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Fourier transform infrared spectroscopy (FTIR)

Rehab Abouelmagd Saad [1,*]

[1] Assistant lecturer, Biomaterial Department, Cairo University
* Corresponding author e-mail: rehab.abouelmagd@dentistry.cu.edu.eg

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Abstract: 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. Functional groups can be associated with characteristic infrared absorption bands, which correspond to the fundamental vibrations of the functional groups. A normal mode of vibration is infrared active (i.e., it absorbs the incident infrared light) if there is a change in the dipole moment of the molecule during the course of the vibration. Thus, symmetric vibrations are usually not detected in infrared.

Keywords: Fourier transform infrared spectroscopy.

I. Introduction

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. An infrared spectroscopy measures 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) (2). Infrared (IR) or Fourier transform infrared (FTIR) spectroscopy has a wide application range, from the analysis of small molecules or molecular complexes to the analysis of cells or tissues. taking advantage of infrared microscopy and of the use of IR radiation, it is used for the mapping of cellular components (carbohydrates, lipids, proteins) to identify abnormal cells.

FTIR spectroscopy has also been increasingly applied to the study of proteins.(1)

Infrared spectroscopy reviews the molecular vibrations. Functional groups can be associated with characteristic infrared absorption bands, which correspond to the fundamental vibrations of the functional groups. A normal mode of vibration is infrared active (i.e., it absorbs the incident infrared light) if there is a change in the dipole moment of the molecule during the course of the vibration. Thus, symmetric vibrations are usually not detected in infrared. In particular, when a molecule has a centre of symmetry, all vibrations which are symmetrical with respect to the centre are infrared inactive. In contrast, the asymmetric vibrations of all molecules are detected. This lack of selectivity allows us to review the properties of almost all chemical groups in one sample, and notably of amino acids and water molecules which can hardly be observed by other spectroscopic techniques. (1)

While this approach suffers from several limitations, it delivers unique information by addressing directly the properties of cofactors, amino acids, and water molecules, with very high sensitivity to structural parameters and electronic interactions. This justifies the experimental efforts that have been made to optimize its use and the interpretation of the data. (1)

Brief history:

The development of spectroscopy in non-visual wavelengths (IR region) was advanced simultaneously with the development of visual spectroscopy. 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). He was really surprised when he found that not only the thermometers register heat beyond the red end of the visible spectrum, but the greatest amount of heat was found in this region. 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. Jacquinot, Fellgett and Connes are the famous researchers along with other known scientists for their work in the early history of spectroscopy. The work of Rubens and Wood on FTIR interferogram and Rubens and von Baeyer in spectroscopy was known before the advent of Michelson interferometer. However, before 1980 some domestic high-resolution FTIR spectrometers were also reported. In the mid1960s, progress has been made in the infrared microscopy and developed techniques which enhanced the signal-to-noise ratio. In the late 1970s, the infrared microscope systems were introduced in the market and in the early stages of 1980s by Digilab and Spectra-Tech Company. (2)

The real advancement was made in FTIR spectroscopy with the availability of commercially accessible high-resolution instruments. Previous to 1980, the FTIR spectrometers resolution was 0.04 cm−1 which is inadequate and less efficient than the old-fashioned grating apparatuses. Revolution attained with the Bomem instruments having a maximum optical path difference (d MOPD) = 250 cm−1. In the traditional IR spectroscopy, specific IR radiations are selected for the analysis, which is a dull and time-consuming process. For example, a molecule containing O-H and C=O functional groups, different ranges of IR radiation were applied for the determination of O-H and C=O functional groups. This problem was solved with the advent of Fourier transform infrared spectroscopy (FTIR), where a pulse (eruption 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 time domain spectrum (interferogram) is converted to frequency domain spectrum by the application of mathematical procedure known as Fourier transform. (2)

Principle of FTIR:

When infrared radiation is bombarded on a sample, it absorbs the light and creates various vibration modes. This absorption relates precisely to the nature of bonds in the molecule. The frequency ranges are measured as wavenumbers typically over the range of 4000–600 cm−1. 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. Prior to the sample analysis, the background is recorded, to avoid air and water vapor contamination peaks. The proportion of the background and the sample spectrum are directly related to the absorption spectrum of the sample. The absorption spectrum indicating various vibrations of the bonds presents in the sample molecule.

