in the dipole moment, the higher is the intensity of absorption. Hence the vibrational absorption bands in simple hydrocarbons are weak while bands associated with bonds connecting atoms with considerable electronegativity difference give strong bands.

### 5. Selection Rule

IR-radiation is absorbed only when a change in dipole moment of the molecule takes place. Complete symmetry about a bond may eliminate certain absorption bands. Therefore number of absorption bands observed is not exactly equal to the fundamental vibrations, some of the fundamental vibrations are IR-active while others are not. This is governed by selection rule described below.

- 1) In a molecule with a centre of symmetry, the vibrations symmetrical about the centre of symmetry are IR-inactive.
- 2) The vibrations which are not symmetrical about the centre of symmetry are IR-active.



**Here are some examples which could explain the selection rule.**

- All the symmetrical diatomic molecules such as  $H_2$ ,  $N_2$  and  $Cl_2$  etc. are IR-inactive.
- The symmetrical stretching of the  $C=C$  bond in ethylene (centre of symmetry) is IR-inactive.
- The symmetrical stretching in  $CO_2$  is IR-inactive, whereas asymmetric stretching is IR-active.
- Cis-dichloro-ethylene molecule shows  $C=C$  stretching bands whereas trans molecule does not show this band.

## 6. Fundamental Vibrations

The IR spectrum of a compound may show more than one vibrational absorption bands. The number of these bands corresponds to the number of fundamental vibrations in the molecule which can be calculated from the degree of freedom (DOF) of the molecule. A molecule comprising of  $n$  atoms has a total of  $3n$  DOF. In a nonlinear molecule, three of these degrees of freedom are rotational and three are translational and the remaining  $(3n-6)$  correspond to vibrational degree of freedom or fundamental vibrations. Whereas in a linear molecule, only two degrees of freedom are rotational (because rotation about its axis of linearity does not change the positions of the atoms) and three are translational. The remaining  $(3n-5)$  degrees of freedom are vibrational degree of freedom or fundamental vibrations.

Simple diatomic molecules have only 1 bond and only 1 vibrational band. If the molecule is symmetrical such as hydrogen, nitrogen, and chlorine, the band is not observed in the IR spectrum. Asymmetrical diatomic molecules, e.g. CO and iodine chloride absorb in the IR spectrum..

It has been observed that in actual IR spectrum, the theoretical number of fundamental bands is seldom observed because there are certain factors which may increase or decrease the number of bands. Some fundamental vibrations lie outside the IR region ( $4000-400\text{ cm}^{-1}$ ), whereas some are too weak to be observed. Few fundamental vibrations are too close that they merge into one another. The occurrence of degenerate bands (bands of same frequency) also cause decrease in the fundamental vibrational bands.

For example: Carbon dioxide,  $CO_2$  is linear and has four fundamental vibrations but actually it shows only two bands ( $666\text{ cm}^{-1}$  and  $2350\text{ cm}^{-1}$ ). The symmetrical stretching vibration of  $CO_2$  is inactive in the IR because this vibration produces no change in the dipole moment of the molecule. The two scissoring or bending vibrations are equivalent and therefore have the same frequency (degenerate) at  $666\text{ cm}^{-1}$ . The asymmetrical stretch of  $CO_2$  gives a strong band in the IR at  $2350\text{ cm}^{-1}$ .

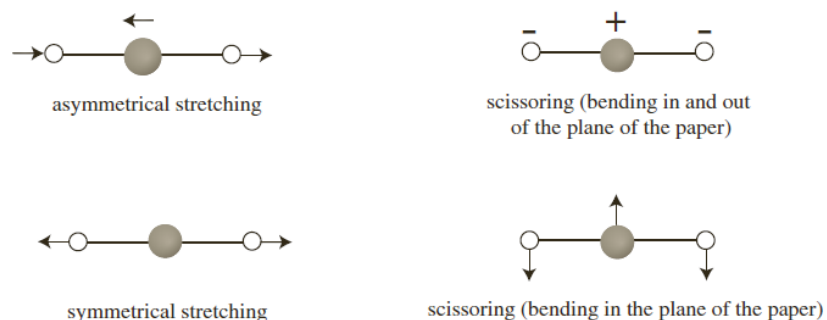


Figure 15.5 : Stretching and bending vibrational modes for CO<sub>2</sub>

The appearance of certain types of non-fundamental (overtone, combinations of fundamental vibrations or difference of fundamental vibrations) bands increases the number of bands as compared to that expected from the theoretical number of fundamental bands. All these bands have very weak intensity than the fundamental vibration bands.

