Module-2 Unit-5
Principles and instrumentation FTIR spectroscopy

Principle:

Infrared or IR spectroscopy is animportant system in organic chemistry which can identify particular functional groups present in the molecule. Additionally, the unique group of absorption bands can readily ascertain the characteristics of pure compounds and can also locate specific impurities. Infrared spectroscopy works on principle that the molecules vibrate at specific frequencies [1]. These frequencies ($\sim$ 4000 to $\sim$ 200 cm^{-1}) fall in IR portion of electromagnetic spectrum. When IR radiation is incident on a sample, it absorbs radiation at frequencies similar to its molecular vibration frequencies, and transmits other frequencies. Frequencies of absorbed radiation are detected by infrared spectrometer, and a plot of absorbed energy against frequency, called'infrared spectrum', can be obtained. Since dissimilar materials possess dissimilar vibrations and give distinct infrared spectra, a particular molecule can be identified. A nonlinear molecule, which has N atoms, exhibits 3N-6 vibrational motions for its atoms, also called fundamental vibrations or normal modes. Only those molecular vibrations appear in the IR spectrum which are IR active (or absorb IR light). For a mode to be IR active, the vibration must induce a change in dipole moment of the vibrating molecule. Therefore, symmetric vibration do not appear in IR spectrum. In a molecule with centre of symmetry, the vibrations symmetric with respect to the centre are IR inactive. However, all such molecular vibrations which are asymmetric are IR active and thus appear in the spectrum. This results in simultaneous detection of all chemical groups present in the material. Interestingly, this technique can readily detect the amino acids as well as water molecules which are difficult to detect by other spectroscopies. Chemical groups which possess permanent dipole (e.g., polar bonds) exhibit strong absorption in infrared. Thus, IR spectra of proteins include absorption peaks caused by carbonyl groups of polypeptide chains.

Main vibrations observed in mid IR region (4,000 to 1,000 cm^{-1}) are:
   a. **Stretching vibrations (v):** These are the vibrations along the bonds, and cause changes in length of the bonds.
   b. **Bending vibrations:** These cause changes in the bond angle. These involve: d (in plane), and p (out of plane) vibrations.

Harmonic oscillator is usually employed to model these vibrations (as shown in **Figure 1**) wherein a chemical bond is depicted as the spring linking two point masses. Spring tension 'k' denotes the bond strength (or molecular force field) and the mass of the atoms or chemical groups is represented by the point masses $m_1$and m_2. The frequency of oscillations,v, is expressed as:

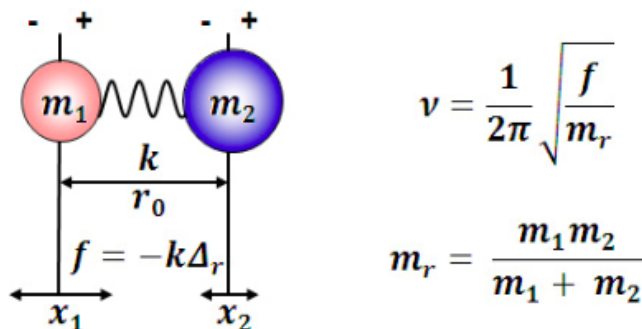$$v = (1/2\pi c) \sqrt{(k (m_1 + m_2) / m_1 m_2)}$$ (1)

Figure 1 Classic harmonic oscillator model[2].

Thus, the bond strength decides the vibration frequencies (v) such that triple or double bonds cause higher frequency than the single bonds. Consequently, frequencies are highly sensitive to the type of chemical group, electronegativity of adjacent atoms or molecules, and the interactions involving hydrogen bonds.If one atom is involved in hydrogen bonding, the bond will be weakened, causing a downshift in the stretching mode frequency of chemical moiety. Therefore, the stretching mode frequencies can provide structural details of certain chemical groups, such as carbonyl or carboxylic moieties in proteins. This can be achieved by monitoring the formation or disruption in hydrogen bonds. Another factor affecting the vibration frequency is mass of the atoms involved in vibrations. Consequently, the vibration frequency can also be altered by isotope labelling of the atoms involved.

