

Fourier Transform Infrared Spectroscopy

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Background

- The interaction of matter with any part of the electromagnetic spectrum is called spectroscopy, which is an instrumentally assisted study between matter and electromagnetic radiation of any range.
- Infrared light was first discovered by Sir Frederick William Herschel during his experiment, which was performed with mercury-in-glass thermometers illuminated by sunlight dispersed through a glass prism (Herschel 1800).
- Later on, various scientists, including William Herschel's son, Sir John Frederick William Herschel, contribute to the infrared spectroscopy very effectively to measure the infrared spectrum practically.
- The IR region is lying between visible and microwave end of the electromagnetic radiation spectrum.
- It is basically divided into three main portions:
 - near IR (14000– 4000 cm^{-1}),
 - mid-IR (4000–400 cm^{-1}), and
 - far IR (400–40 cm^{-1})
- In the traditional IR spectroscopy, specific IR radiations are selected for the analysis, which is a tedious and time-consuming process.

Fourier transform infrared spectroscopy (FTIR)

- Fourier transform infrared spectroscopy (FTIR) is a largely used technique to identify the functional groups in the materials (gas, liquid, and solid) by using the beam of infrared radiations.
- This problem associated with traditional IR spectroscopy was solved with the advent of Fourier transform infrared spectroscopy (FTIR), where a pulse (burst of energy) is bombarded on molecules; as a result, different parts of the same molecules received its characteristics IR radiation and displayed a time domain spectrum called interferogram.
- The interferogram is converted to frequency domain spectrum by the application of mathematical procedure known as Fourier transform.
- An infrared spectroscopy measured the absorption of IR radiation made by each bond in the molecule and as a result gives spectrum which is commonly designated as % transmittance versus wavenumber (cm^{-1}).
- A diverse range of materials containing the covalent bond absorbed electromagnetic radiation in the IR region.

... Fourier transform infrared spectroscopy (FTIR)

- The lower energy radiation in the infrared (IR) region of the electromagnetic spectrum can interact with atoms, and molecules can produce changes within these entities.
- This type of radiation is not energetic enough to excite electrons, but it can cause the chemical bonds in molecules to vibrate in different ways.

IR Active Molecules

- For the determination of functional groups in a molecule, it must be IR active.
- An IR active molecule is the one which has dipole moment.
- When the IR radiation interacts with the covalent bond of the materials having an electric dipole, the molecule absorbed energy, and the bond starts back and forth oscillation.
- Therefore, the oscillation which caused the change in the net dipole moment of the molecule should absorbed IR radiations.
- **The dipole moment is determined by the magnitude of the charge difference and the distance between the two centers of charge.**

Why IR Active?

- A single atom doesn't absorb IR radiation as it has no chemical bond.
- Symmetrical molecules also do not absorb IR radiation, because of zero dipole moment.

IR Inactive molecule: example H₂

- For instance, H₂ molecule has two H atoms; both cancelled the effect of each other and giving zero dipole moment to H₂ molecule.
- Therefore, H₂ molecule is not an IR active molecule.

IR Active molecule: Example H-F (hydrogen fluoride)

- H-F is an IR active molecule, because when IR radiation interacts with H-F molecule, the charge transferred toward the fluorine atom and as a result fluorine becomes partial negative and hydrogen becomes partial positive, giving net dipole moment to H-F molecule.
- It should be noted here that a particular IR radiation (frequency) will be absorbed by a particular bond in the molecule, because every bond has their particular natural vibrational frequency.
- Thus two molecules with different structures don't have the same infrared spectrum, although some of the frequencies might be same.

Modes of Vibration & IR Activity

- Organic molecules mostly contain covalent bonds between the atoms, which are not stiff but rather behave like springs and always agitating at room temperature.
- This movement of the bonds in molecule gives various modes of vibration.
- There are two modes of vibrations: stretching and bending vibration.

