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Introductory Chapter

Introduction to Infrared Spectroscopy

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1. Introduction

1.1 Short history of the technique

Infrared radiation was discovered by Sir William Herschel in 1800 [1]. Herschel was investigating the energy levels associated with the wavelengths of light in the visible spectrum. Sunlight was directed through a prism and showed the well known visible spectrum of the *rainbow colors*, i.e, the visible spectrum from blue to red with the analogous wavelengths or frequencies [2, 3] (see Fig.1).
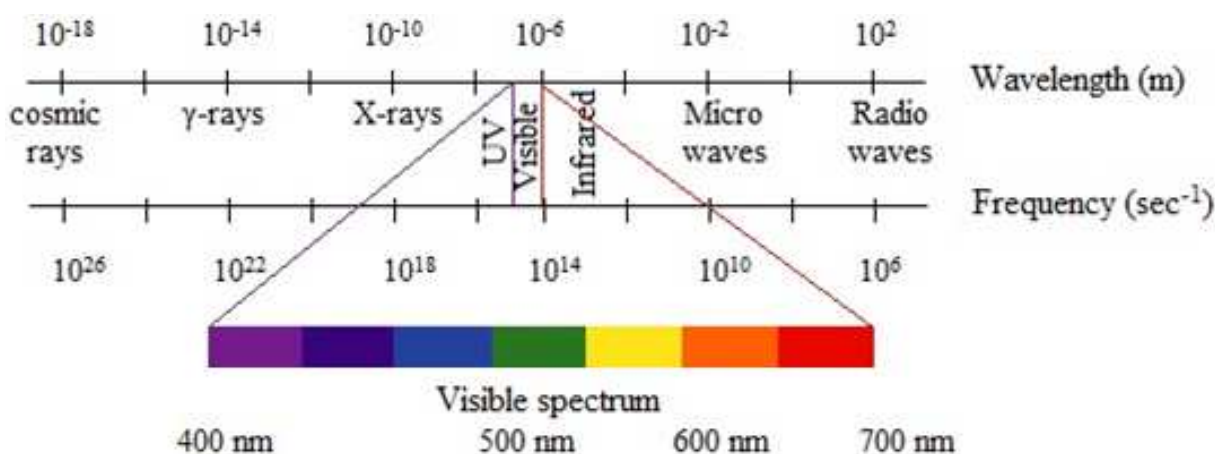

Fig. 1. The electromagnetic spectrum.

Spectroscopy is the study of interaction of electromagnetic waves (EM) with matter. The wavelengths of the colors correspond to the energy levels of the rainbow colors. Herschel by slowly moving the thermometer through the visible spectrum from the blue color to the red and measuring the temperatures through the spectrum, he noticed that the temperature increased from blue to red part of the spectrum. Herschel then decided to measure the temperature just below the red portion thinking that the increase of temperature would stop outside the visible spectrum, but to his surprise he found that the temperature was even higher. He called these rays, which were below the red rays "non colorific rays" or invisible rays, which were called later "infrared rays" or IR light. This light is not visible to human eye. A typical human eye will respond to wavelengths from 390 to 750 nm. The IR spectrum starts at 0.75 nm. One nanometer (nm) is 10^{-9} m The Infrared spectrum is divided into, Near Infrared (NIRS), Mid Infrared (MIRS) and Far Infrared (FIRS) [4-6].

1.2 The three Infra red regions of interest in the electromagnetic spectrum

In terms of wavelengths the three regions in micrometers (μm) are the following:

i.   NIRS, (0.7 μm to 2,5 μm)
ii.   MIRS (2,5 μm to 25 μm)
iii. FIRS (25 μm to300 μm).

In terms of wavenumbers the three regions in cm^{-1} are:

1.   (NIRS), 14000-4000 cm^{-1}
2.   (MIRS), 4000-400 cm^{-1}
3.   (FIRS), 400-10 cm^{-1}

The first region (NIRS) allows the study of overtones and harmonic or combination vibrations. The MIRS region is to study the fundamental vibrations and the rotation-vibration structure of small molecules, whereas the FIRS region is for the low heavy atom vibrations (metal-ligand or the lattice vibrations).Infrared (IR) light is electromagnetic (EM) radiation with a wavelength longer than that of visible light: ≤0.7μm. One micrometer (μm) is 10^{-6}m.