Thus, depending upon the type of atoms present, a specific chemical/functional group exhibits vibrational frequencies in particular region. Again, the frequencies in these regions are affects by the environment (solvents) of the chemical group. Thus, a detailed analysis of simplified model compounds in varying environments is required for establishing a clear relationship between the IR mode frequency and structure of the compound. Moreover, from absorption frequencies the presence or absence of various chemical groups in a chemical structure can be ascertained. Other than the characteristic position of the absorption peaks, their magnitude is concentration dependent. Therefore, both quantitative and qualitative information can be obtained.

Fourier Transform Infrared (FTIR) spectrometry is meant to overcome the difficulties experienced in dispersive instruments. An important limitation was the long time required for scanning process. It is desirable to simultaneously measure all IR frequencies. The solution used a simple optical device called interferometer to produce a signal composed of all infrared frequencies "embedded" within it. The signal is recorded very rapidly, typically within a few seconds. Therefore, measurement time per sample was abridged to a few seconds. Interferometers generally use a beam splitter to split the incoming IR beam in two optical beams. One beam is reflected off of a flat mirror that is fixed while the second beam is reflected off of another flat mirror which is on a system allowing this mirror to shift some distance away from beam splitter. Both the beams reflect off of their respective mirrors and then are reunited when they assemble again at beam splitter. Since path of one beam is fixed and for other is continuously varying when its mirror shifts, signal exiting the interferometer is result of these two "interfering" beams. The resultant signal is described as interferogram and exhibit such property that each data point in the signal contains information of all IR frequencies coming from source. Consequently, all frequencies are simultaneously measured when the interferogram is recorded. In this way, the interferometer leads to extremely quick measurements. Since a frequency spectrum (intensity vs. frequency plot) is required for analysing the compound, the recorded interferogram cannot be directly interpreted and some methods to "decode" individual frequencies are necessary. This is achieved by using the well known mathematical technique called Fourier transformation and the result of the transformation provides the required spectral information for analysis.

Instrumentation:

Theessential component of an FTIR system are included in Figure 2.2. IR source emits a broad band radiation having various IR wavelengths. Usually a SiC ceramic heated around 1550 Kelvin is used as IR source. Rather thanamonochromator, a Michelson interferometer is oftenemployedto analyse theinfraredbeam after passing through sample.

The IR radiation passes from the interferometer which modulates it by performing optical inverse Fourier transform on this radiation. Modulated IR beam is then passed from a gas specimen which absorbs it at different wavelengths due to different molecules present in it. Finally, a detector detects the intensity of IR radiation. A computer digitises and performs Fourier transform on detected signal to produce IR spectrum of gas sample [3].
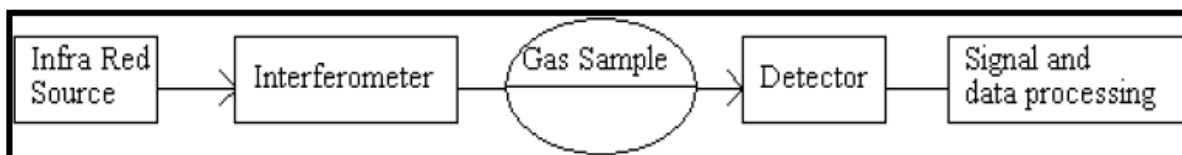
Figure 2 Fundamental components of FTIR.

Fundamental components of an FTIR system

1. The Source:- A glowing black body emits the IR radiation. This beam is passed to an aperture that limits amount of energy incident on sample.

2. Interferometer:- Interferometer performs "spectral encoding" on incoming radiation and exiting signal contains all the IR frequency components.

3. Sample:- Beam is either transmitted through or reflected off of the sample surface, depending on type of investigations being performed. Sample absorbs energies at frequencies characteristic to it.