**Overtone bands:** In addition to the fundamental vibrations, other frequencies can be generated by modulations of the fundamental bands. An overtone band occurs when the molecule makes a transition from the ground state ( $v=0$ ) to the second excited state ( $v=2$ ), where  $v$  is the vibrational quantum number. The intensity of the overtone band is very low as compared to the fundamental band and they are usually found in the near infrared region. Based on the harmonic oscillator approximation it has been found that the energy of the overtone transition is about  $n$  times of the fundamental vibration associated with that particular transition. Suppose a compound shows strong absorptions at  $x$  and  $y$   $\text{cm}^{-1}$  then it may also give rise to weaker absorptions at  $2x$ ,  $2y$ ,  $3x$  and  $3y$   $\text{cm}^{-1}$ , respectively. The intensity of overtone bands decreases as the order of the overtone increases, i.e. the intensity of  $3x$  or  $3y$  overtones will be less than the  $2x$  and  $2y$ . Therefore second and third overtones are rarely observed.

**Combination Bands:** Combination bands are observed when two or more than two fundamental vibrations are excited simultaneously. If there are two fundamental vibrations at  $x$  and  $y$   $\text{cm}^{-1}$  then it may also give rise to absorption bands at  $(x+y)$ ,  $(x+2y)$ ,  $(2x+y)$   $\text{cm}^{-1}$ .

**Difference bands:** It is also possible to have a difference band where the frequencies of two fundamental bands are subtracted, i.e.  $(x-y)$ ,  $(x-2y)$ ,  $(2x-y)$   $\text{cm}^{-1}$ .

**Fermi bands/resonance:** When a fundamental vibration couples with an overtone or combination band, the coupled vibration is called Fermi resonance. As a result, two strong bands are observed in the spectrum, instead of the expected strong and weak bands. Fermi resonance is often observed in carbonyl compounds.

A practical use for understanding overtones and combination bands is applied to organic solvents used in spectroscopy. Most organic liquids have strong overtone and combination bands in the mid-infrared region, therefore, acetone, DMSO, or acetonitrile should only be used in very narrow spectral regions. Solvents such as  $\text{CCl}_4$ ,  $\text{CS}_2$  and  $\text{CDCl}_3$  can be used above  $1200$   $\text{cm}^{-1}$ .



## 7. Sample Preparation

IR spectrum of a compound can be recorded in many different forms, such as liquid, solid, gas and solution. Some of the materials are opaque to infrared radiation, so in order to obtain spectra they must be dissolved or diluted in a transparent matrix. For recording IR spectra, the sample should be properly dry as water absorb near  $3710$  and  $1630\text{ cm}^{-1}$ . The samples should be perfectly dried, since cell materials (NaCl, KBr) are usually spoiled by the moisture.

**1) Solid samples:** There are several methods by which an IR spectrum of a solid sample can be recorded.

**a) As a pressed disc:** The first common method involves the mixing of finely ground solid sample with powdered potassium chloride. A translucent pellet of this powder mixture is formed by pressing it in a mechanical pressure. The main advantage of using KBr is that it does not interfere with the bands due to compound since KBr is transparent to IR radiation  $4000\text{-}650\text{ cm}^{-1}$  and thus gives better spectra. The disadvantage of this method is that KBr absorbs water quickly which may interfere with the spectra that is obtained.