Experiments continued with the use of these infrared rays in spectroscopy called, Infrared Spectroscopy and the first infrared spectrometer was built in 1835. IR Spectroscopy expanded rapidly in the study of materials and for the chemical characterization of materials that are in our planet as well as beyond the planets and the stars. The renowned spectroscopists, Hertzberg, Coblenz and Angstrom in the years that followed had advanced greatly the cause of Infrared spectroscopy. By 1900 IR spectroscopy became an important tool for identification and characterization of chemical compounds and materials. For example, the carboxylic acids, R-COOH, show two characteristic bands at 1700 cm^{-1} and near 3500 cm^{-1}, which correspond to the C=O and O-H stretching vibrations of the carboxyl group, -COOH. Ketones, R-CO-R absorb at 1730-40cm^{-1}. Saturated carboxylic acids absorb at 1710 cm^{-1}, whereas saturated/aromatic carboxylic acids absorb at 1680-1690 cm^{-1} and carboxylic salts or metal carboxylates absorb at 1550-1610 cm^{-1}. By 1950 IR spectroscopy was applied to more complicated molecules such as proteins by Elliot and Ambrose [2]. These later studies showed that IR spectroscopy could also be used to study biological molecules, such as proteins, DNA and membranes and could be used in biosciences, in general [2-8].

Physicochemical techniques, especially infrared spectroscopic methods are non distractive and may be the ones that can extract information concerning molecular structure and characterization of many materials at a variety of levels. Spectroscopic techniques those based upon the interaction of light with matter have for long time been used to study materials both *in vivo* and in *ex vivo* or *in vitro*. Infrared spectroscopy can provide information on isolated materials, biomaterials, such as biopolymers as well as biological materials, connective tissues, single cells and in general biological fluids to give only a few examples. Such varied information may be obtained in a single experiment from very small samples. Clearly then infrared spectroscopy is providing information on the energy levels of the molecules in wavenumbers(cm^{-1}) in the region of electromagnetic spectrum by studying the vibrations of the molecules, which are also given in wavelengths (μm).

Thus, infrared spectroscopy is the study of the interaction of matter with light radiation when waves travel through the medium (matter). The waves are electromagnetic in nature and interact with the polarity of the chemical bonds of the molecules [3]. If there is no

polarity (dipole moment) in the molecule then the infrared interaction is inactive and the molecule does not produce any IR spectrum.

1.3 Degrees of freedom of vibrations

The forces that hold the atoms in a molecule are the chemical bonds. In a diatomic molecule, such as hydrochloric acid (H-Cl), the chemical bond is between hydrogen (H) and chlorine (Cl). The chemical forces that hold these two atoms together are considered to be similar to those exerted by massless springs. Each mass requires three coordinates, in order to define the molecule's position in space, with coordinate axes x,y,z in a Cartesian coordinate system. Therefore, the molecule has three independent **degrees of freedom** of motion. If there are N atoms in a molecule there will be a total of **3N degrees of freedom** of motion for all the atoms in the molecule. After subtracting the translational and rotational degrees of freedom from the 3N degrees of freedom, we are left with 3N-6 internal motions for a non linear molecule and 3N-5 for a linear molecule, since the rotation in a linear molecule, such as H-Cl the motion around the axis of the bond does not change the energy of the molecule. These internal vibrations are called the normal modes of vibration. Thus, in the example of H-Cl we have one vibration,(3x2)-5=1, i.e. only one vibration along the H-Cl axis or along the chemical bond of the molecule. For a non linear molecule as H_2O we have (3x3)-6=3 vibrations, the two vibrations along the chemical bonds O-H symmetrical (v_s) and antisymmetrical (v_{as}) O-H bonds and the bending vibration (δ) of changing the angle H-O-H of the two bonds [3,4]. In this way we can interpret the IR-spectra of small inorganic compounds, such as, SO_2, CO_2 and NH_3 quite reasonably. For the more complicated organic molecules the IR spectrum will give more vibrations as calculated from the 3N-6 vibrations, since the number of atoms in the molecule increases, however the spectrum is interpreted on the basis of characteristic bands.

2. Theory

2.1 Interaction of light waves with molecules

The interaction of light and molecules forms the basis of IR spectroscopy. Here it will be given a short description of the Electromagnetic Radiation, the energy levels of a molecule and the way the Electromagnetic Radiation interacts with molecules and their structure [5, 6].