4. The Detector:- Detector measures the interferogram signal.

5. The Computer:- It performs Fourier transformation to obtain final IR spectrum for examination.

The components of optical system in FTIR spectrometer include an interferometer, which has two mirrors, IR source and IR detector, anda beamsplitter.
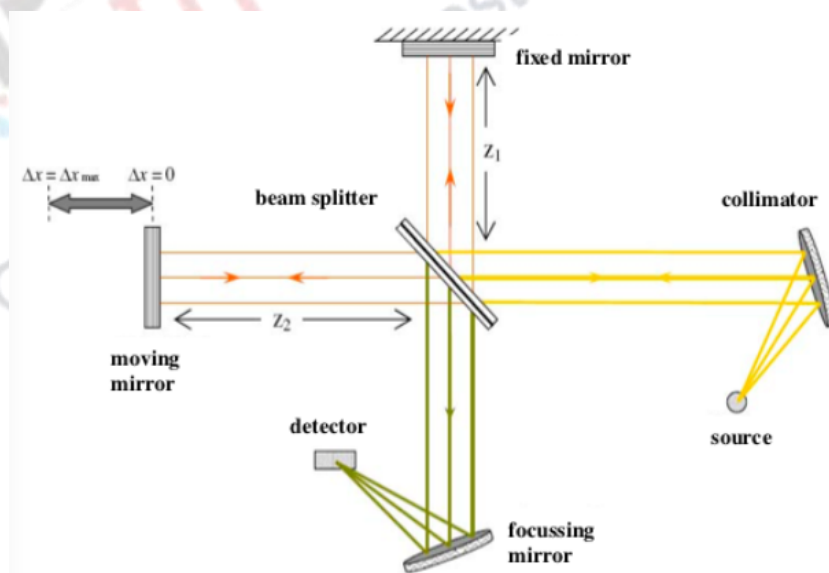

Figure 3 Michelson interferometer.

Beamsplitter, a half-silvered mirror, is central to the functioning of the interferometer. When light is incident on it, half of the incident light reflected while the remaining half is transmitted. The rotating mirror and stationary mirror of the interferometer, both receive each half of these beams. These beams

again reach the beamsplitter after being reflected from the two mirrors. The beamsplitter again splits each half beam into reflected and transmitted half beams. Two output beams result: one travels to the source and other to the detector. When these two beams come back to the beamsplitter, an interference pattern is generated, which is called interferogram. The displacement of the moving mirror causes difference in path length in the two arms of the interferometer, which in turn varies the interference pattern. The interference pattern is detected by the IR detector as variations in IR energy level and ultimately yields spectral information.

The working of interferometer can further be elucidated by explaining the alterations light undergoes in it. Let us consider an interference pattern produced when a monochromatic (e.g., generated by HeNe laser) light is used as light source. An ideal beamsplitter has the following charatceristics:

1. It does not generate or absorb radiation
2. Half of the incident light is transmitted by it
3. The remaining half of all the incident light is reflected.

Thus, the light entering the interferometer from the source, is either sent back to the source or directed towards IR detector. The moving mirror, while scanning back and forth, causes greater or less than half of total light, entering the interferometer, to reach the detector. The light which does not go to the detector is sent to the source. There is no other sink of the light.

If the mirror in interferometer are equidistant from beamsplitter, both light beams travel the same distance. When these beams return to beamsplitter, each of them is again split and recombined with half of the light from the other arm of the interferometer. The two component beams which are sent to the detector as output, are entirely in phase with each other, leading to constructive interference. Whereas, the two component beams sent to the source are completely out of phase to each other, resulting in destructive interference. Thus, the entire incident light reaches the detector and none reaches the source. On the contrary, if moving mirror is displaced by $\lambda/4$ (where λ is the wavelength of the incident light), the light from moving mirror coming to beamsplitteris $\lambda/2$ out of phase with the light from fixed mirror. This causes destructive interference in the component lights reaching the detector, and constructive interference in the components reaching the source. Thus, no light reaches the detector and entire light is sent back to the source.