**b) As a mull or paste:** Finely ground compound is mixed with an oily mulling agent (usually Nujol) using a pestle and mortar. A thin film of the mull is placed between two flat plates of NaCl and the spectrum is measured. The main disadvantages of this method is that nujol has absorption bands at  $2924\text{-}2860$ ,  $1462$ ,  $1380\text{ cm}^{-1}$ , therefore no information about the observed compound can be obtained in this region.

**c) As a film:** The third method is to dissolve the solid sample in a suitable, non-hygroscopic solvent usually methylene chloride or carbon tetra chloride. A drop of this solution is deposited on surface of Potassium bromide or Sodium chloride plate. The solution is then evaporated to dryness and the film thus formed on the KBr disc is analysed directly to obtain the IR spectrum. The most important thing is that the film should not be too thick otherwise light cannot pass through it. This method gives good results with dilute solution of the compound in a non-polar solvent.

**2) Liquid samples:** Liquids are studied neat or in solution. A drop of neat liquid sample or a solution of the sample in an appropriate solvent is placed between two plates of a salt (sodium chloride or potassium bromide) to give a thin film and analysed to obtain the spectrum. The plates are transparent to the infrared light and do not introduce any lines onto the spectra. Salt plates break easily and are water soluble therefore compounds analysed by this method should be free from water. Spectrum obtained by this method is known as neat spectrum since no solvent is used in recording the spectrum.

**3) Gaseous samples:** The gas is introduced into a special cell with a long path length and the walls of its both the ends are normally made up of NaCl. Gases have very less densities compared to liquids, and hence path lengths should be correspondingly greater, usually  $10\text{ cm}$  or longer. The vapor phase technique is limited because most of the organic compounds have too low vapor pressure to produce a useful absorption spectrum.

**It is important to note that spectra obtained from different sample preparation methods will look slightly different from each other due to differences in the samples' physical states.**

## 8. IR-spectrometer

Traditionally, dispersive infrared spectrophotometers, developed in 1940s, were used to obtain infrared spectra. In 1960s, a new method was developed known as Fourier-transform infrared (FT-IR) spectrometers. But due to high cost of the instrument, this was tended to be used for advanced research only at that time. Gradually, technology advancements in computers and instruments have reduced the cost and enhanced the capabilities of an FT-IR spectrophotometer. Today they are predominantly used and have improved the acquisition of infrared spectra dramatically.

## 9. Dispersive Infrared Spectrometer

The basic components of a dispersive IR spectrometer include a radiation source, Sample and reference cells, monochromator, detector, amplifier and recorder. A schematic diagram of a typical dispersive spectrometer is shown in Fig.

**Radiation source:** The common IR radiation source are inert solids that are heated electrically to 1000 to 1800 °C to promote thermal emission of radiation in the infrared region of the EM spectrum. The most common sources are Nernst filament (composed of rare-earth oxides such as zirconium, cerium and thorium), Globar (composed of silicon carbide), and Nichrome coil. They all produce continuous radiations, but with different radiation energy profiles. The beam from the source is divided into two equivalent beams, one passing through the sample and the other as reference beam.

**Sample and reference cells:** Like UV sample tubes (cuvettes) glass or quartz cannot be used to make the sample cells for IR-spectroscopy, because they absorb strongly in most of the IR region. Alkali metal halides such as KCl, NaCl are commonly used as they are transparent to the IR-region.

**Monochromator:** The monochromator is a device used to disperse or separate a broad spectrum of IR radiation into a continuous spectrum of frequencies of Infrared light. The monochromator consists of rapidly rotating chopper that passes the two beams alternately to a diffraction grating. The slowly rotating diffraction grating varies the frequency or wavelength of radiation and sends it the individual frequency to the thermocouple detector which generates an electrical signal as a response.

**Detectors and Amplifier:** Detectors are devices that convert the radiant energy into an electrical signal. The detector determines the ratio between the intensities of the reference and sample beams. Due to the difference in the intensities of the two beams falling on the detector, an alternating current starts flowing from the detector to the amplifier, where it is amplified and relayed to the recorder.