Fig. 9.4 Representation of stretching vibration in diatomic linear molecule hydrogen fluoride (H-F) and bending vibration in triatomic molecule water (H₂O)

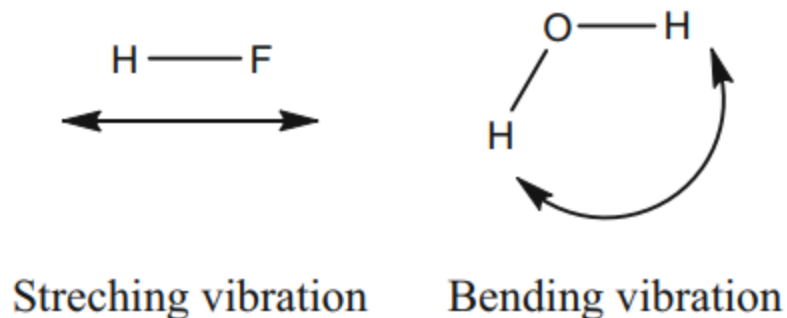
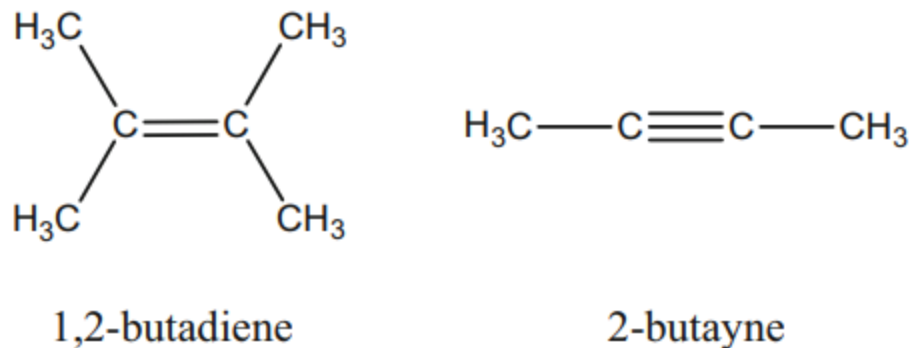
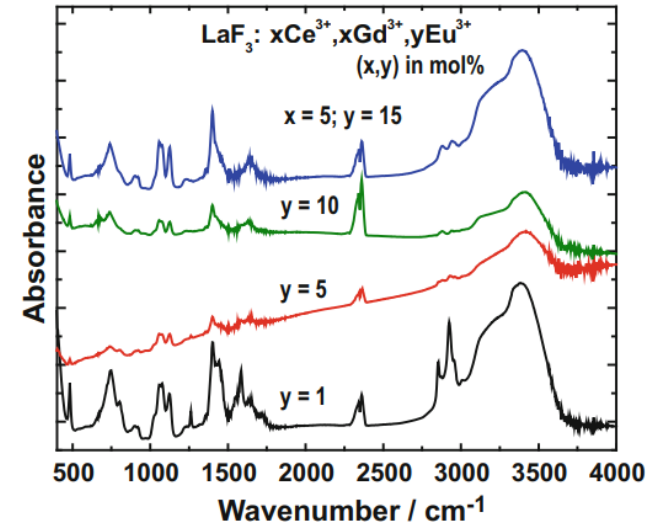


Fig. 9.5 IR inactive molecules with double and triple bond



Infrared Spectrum

- The plot of measured infrared light intensity (absorbance or % transmittance) versus its property, such as energy range expressed in wavenumber (cm^{-1}), is called an infrared spectrum.
- The FTIR spectrum is measured as wavenumber because wavenumber is directly related to the energy and frequency, thus providing an easy way for interpreting the spectrum.
- The infrared spectrum is conventionally plotted with high wavenumber to the left and low wavenumber to the right in its x-axis.
- However, in certain articles the contrary profile of FTIR spectra are also reported.
- The IR spectrum is recorded in absorbance mode, which measures the amount of light absorbed by a sample, and its intensity at y-axis is plotted in absorbance unit.