Figure 4Left: Constructive, and right: destructive interference.

Thus, with the back and forth movement of the moving mirror,the detector perceives light and dark bands resulting total or partial constructive/destructive interference. In this case, the interferogram is a cosine function, having full intensity when both mirrors are equidistant from beamsplitter, to zero intensity when there is $\lambda/4$ path difference between them. If the moving mirror is displaced by $\lambda/2$ or multiples of $\lambda/2$, then also full intensity in output is obtained. Likewise, a displacement of $\lambda/4$ or multiples of $\lambda/4$ result in zero intensity.

Since the IR source is polychromatic, it emits light with a wide frequency range. Each emitted frequency produces a separate cosine signal, and the resulting interferogram is the sum of all cosine waves produced by each individual IR frequency. In this case, complete constructive interference occurs only when both mirrors are equidistant from the beamsplitter, as at this point all waves

simultaneously interfere in constructive manner. At all other points, there is only apartial constructive interference. The frequency as well as intensity of each cosine wave present in the interferogram is resolved by Fourier transform. Thus, a plot of intensity as a function of frequency is obtained in the form of a spectrum [4].
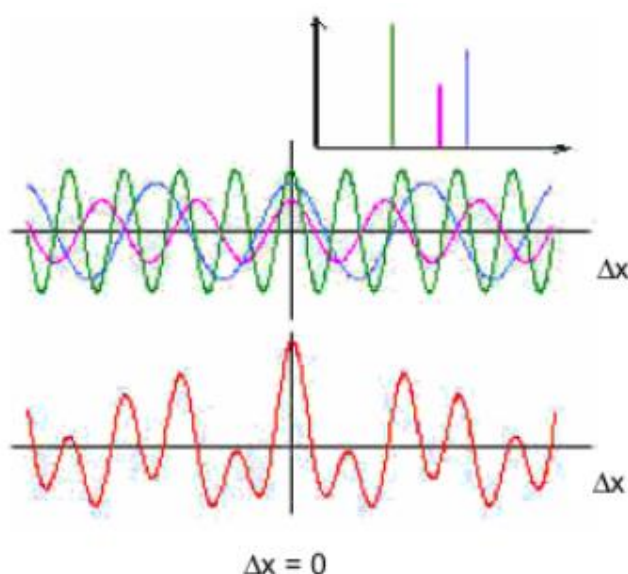

Figure 5*Top:* **a hypothetical spectrum having three frequencies with different amplitudes,***middle:***interferograms for these frequencies, and** *bottom:***Interferogram for the three mixed frequencies.**

SUGGESTED READINGS:

1. http://www.chem.ucla.edu/~harding/ec_tutorials/tutorial33.pdf
2. Infrared Spectroscopy Absorption tables.
3. Joachim Oelichmann, Surface and depth-profile analysis using FTIR spectroscopy; Fresenius Z Anal Chem (1989) 333:353-359.

REFERENCES:

1. Meier RJ. Vibrational spectroscopy: a 'vanishing' discipline? ChemSoc Rev 2005; 34: 7 43-752.
2. Giuseppe Bellisola, Claudio Sorio Infrared spectroscopy and microscopy in cancer research and diagnosis; Am J Cancer Res 2012;2(1):1-21
3. Chalmers JM, Griffiths PR. Handbook of vibrational spectroscopy. New York: J. Wiley, 2002.
4. Griffiths PR, De Haseth JA. Fourier transform infrared spectrometry. Hoboken, NJ: Wiley-Interscience, 2007.

GLOSSARY:

1. Bond strength –

Itis the strength with which two atoms are held together via chemical bonds. It is typically measured as the amount of energy(in kilocalories/mole)needed to dissociate the bond.

2. Black Body –

Black body, by definition, is one which absorbs all the radiation it receives and does not reflect any ('black'!).

3. Interferogram –

It is a photographic record produced by an apparatus which records optical interference.