Several modes arise due to the various bond vibrations. So, in this way one can easily identify the functional group in a molecule.

During an absorption process, the molecule absorbs only those frequencies of IR radiation which matched with the natural vibrational frequency of the bonds and hence increases the amplitude of vibrational modes of the molecules. However, all the bonds in a molecule cannot absorb the IR radiation irrespective to the matching frequency of IR radiations, until and unless it has a net dipole moment. 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. (2)

Sample forms and preparation for FTIR analysis:

Fourier transform infrared (FTIR) is one of the important analytical techniques that can be used for characterizing samples in the forms of liquids, solutions, pastes, powders, films, fibres, and gases. This characterization analysis is quite rapid, good in accuracy, and relatively sensitive. In the FTIR analysis procedure, samples are subjected to contact with infrared (IR) radiation. The IR radiations then have impacts on the atomic vibrations of a molecule in the sample, resulting the specific absorption and/or transmission of energy. This makes the FTIR useful for determining specific molecular vibrations contained in the sample (3). In short, the IR spectrum is divided into three wavenumber regions: far-IR spectrum (<400 cm-1), mid-IR spectrum (400-4000 cm -1), and near-IR spectrum (400013000 cm-1). The mid-IR spectrum is the most widely used in the sample analysis, but far- and near-IR spectrum also contribute in providing information about the samples investigated.

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. NaCl is absorbed at 650 cm−1, and very few bands are supposed to absorb in this region; therefore, it is commonly used in the routine experiment. The CO2 and H2O from the atmosphere usually appeared in the compound spectrum which causes problem during the interpretation of the spectrum. Therefore, it is very important to run background spectrum so that it is automatically subtracted from the compound spectrum. Between the polished NaCl or KBr plates, a drop of liquid is placed, known as salt plate. After pressing the plates, a thin film is formed. The pair of plates is inserted in the holders. The spectrum obtained during this method is called as neat spectrum because it is free of solvent. Moreover, being ionic in nature, these salt plates are easily soluble in water; therefore, it is recommended that the compounds must be free of water. Three methods are available for solid sample. In the first method, the compounds are finely grounded with KBr salt and then pressed at high pressure to form pellets called KBr pellets. However, KBr absorb water which gives water peaks in the spectrum and hindered the peaks originated from the compounds. Nevertheless, if KBr plates are prepared carefully by avoiding the absorption of moisture, no peak will appear in the spectrum. The other advantage is that KBr is transparent below 400 cm−1. 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 might interfere with compounds having peak in these regions. In the third method, the compound is dissolved in solvent Chloroform (CCl4) is mostly used, because it dissolves most of the organic compounds; however, like Nujol the CCl4 peaks appeared and interfere with the compounds peak at approximately 700 cm-1.

Attenuated total reflection (ATR)-FTIR:

Due to the drawbacks associated with KBr pellets and liquid cells method, FTIR measurements are largely achieved in attenuated total reflection (ATR) mode because of its simplicity as compared to the conventional transmission mode. Various samples such as liquids, solids, pastes, fiber pellets, powders, slurries, and many other are placed without any treatment on the ATR crystal. It is a fast technique and the data is obtained in a few seconds. This can be achieved practically without any major sample preparation. IR-ATR provided an advantage that the sample can be investigated without interruption. Thus, biofilm removal from its support, which modifies its structure significantly from its natural form, can be avoided. Additionally, very thin films and surface coverings can be examined, which are not available to normal chemical approaches. Particularly ATR is an extremely good technique for polymer and membrane science. The key advantage of ATR is its capacity for the measurement of varieties of samples such as solid and liquid samples without the need of complex steps. In this approach, the IR ray enters the ATR crystal at 45◦ relative to the crystal surface and is entirely reflected at the crystal to sample interface. Because of its wavelike properties, the light is not reflected directly by the boundary surface but by a computer-generated layer within the optically less dense sample. Evanescent wave is a fraction of light which reached to the sample. The penetration depth depends on the wavelength, the refractive indices of the ATR crystal and the sample, as well as the angle of the incident light. Characteristically, it is of the order of a few microns (0.5–3 μm). The evanescent wave is attenuated in the spectral regions, where the sample absorbs energy. After one or numerous internal reflections, the IR beam exits the ATR crystal and is directed to the IR detector.

Instrumentation:

The typical FTIR spectrometer consists of an IR light source, interferometer, sample compartment, detector, amplifier, and computer. The light source generates radiation which strikes the sample passing through the interferometer and reaches the detector. Then the signal is amplified and converted to digital signal (interferogram) by the amplifier and analog-to-digital converter, respectively. Eventually, the interferogram is translated to spectrum through the Fast Fourier Transform (FFT) algorithm. Michelson interferometer is the main core of FTIR spectrometer.it consists of a beam splitter, fixed mirror, and a moveable mirror that translates back and forth, very precisely. The beam splitter is made of a special material that transmits half of the radiation striking it and reflects the rest half of the radiation. It works on the basis of principle that the light from the source is collected by collimating mirror and made its rays parallel, which strikes beam splitter and consequently splits into two beams. One beam is transmitted through the beam splitter to the fixed mirror, and the second is reflected off the beam splitter to the moving mirror. The fixed and moving mirrors reflect the radiation back to the beam splitter. Accordingly, both of these reflected radiations are recombined at the beam splitter, resulting in one beam that leaves the interferometer and interacts with the sample and strikes the detector. Principally, FTIR (Fourier transform infrared) is a method of obtaining infrared spectra, which includes initially the collection of an interferogram of a sample signal using an interferometer and then performance of a Fourier transform (FT) on the interferogram to obtain the spectrum. An FTIR spectrometer collects and digitizes the interferogram, performs the FT function, and displays the spectrum. (2)

Advantages:

Some of the major advantages of FTIR over the dispersive technique include:

Speed: Because all of the frequencies are measure simultaneously, most FTIR measurements are made in seconds rather than several minutes.

Sensitivity: Sensitivity is dramatically improved with FTIR for many reasons. The detectors employed are much more sensitive, the optical throughput is much higher (referred to as the Jacquinot Advantage) which results in much lower noise levels, and the fast scans enable the co-addition of several scans in order to reduce the random measurement noise to any desired level (referred to as signal averaging).

Mechanical simplicity: The moving mirror in the interferometer is the only continuously moving part in the instrument. Thus, there is very little possibility of mechanical breakdown.

Internally calibrated: These instruments employ a He-Ne reference laser as an internal wavelength calibration standard (referred to as the Connes Advantage). These instruments are self-calibrating and never need to be calibrated by the user. (1)

These advantages, along with several others, make measurements made by FTIR extremely accurate and reproducible. Thus, it is a very reliable technique for the positive identification of virtually any sample. The sensitivity benefits enable identification of even the smallest of contaminants. This makes FTIR an invaluable tool for quality control or quality assurance applications whether it be batch-to-batch comparisons to quality standards or analysis of an unknown contaminant. In addition, the sensitivity and accuracy of FTIR detectors, along with a wide variety of software algorithms, have dramatically increased the practical use of infrared for quantitative analysis. Quantitative methods can be easily developed, calibrated, and can be incorporate into simple procedures for routine analysis. Thus, the Fourier transform infrared (FTIR) technique has brought significant practical advantages to infrared spectroscopy. It has made possible the development of many new sampling techniques which were designed to tackle challenging problems that were impossible by older technology.