... Infrared Spectrum

- The absorbance spectrum of a sample is calculated from the following relation:

$$A = \log (I^0/I)$$

- Where A , absorbance; I^0 , intensity in the background spectrum; and I , intensity in the spectrum of sample.
- The absorbance can be also correlated with the concentration of molecules in a sample through the equation called as Beer's law:

$$A = \epsilon lc$$

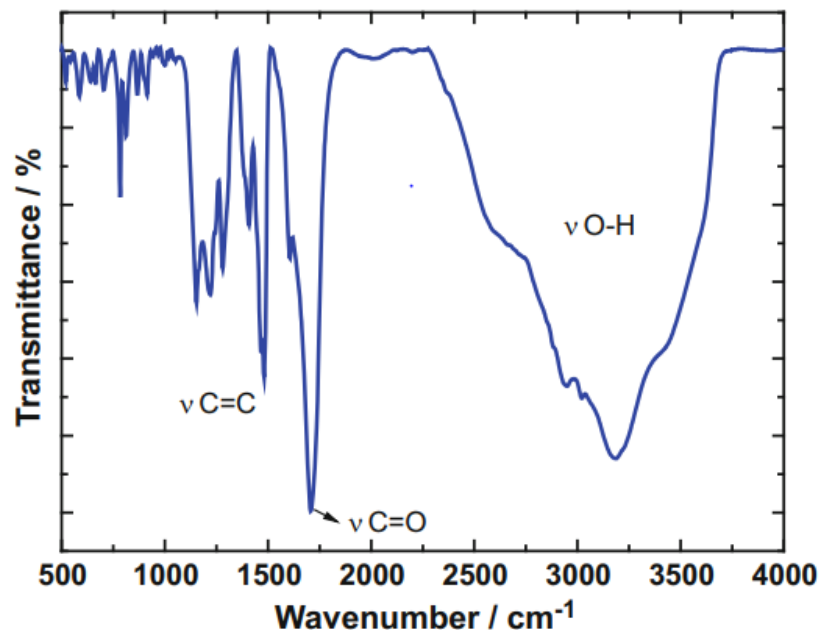
- where, A absorbance; ϵ , molar absorptivity; l , path length; and c , concentration of the sample.
- The height or area of a peak in an absorbance spectrum is proportional to concentration; therefore Beer's law can be used to determine the concentrations of molecules in samples.

... Infrared Spectrum

- On the other hand, the y-axis of an infrared spectrum can be also plotted in unit called percent transmittance (% T), which measures the percentage of light transmitted by the compound and can be calculated as follows:

$$\%T = 100 \times (I/I^0)$$

- Where, % T, percent transmittance; I^0 , intensity in the background spectrum; and I , intensity in the sample spectrum.