2.2 Electromagnetic radiation

The EM radiation is a combination of periodically changing or oscillating electric field (EF) and magnetic field (MF) oscillating at the same frequency, but perpendicular to the electrical field [7] (see Fig.2).

The wavelength is represented by λ [6], which is the wavelength, the distance between two positions in the same phase and frequency (v) is the number of oscillations per unit time of the EM wave per sec or vibrations/unit time. The wavenumber is the number of waves/unit length [7]. It can be easily seen [3] that c is given by equation 1:

$$c = \lambda v \tag{1}$$

where, c is the velocity of light of EM waves, or light waves, which is a constant for a medium in which the waves are propagating, c=3x 10^8m/s
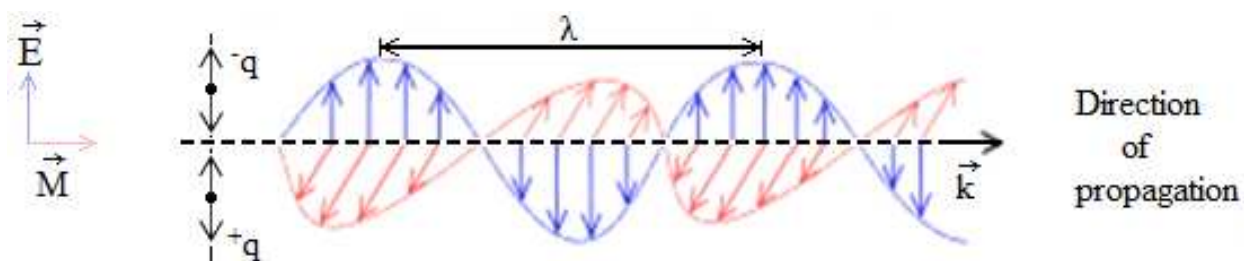
Fig. 2. An Illustration of Electromagnetic Radiation can be imagined as a self-propagating transverse oscillating wave of electric and magnetic fields. This diagram shows a plane linearly polarized wave propagating from left to right. The electric field is in a vertical plane (E) blue and the magnetic field in a horizontal plane (M) red

The wavelength (λ) is inversely proportional to the frequency, $1/v$. The Energy in quantum terms [8]: is given by Planck's equation:

$$E = hv \tag{2}$$

Which was deduced later also by Einstein, where, E is the energy of the photon of frequency v and h is Max Planck's constant [8], h=6.62606896x 10^{-34} Js or h =4.13566733x 10^{-15} ev. Wave number and frequency are related by the equation

$$v = c\tilde{v} \tag{3}$$

The EM spectrum can be divided as we have seen into several regions differing in frequency or wavelength. The relationship between the frequency (v) the wavelength (λ) and the speed of light(c) is given below:

$$v = \frac{c}{\lambda} \quad v = \frac{E}{h} \quad E = \frac{hc}{\lambda} \tag{4}$$

The frequency in wavenumbers is given by the equation:

$$\tilde{v} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}} \quad (cm^{-1}) \tag{5}$$

Where, k=bond spring constant, μ= reduced mass, c=velocity of light (cm/sec),

μ is the reduced mass of the AB bond system of masses and m= mass of the atoms, m_A=mass of A and m_B= mass of B. The isotope effect can also be calculated using the reduced mass and substituting the isotopic mass in the equation of the frequency in wavenumbers.

Example, the H-Cl molecule

$$\mu = \frac{m_H m_{Cl}}{m_H + m_{Cl}}$$

m_H and m_{Cl} are the atomic masses of H and Cl atoms.

2.3 Energy of a molecule

The name *atom* was coined by Democritus [9] from the Greek, α-τέμνω, meaning in Greek it cannot be cut any more or it is indivisible. This is the first time that it was postulated that the atom is the smallest particle of matter with its characteristics and it is the building block of all materials in the universe. Combinations of atoms form molecules.