4. Monochromator –

An optical device used for transmitting a mechanically selectable narrow band ofwavelengthsoflightor other radiation, selected from a broader range of wavelengths available at the input. Greek word*mono-* means 'single', and *chroma*, implies 'color'. The suffix *-ator*means an agent.

TIME LINE:

Chemical IR spectroscopy evolved as a science in 1880s. Interferometer was discovered byA. A. Michelson in 1890s, during his studies on the speed of light. Till early 1940s, it was an immature scientific field. However, in late 1940s, the commercial development of the optical null dispersive spectrophotometer popularized chemical IR spectroscopy. IR analysis relied on dispersive instruments, and began to be widely used inlaboratories for organic characterizations.

The first Fourier transform infrared (FTIR) spectrum was generated by Peter Fellgett in 1949, when hemeasured the light from celestial bodies by using an interferometer. However, for many years, FTIR was only limited to a few advanced research groups who had access to large and expensive computers and with personnel able to wait up to 12 hours to transform an interferogram into a spectrum. FTIR wasusedonly forsolving problems which could not be studied via dispersive techniques.

Commercial FTIR spectrometers only appeared with micro-computers in late 1960s. This success was owing to the development of Cooley-Tukey algorithm in 1966, which could quickly generate the FTIR spectrum. Nonetheless, the earliest FTIRs were still bulky and expensive, which with advancement of technology were developed into low cost and relatively compact instruments, which we today see in most of the laboratories.

SELF ASSESSMENT:

Objective Questions:

1) How is the wavelength controlled in an FTIR spectrometer?
   a. By a Michelson Interferometer
   b. By a computer
   c. By a laser
   d. By calibration with a standard sample

2) What type of technique is FTIR spectroscopy?
   a. A dispersive technique?
   b. An emission technique
   c. An absorbance technique
   d. A UV-Vis technique
   e. A reflectance technique

3) How is the detector on the Mattson RS/1 FTIR spectrometer cooled?
   a. With water
   b. With liquid nitrogen

c. With a fan

d. By Peltier cooling

e. It's not.

4) What does the spectrum of Nitrogen(N2) look like?

a. The same as that of air

b. It has only p- and r-branches

c. The same as that of carbon monoxide

d. It doesn't have one!

5) What are the selection rules for FTIR absorption?

A: Absorption only occurs for symmetrical molecules

B: Absorption only occurs with a dipole change

C: Absorption requires an odd vibrational quantum number

D: Absorption requires promotion to a new quantum level

a. C and D

b. All A, B, C AND D

c. A and D

d. A, B and C

e. B and D

6) What occurs when the moving mirror in an FTIR spectrometer is the same distance from the beamsplitter as the static mirror?

a. Constructive interference

b. Destructive interference

c. Radio interference

d. The spectrum is measured

7) Which infrared technique can measure two spectra at once?

a. FTIR spectroscopy

b. FTIR-ATR spectroscopy

c. Dispersive infrared spectroscopy

d. FTIR microscopy

e. none

8) Which spectrometer is the more complicated: dispersive or FTIR?

a. Dispersive

b. FTIR
c. neither

9) In what region of the spectrum does infrared radiation occur?
   a. At the low-energy end
   b. Between the visible and ultraviolet regions
   c. Between the visible and microwave regions
   d. Between the visible and x-ray regions
   e. At the high-energy end

10) What occurs when a molecule absorbs infrared radiation?
    a. It warms up
    b. It flies around
    c. It spins faster
    d. It vibrates faster
    e. It emits light

Subjective Questions:

11) Modern FTIRs dominate the market, why are they favoured over dispersive (monochromator based) instruments?

12) For near IR one needs good S/N and broad spectral coverage to get band shapes, why are dispersive instruments still used (actually FTIR is also used)?

13) Explain why IR sampling is such a major issue, i.e. why do you not just use standard cuvettes?

14) Why do IR experiments require high concentrations?

15) Give an example where dispersive IR is favoured over FTIR and explain why.