Applications:

FTIR for Materials Characterization is an efficient spectroscopic technique to characterize the structure of the following materials.

1. Organic Compounds: FTIR is largely used for the study of organic molecules, which brought mainly two types of changes in the molecules: stretching vibration causes of change in the bond length and bending vibration causes of change in the bond angle. Change in the bond length usually occurred at higher frequency or energy because stretching required higher energy as compared to bending vibrations. (2)

2.Nanomaterials: Any solid materials with one of its dimensions fewer than about 100 nm are known as nanoscale materials or nanomaterials. This small size of the particle, abruptly, increases the surface/volume ratio, and, therefore, many vital physical and chemical characteristics are expressively improved, which are completely different from their bulk counterparts. Although, nanomaterials and their bulk counterparts organize the same materials, but smaller particles indicate absolutely diverse physicochemical or electromagnetic properties from their bulk counterparts.

3-FTIR in Biomedical Imaging: FTIR spectroscopic imaging is a chemical imaging technique which is very important to investigate the biological samples. 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 labelling or visualization in various sample, and its application is largely reported in medical imaging samples. For instance, it is used in human colorectal adenocarcinoma studies. Similarly, the deposition of β-amyloid protein in human brain tissue slice, comprises the Alzheimer's diseases, have been investigated through FTIR spectroscopic imaging techniques. The ATR-FTIR imaging technique is important in the biomedical field. it is the key for the potential characterization of biomedical samples in tissue engineering. (2)

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 can be analyzed with the help of this technique. different natural samples such as gummy materials, solids, liquids, and solutions can also be investigated and identified with the help of FTIR. The identification of diverse range of organic and inorganic compounds can be studied through this technique. Polymers and polymer blends as well as indirect verification of trace organic contaminants on surfaces of various materials, routine qualitative and quantitative analyses can be performed. With the help of FTIR adhesives, coatings and adhesion promoters or coupling agents as well as thin film can be easily analyzed. The gaseous samples can be investigated using a gas cell for the headspace analysis or environmental monitoring process. (2)

Why Raman is Different from IR? (4)

IR requires change in dipole moment

Raman requires change in polarizability

Selection rules are therefore different and can be exclusive for centrosymmetric molecules which are IR inactive.

What is Raman spectroscopy?

Raman Spectroscopy is a popular technique for the analysis of molecular structure and is now considered complementary to infrared spectroscopy. Raman spectroscopy is based on the Raman effect, which was first found by the Indian physicist Chandrasekhara Venkata Raman in 1928. According to quantum mechanics, when photons interact with a molecule, the molecule may be advanced to a virtual state of higher energy. From this higher energy state, there can be a few possible outcomes. One such outcome can be that the molecule comes down to some vibrational energy level different than that of its beginning state, by producing a photon of some different energy. The difference between the energy of that scattered photon and the energy of the incident photon is the called the Raman Shift 1. Raman spectra are measured by exciting a sample using a high-intensity laser beam and passing the scattered light through a spectrometer. The energy difference between the incident light and the scattered light is called the Raman Shift. In the obtained spectrum, horizontal axis is the wavenumber of the Raman shift (cm−1) and the vertical axis is the intensity of the scattered light.

Comparison of Infrared vs. Raman:

Both spectroscopic techniques measure the same thing, vibrational energy, in different ways.

IR is an absorption measurement, while Raman measures scattered light from a laser source, which is superimposed with the vibrational structure of the molecule.

The selection rules are different: IR bands are active if the dipole moment of the vibrating molecule changes. While Raman band are active if the polarizability of the molecule changes.

Molecules of high symmetry frequently will not show IR activity

Example of FTIR analysis of dental Root canal sealer:ZnO/Siwak:(6)

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