The energy of a molecule is the sum of 4 types of energies [3]:

$$E = E_{ele} + E_{vib} + E_{rot} + E_{tra} + E_{nuc} \qquad (6)$$

E_{ele}: is the electronic energy of all the electrons of the molecule
E_{vbr}: is the vibrational energy of the molecule, i.e., the sum of the vibrations of the atoms in the molecule
E_{rot}: is the rotational energy of the molecule, which can rotate along the three axes, x,y,z
E_{tra}: is the translational energy of the molecule, which is due to the movement of the molecule as a whole along the three cartesian axes, x, y, z .
E_{nuc}: is the nuclear energy

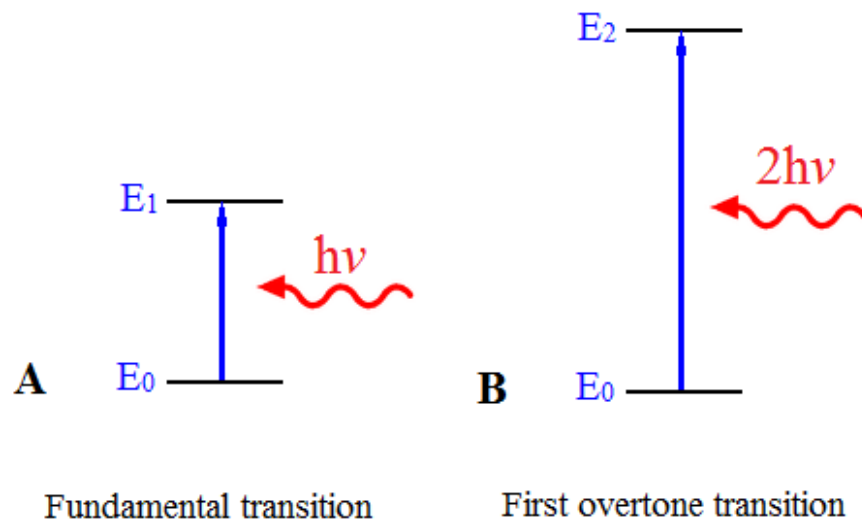Energy level electronic transitions (see Figs 3A, 3B):

Fig. 3. A: Increasing the energy level from E_0 to E_1 with the wave energy $h\nu$, which results in the fundamental transition, B: Increasing the energy level from E_0 to E_2 leads to the first overtone transition or first harmonic.

3. The techniques of infrared spectroscopy

We have two types of IR spectrophotometers: The classical and the Fourier Transform spectrophotometers with the interferometer

3.1 The classical IR spectrometers [3, 4]

The main elements of the standard IR classical instrumentation consist of 4 parts (see Fig.4)

1. A light source of irradiation
2. A dispersing element, diffraction grating or a prism

3.   A detector
4.   Optical system of mirrors

Schematics of a two-beam absorption spectrometer are shown in. Fig. 4.
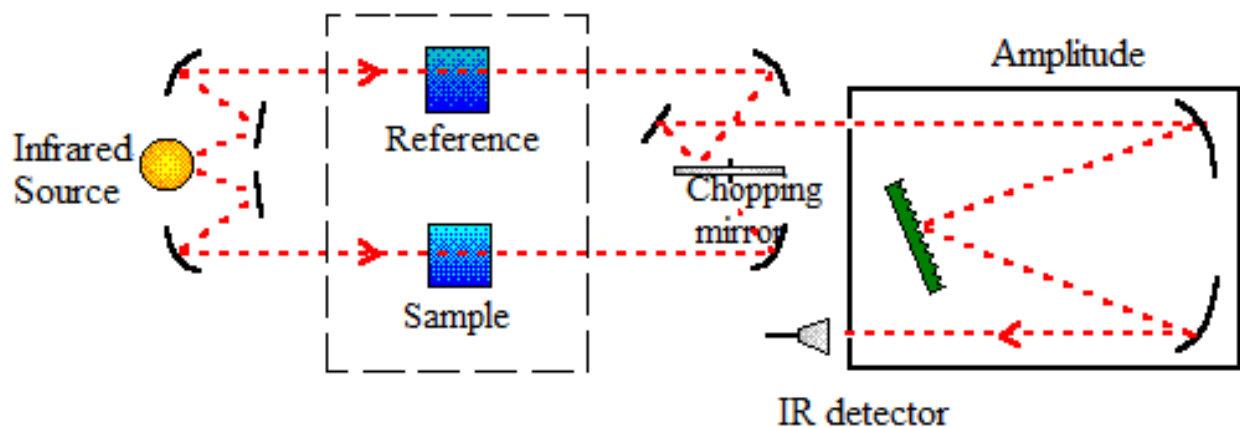

Fig. 4. A schematic diagram of the classical dispersive IR spectrophotometer.