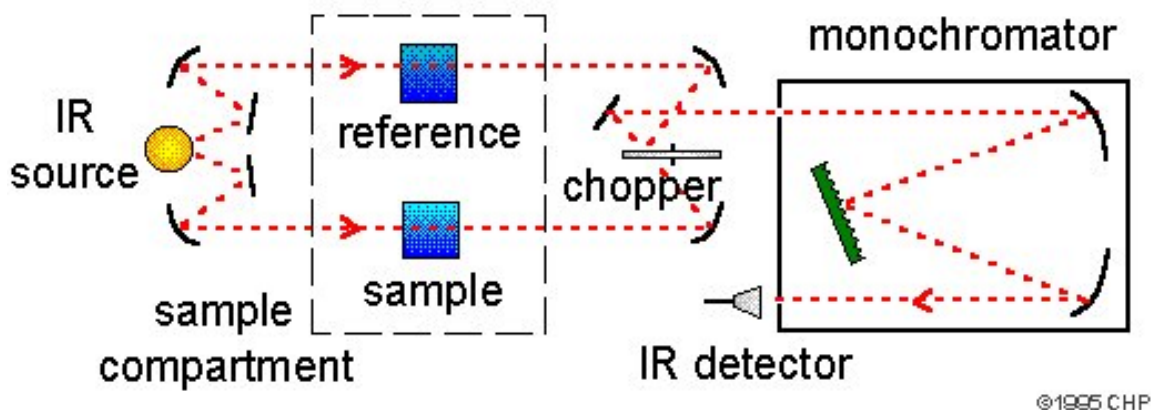
The detectors used in IR spectrometers can be categorized into two classes: thermal detectors and photon detectors. Thermal detectors consists of several thermocouples connected together to produce greater sensitivity. They measure the heating effect produced by infrared radiation that causes the flow of current. The current produced is proportional to the intensity of radiation falling on the thermal detector. Photon detectors rely on the interaction of IR radiation and a semiconductor material. Non-conducting electrons are excited to a conducting state and therefore producing a small current or voltage.

**Recorder:** It records IR-spectrum as a plot of frequency of absorbed radiation and intensity of absorption in terms of transmittance. Unlike UV-spectroscopy, here we use the wavenumber unit. As the detector records the ratio of the intensities of the two beams therefore percent transmittance is recorded.

$$\text{Transmittance (T)} = I/I_0$$

$$\text{Percent transmittance (\%T)} = I/I_0 \times 100$$

Where  $I_0$  is the intensity of the incident radiation and  $I$  is the intensity of the radiation emerging from the sample.



**Figure 1: Schematic diagram of a dispersive IR spectrometer**

## 10. Fourier-Transform Infrared Spectrometer

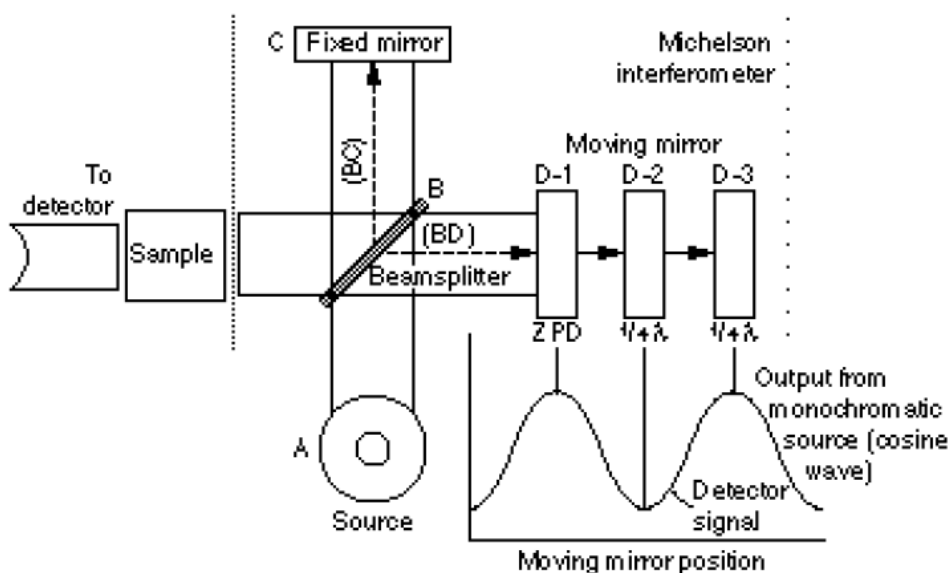
Fourier transform spectrometers have recently replaced dispersive instruments for most applications due to their superior speed and sensitivity. They have greatly extended the capabilities of infrared spectroscopy and have been applied to many areas that are very difficult or nearly impossible to analyze by dispersive instruments. Instead of viewing each component frequency sequentially, as in a dispersive IR spectrometer, all frequencies are examined simultaneously in Fourier transform infrared (FTIR) spectroscopy.