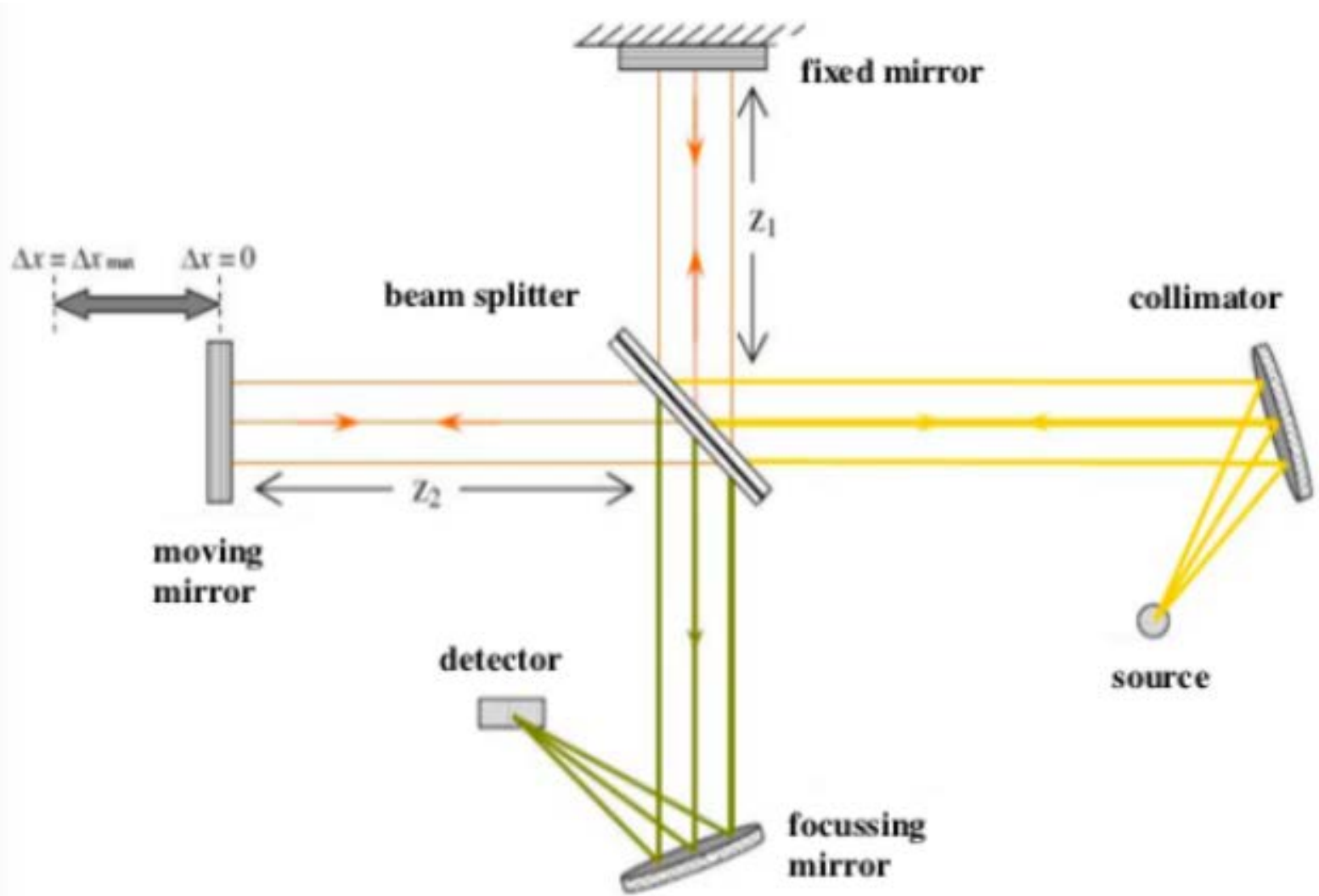
***Prior to the sample analysis, the background is recorded, to avoid air and water vapor contamination peaks.**

Instrumentation

- The normal instrumental process is as follows:
 - 1. The Source:** Infrared energy is emitted from a glowing black-body source.
 - This beam passes through an aperture which controls the amount of energy presented to the sample (and, ultimately, to the detector).
 - 2. The Interferometer:** The beam enters the interferometer where the “spectral encoding” takes place.
 - The resulting interferogram signal then exits the interferometer.
 - 3. The Sample:** The beam enters the sample compartment where it is transmitted through or reflected off of the surface of the sample, depending on the type of analysis being accomplished.
 - This is where specific frequencies of energy, which are uniquely characteristic of the sample, are absorbed.
 - 4. The Detector:** The beam finally passes to the detector for final measurement.
 - The detectors are specially designed to measure the special interferogram signal.
 - 5. The Computer:** The measured signal is digitized and sent to the computer where the Fourier transformation takes place.
 - The final infrared spectrum is then presented to the user for interpretation.