The infrared radiation from the source by reflecting to a flat mirror passes through the sample and reference monochromator then through the sample. The beams are reflected on a rotating mirror, which alternates passing the sample and reference beams to the dispersing element and finally to detector to give the spectrum (see Fig 4). As the beams alternate the mirror rotates slowly and different frequencies of infrared radiation pass to detector.

3.2 Fourier Transform IR spectrometers

The modern spectrometers [7] came with the development of the high performance Fourier Transform Infrared Spectroscopy (FT-IR) with the application of a Michelson Interferometer [10]. Both IR spectrometers classical and modern give the same information the main difference is the use of Michelson interferometer, which allows all the frequencies to reach the detector at once and not one at the time/

In the 1870's A.A. Michelson [11] was measuring light and its speed with great precision(3) and reported the speed of light with the greatest precision to be 299,940 km/s and for this he was awarded the Nobel Prize in 1907. However, even though the experiments in interferometry by Michelson and Morley [12] were performed in 1887 the interferograms obtained with this spectrometer were very complex and could not be analyzed at that time because the mathematical formulae of Jean Baptiste Fourier series in 1882 could not be solved [13]. We had to wait until the invention of Lasers and the high performance of electronic computers in order to solve the mathematical formulae of Fourier to transform a number of points into waves and finally into the spectra [14]

The addition, of the lasers to the Michelson interferometer provided an accurate method (see Figs. 5A & 5B) of monitoring displacements of a moving mirror in the interferometer with a high performance computer, which allowed the complex interferogram to be analyzed and to be converted *via* Fourier transform to give spectra.

Fig. 5A. Michelson FT-IR Spectrometer has the following main parts:

1. Light source
2. Beam splitter (half silvered mirror)
3. Translating mirror
4. Detector
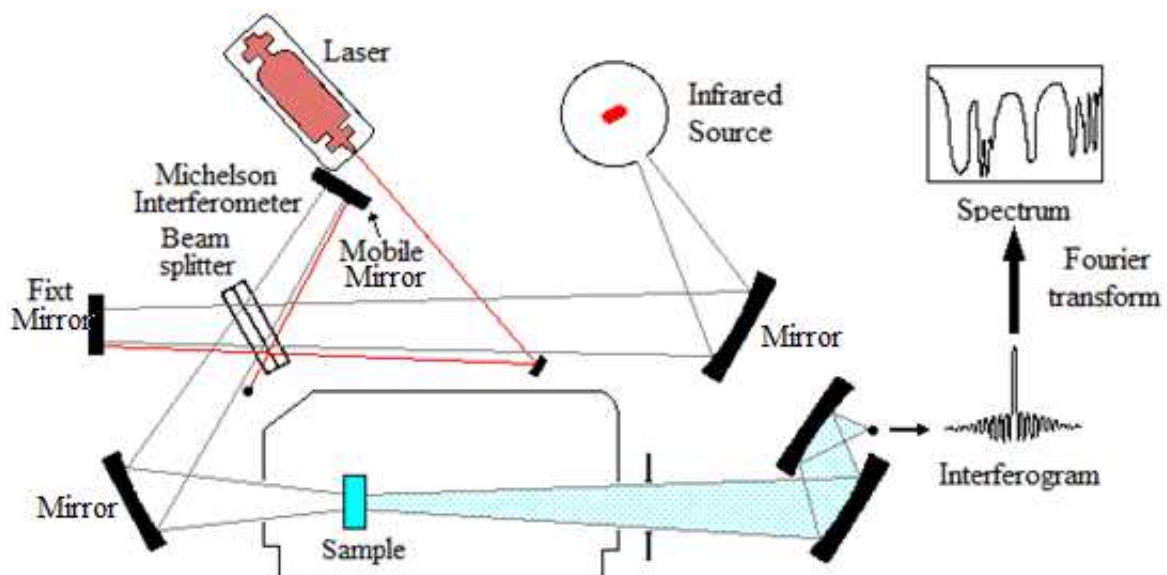5. Optical System (fixed mirror)

Fig. 5B. Schematic illustration of a modern FTIR Spectrophotometer.