The basic components of an FTIR spectrometer are shown schematically in Figure 2.3. The radiation emerging from the source is passed through an interferometer to the sample before reaching a detector. Then the signal is amplified and converted to digital form by an analog-to-digital converter and transferred to the computer in which Fourier transform is carried out. Interferometer divides radiant beams, generates an optical path difference between the beams and then recombines them in order to produce repetitive interference signals measured as a function of optical path difference by a detector. Thus interferometer produces interference signals, which contain infrared spectral information generated after passing through a sample.

The most commonly used interferometer is a Michelson interferometer. It consists of three active components: a moving mirror, a fixed mirror, and a beam splitter (Fig. 15.4). The two mirrors are perpendicular to each other. The beam splitter is a semi-reflecting device and bisects the plane of

these two mirrors. The beam splitter is often made by coating a thin film of germanium or iron oxide onto an 'infrared-transparent' substrate such as potassium bromide or cesium iodide.

The energy goes from the source to the beam splitter which splits the beam into two parts. One part is transmitted to a moving mirror; one part is reflected to a fixed mirror. The moving mirror moves back and forth at a constant velocity. The two beams are reflected from the mirrors and recombined at the beam splitter. The beam from the moving mirror has traveled a different distance than the beam from the fixed mirror. When the beams are combined an interference pattern is created. Since some of the wavelengths recombine constructively and some destructively. This interference pattern is called an interferogram. This interferogram then goes from the beam splitter to the sample, where some energy is absorbed and some is transmitted. The transmitted portion reaches the detector. The detector reads information about every wavelength in the infrared range simultaneously.



**Figure: Schematic Presentation of a typical FTIR spectrometer**

The moving mirror produces an optical path difference between the two arms of the interferometer (the relative position of moving mirror to the fixed mirror). If the two mirrors are at equal distance from the beam splitter, the two beams travel the same path length. Therefore two beams are totally in phase with each other and hence they interfere constructively and lead to a maximum intensity reaching to the detector. When the moving mirror travels in either direction by the distance  $\lambda/4$ , the optical path is changed by  $2(\lambda/4)$ , or  $\lambda/2$ . The two beams are  $180^\circ$  out of phase with each other, and thus interfere destructively resulting minimum intensity reaching the detector. If the moving mirror further travels by  $\lambda/4$ , then the optical path difference will be  $2(\lambda/4)$ , or  $\lambda$ . The two beams are again in phase with each other and result in another constructive interference again giving a maximum response in the detector. Such a maximum will be observed whenever the path difference is an integral multiple of  $\lambda$ .

Thus moving mirror is the key component of interferometer, because alternate light and dark images will reach the detector if the mirror is slowly moved either away from or towards the beam splitter. When the mirror is moved at a constant velocity, the intensity of radiation reaching the detector varies in a sinusoidal manner to produce the interferogram output shown in Fig. 15.4. The interferogram is a complex signal but its wave like pattern contains all the frequencies that make up the infrared spectrum. It is actually a time domain spectrum and records the detector response changes versus time. If the sample happens to absorb at this frequency, the amplitude of the sinusoidal wave is reduced by an amount proportional to the amount of sample in the beam.