Working Principle

- A method for measuring all of the IR frequencies simultaneously was developed employing a very simple optical device called an interferometer.
- The interferometer produces a unique type of signal which has all of the infrared frequencies “encoded” into it.
- The signal can be measured very quickly, usually on the order of one sec. or so.
- Thus, the time element per sample is reduced to a matter of a few seconds rather than several minutes.
- **Most interferometers** employ a beam splitter which takes the incoming infrared beam and divides it into two optical beams.
- One beam reflects off of a flat mirror which is fixed in place.
- The other beam reflects off of a flat mirror which is on a mechanism which allows this mirror to move a very short distance (typically a few millimeters) away from the beam splitter.
- The two beams reflect off of their respective mirrors and are recombined when they meet back at the beam splitter.
- Because the path that one beam travels is a fixed length and the other is constantly changing as its mirror moves, the signal which exits the interferometer is the result of these two beams “interfering” with each other.

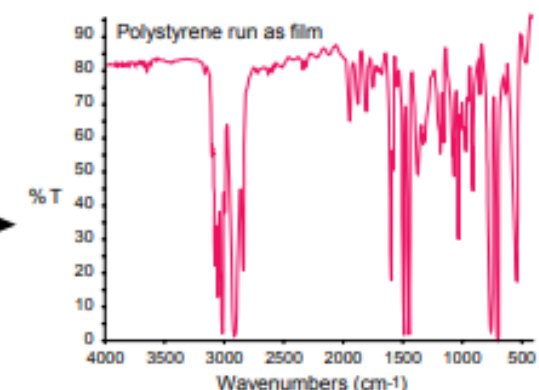
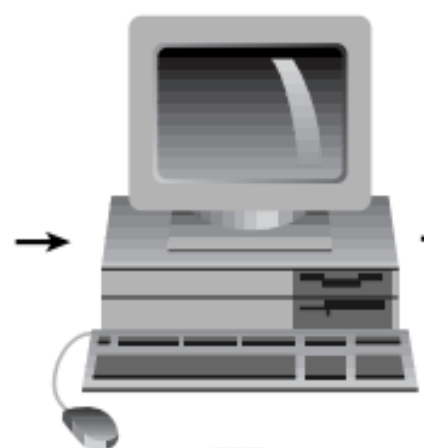
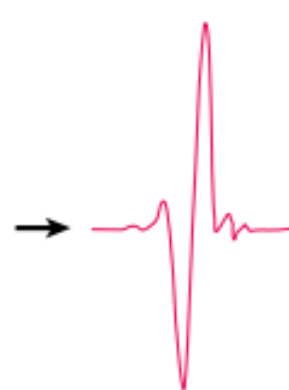
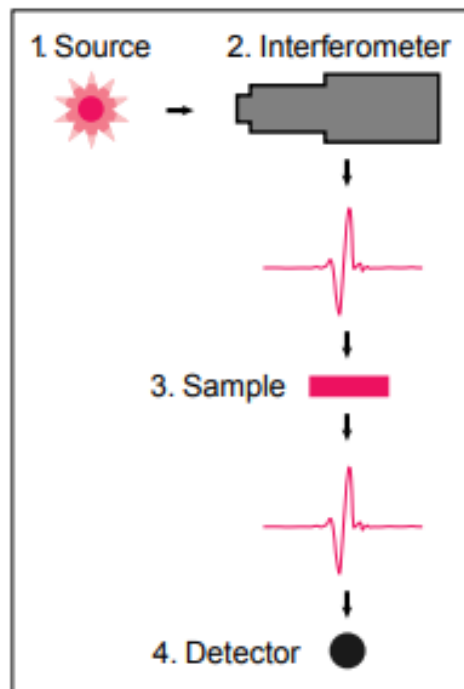