Infrared spectroscopy underwent tremendous advances after the second world war and after 1950 with improvements in instrumentation and electronics, which put the technique at the center of chemical research and later in the 80's in the biosciences in general with new sample handling techniques, the attenuated total reflection method (ATR) and of course the interferometer [13]. The Fourier Transform.IR spectrophotometry is now widely used in both research and industry as a routine method and as a reliable technique for quality control,

molecular structure determination and kinetics [14-16] in biosciences(see Fig. 6). Here the spectrum of a very complex matter , such as an atheromatic plaque is given and interpreted.

In practice today modern techniques are used and these are the FT-methods. The non- FT methods are the classical IR techniques of dispersion of light with a prism or a diffraction grading. The FT-technique determines the absorption spectra more precisely. A Michelson interferometer should be used today to obtain the IR spectra [17]. The advantage of FT-method is that it detects a broad band of radiation all the time (the multiplex or Fellget advantage) and the greater proportion of the source radiation passes through the instrument because of the circular aperture (Jacquinot advantage) rather than the narrow slit used for prisms or diffraction gratings in the classical instrument.
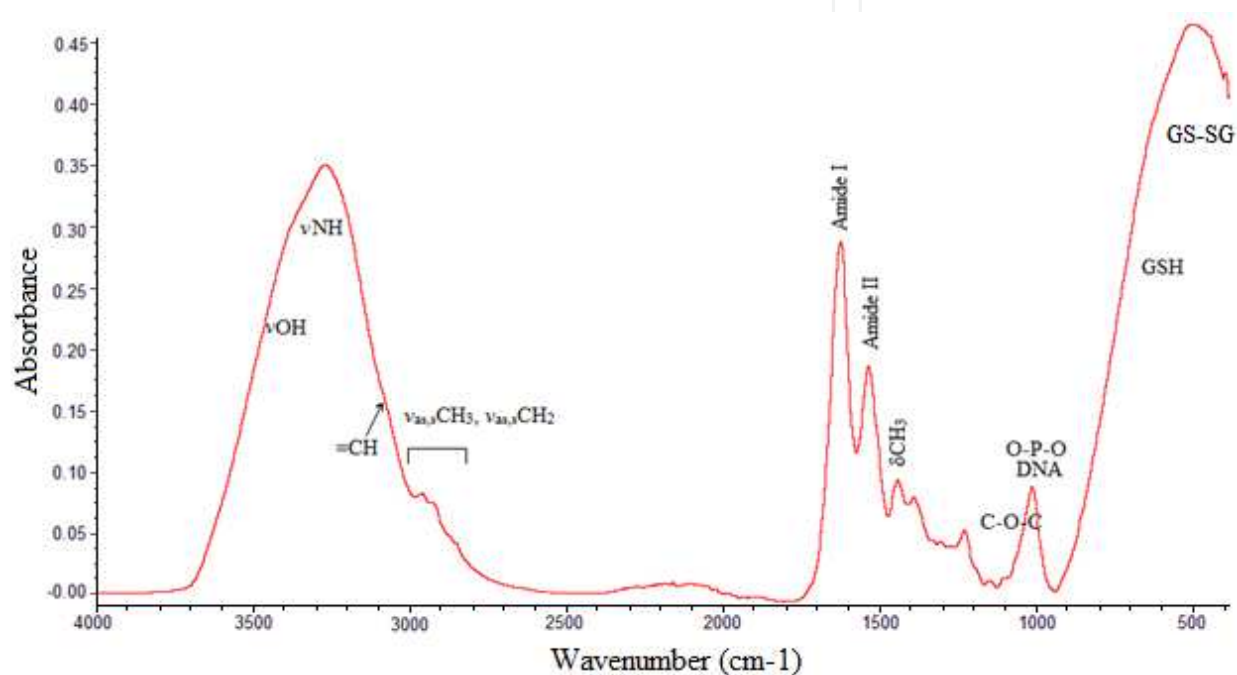

Fig. 6. FT-IR spectrum of a coronary atheromatic plaque is shown with the characteristic absorption bands of proteins, amide bands, O-P-O of DNA or phospholipids, disulfide groups, etc.