Now to obtain the infrared spectrum, the detector signal is sent to the computer, where mathematical operation known as Fourier transformation converts the interferogram (a time domain spectrum displaying intensity versus time) to the final IR spectrum, a frequency domain spectrum showing plot between intensity of signal versus frequency.

## 11. Hands-on Operation of an FTIR Spectrometer

**Step 1:** First step is the sample preparation. Sample preparation has already been discussed in the above section.

**Step 2:** The second step is to obtain an interferogram of the background which consists of the IR-active atmospheric gases carbon dioxide (doublet at  $2360\text{ cm}^{-1}$  and sharp spike at  $667\text{ cm}^{-1}$  in Fig. 6) and water vapors (two irregular groups of lines at about  $3600\text{ cm}^{-1}$  and about  $1600\text{ cm}^{-1}$  in Fig. 6). Nitrogen and oxygen are not IR-active hence do not absorb in IR-region. This interferogram is subjected to Fourier transform which gives the spectrum of background. Figure 6 shows an example of an FTIR background spectrum.

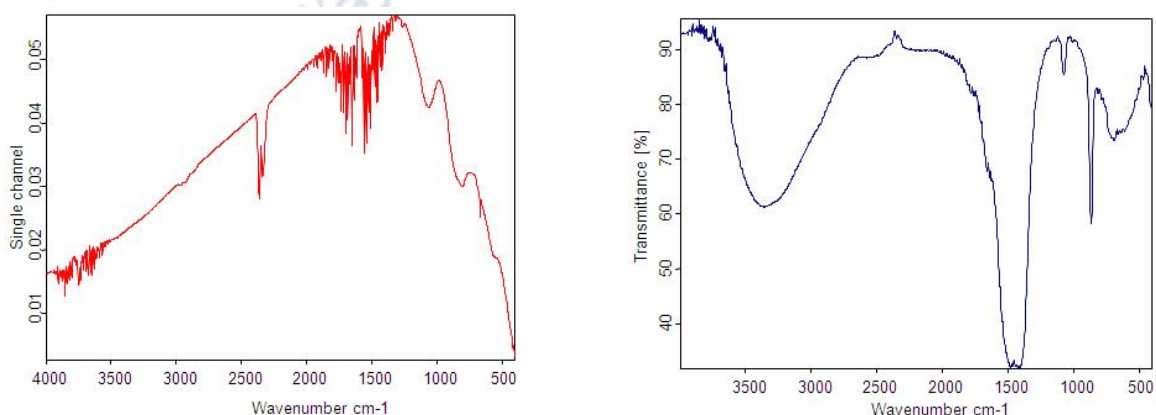


Figure 6: (A) Background IR spectrum; (B) Sample IR spectrum



**Step 3:** In the third step, spectrum of the sample under investigation is obtained by the same procedure. This spectrum contains absorption bands from the sample as well as the background (gaseous or solvent).

**Step 4:** The ratio between the single-beam sample spectrum and the single beam background spectrum gives the spectrum of the sample (**Figure 7**). Computer software automatically subtracts the spectrum of the background from the sample spectrum.

**Step 5:** Finally the data obtained is analyzed by assigning the observed absorption frequency bands in the sample spectrum to appropriate normal modes of vibrations in the molecules.

 **Pathshala**  
पाठशाला  
A Gateway to All Post Graduate Courses



## 12. Summary

1. Absorption of electromagnetic radiation in infrared region can cause changes in the vibrational and rotational energy states.
2. A molecule consisting of  $n$  atoms has a total of  $3n$  degrees of freedom
3. The number of fundamental vibrational bands in a molecule is equal to the degree of freedom of a molecule however these numbers of bands is seldom obtained because of the occurrence of certain non-fundamental bands such as overtones, combinations of fundamental vibrations or difference of fundamental vibration bands.
4. The IR-spectrum can be obtained in all the three states, solid, liquid and gas.
5. Fourier-transform infrared spectrometers are superior than the traditional dispersive spectrometers and gives high resolution spectrum in less time.