Michelson interferometer

... Working Principle

- The resulting signal is called an interferogram has information about every infrared frequency which comes from the source.
- The resultant interferogram signal is transmitted through or bounces from the sample surface, where specific energy wavelengths are absorbed.
- The beam eventually passes through the detector and further passed on to processing computer for Fourier transformation of energy signals.
- **Fourier transform, named in the honor of French mathematician and physicist Jean Baptiste Joseph Fourier (1768–1830).**
- **Because there needs to be a relative scale for the absorption intensity, a background spectrum must also be measured.**
- **This is normally a measurement with no sample in the beam.**
- **This can be compared to the measurement with the sample in the beam to determine the “percent transmittance.”**

Spectrometer



Advantages of FT-IR

- FTIR is the most modern type and preferred over the other dispersive spectrometers.
- It is because of its:
 - high precision,
 - accuracy,
 - speed,
 - enhanced sensitivity,
 - ease of operation,
 - sample nondestructiveness
 - Internally Calibrated: employ a HeNe laser as an internal wavelength calibration standard

Sample Preparation

- The sample preparation is very important for IR spectra analysis where the sample is placed in the cell or in the holder.
- It is very problematic because IR radiations are strongly absorbed by glass and plastic materials throughout the entire IR range.
- The cell is constructed of ionic materials, such as KBr or NaCl.
- The KBr plates are expensive, but they have advantages over NaCl, as they can record IR spectra from 400 to 4000 cm^{-1} .
- However, NaCl plate is also largely used due to its low cost and recorded spectra from 650 to 4000 cm^{-1} .

Methods for solid sample preparation

- The compounds are finely grounded with KBr salt and then pressed at high pressure to form pellets called KBr pellets.
- In another method called Nujol mull, the compound is finely grounded with the mineral oil called Nujol, as a result a thick suspension is formed which is placed between the plates.
- The main drawbacks of this method are the Nujol peaks which appeared at 2924, 1462, and 1377 cm^{-1} that might interfere with for compounds having peak in these regions.
- In the third method, the compound is dissolved in solvent.
- Chloroform (CCl_4) is mostly used, because it dissolves most of the organic compounds; however, like Nujol the CCl_4 peaks appeared and interfere with the compounds peak at approximately 700 cm^{-1} .

...Sample preparation

- **To prepare a liquid sample** to IR analysis, firstly place a drop of the liquid on the face of a highly polished salt plate (such as NaCl, AgCl or KBr), then place a second plate on top of the first plate so as to spread the liquid in a thin layer between the plates, and clamps the plates together.
- **A gas sample** is created by allowing the sample to expand into an evacuated cylindrical cell which has special windows that will not absorb the infrared light.
- Choice of window materials: KBr, BaF₂, coated ZnSe (Zinc selenide).

Applications

- **FTIR in Biomedical Imaging:** For characterizing the biomedical sample, FTIR spectroscopy has advantages over other imaging techniques because it detects specific molecular vibrations in the chemical bonds of molecules.
- FTIR imaging technique does not required the dyes for labeling or visualization in various sample.
- There are several examples, for instance,
 - it is used in human colorectal adenocarcinoma studies.
 - the deposition of β -amyloid protein in human brain tissue slice, comprises the Alzheimer's diseases
- **FTIR in Proteins Study:** In many cases the FTIR can be applied for the structural determination of protein.
- There are two major bands in the FTIR spectrum of protein known as amide I (1600– 1700 cm^{-1}) and amide II.

Miscellaneous Applications of FTIR Spectroscopy

- FTIR is an extremely important tool for the detection of large range samples in different fields.
- For instance, resins, adhesives, paints, coatings, polymers, metal oxides, and large number of drugs.
- Polymers and polymer blends as well as indirect verification of trace organic contaminants on surfaces of various materials can be analyzed.
- Routine qualitative and quantitative analyses can be performed.
- Can also analyze the gaseous samples using a gas cell for the headspace analysis or environmental monitoring process.

Thanks