3.3 Micro-FT-IR spectrometers

The addition of a reflecting microscope to the IR spectrometer permits to obtain IR spectra of small molecules, crystals and tissues cells, thus we can apply the IR spectroscopy to biological systems, such as connective tissues, blood samples and bones, in pathology in medicine [15, 26-27]. In Fig. 7 is shown the microscope imaging of cancerous breast tissues and its spectrum.

4. Applications

Infrared spectroscopy is used in chemistry and industry for identification and characterization of molecules. Since an IR spectrum is the "fingerprint" of each molecule IR is used to characterize substances [16, 17]. Infrared spectroscopy is a non destructive method and as such it is useful to study the secondary structure of more complicated systems such
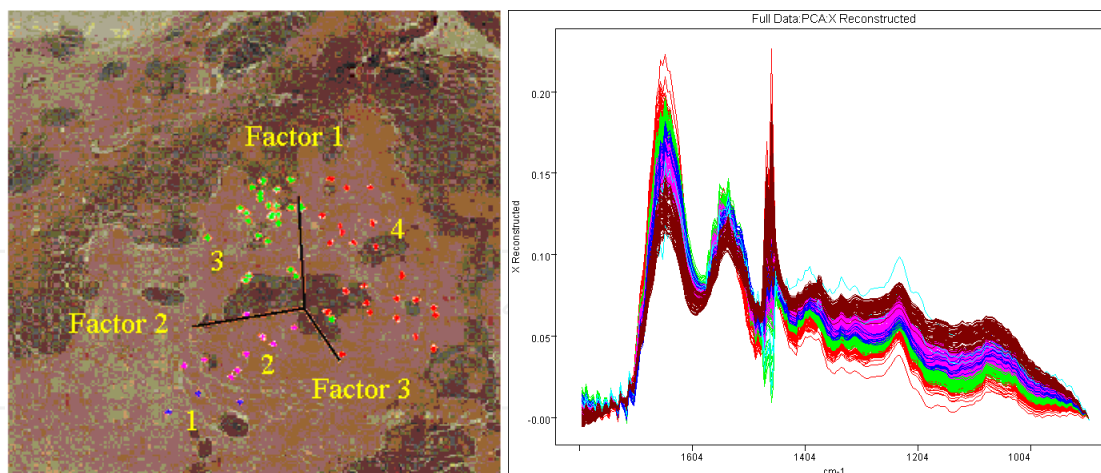
Fig. 7. Breast tissue: a 3-axis diagram and the mean spectral components are shown [25].

as biological molecules proteins, DNA and membranes. In the last decade infrared spectroscopy started to be used to characterize healthy and non healthy human tissues in medical sciences.

IR spectroscopy is used in both research and industry for measurement and quality control. The instruments are now small and portable to be transported, even for use in field trials. Samples in solution can also be measured accurately. The spectra of substances can be compared with a store of thousands of reference spectra [18]. Some samples of specific applications of IR spectroscopy are the following:

IR spectroscopy has been highly successful in measuring the degree of polymerization in polymer manufacture [18]. IR spectroscopy is useful for identifying and characterizing substances and confirming their identity since the IR spectrum is the "fingerprint" of a substance. Therefore, IR also has a forensic purpose and IR spectroscopy is used to analyze substances, such as, alcohol, drugs, fibers, blood and paints [19-28]. In the several sections that are given in the book the reader will find numerous examples of such applications.

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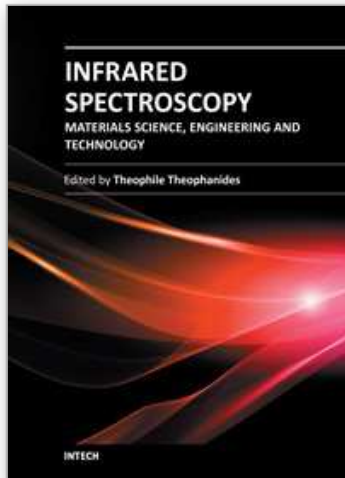
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The present book is a definitive review in the field of Infrared (IR) and Near Infrared (NIR) Spectroscopies, which are powerful, non invasive imaging techniques. This book brings together multidisciplinary chapters written by leading authorities in the area. The book provides a thorough overview of progress in the field of applications of IR and NIR spectroscopy in Materials Science, Engineering and Technology. Through a presentation of diverse applications, this book aims at bridging various disciplines and provides a platform for collaborations among scientists.