Chapter

Introductory Chapter: Infrared Spectroscopy - A Synopsis of the Fundamentals and Applications

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1. History and fundamentals

Spectroscopy is a term that describes the interaction of matter with electromagnetic radiation. Several forms of interaction therefore exist: absorption, emission, diffraction, impedance, resonance, and inelastic scattering of radiation. Therefore, and as a big science, spectroscopy is used to characterize/detect matter (atoms, molecules, and nuclei) based on the produced spectra and following their interaction with radiation. The electromagnetic spectrum, and as the word *spectrum* implies, is a range of frequencies of the electromagnetic radiation and the corresponding wavelengths and photon energies [1, 2]. **Figure 1** shows a schematic portrayal of the electromagnetic spectrum, along with the molecular processes that can occur in each region, e.g., rotation (microwave), vibration (infrared), electronic excitation (ultraviolet-visible), and bond breaking and ionization (X-rays).

As shown in **Figure 1**, the sector of the spectrum extending from the nearly 10^{-3} m (microwave) to the 780 nm (visible) wavelength range is labeled as the infrared (IR) region. Extending from the red edge of the visible region to 1 mm on the wavelength scale, IR radiations were first come across by Sir William Herschel in the nineteenth century by sensing the temperature escalation across the visible zone and then from the visible zone to beyond, which was then soon identified as the IR region [3–5]. Akin to the situation in the ultraviolet region, the IR radiations are invisible to the human eye. As shown on the wavelength scale in **Figure 1**, IR radiations appear at a longer wavelength compared to the visible region. Accordingly, and since electromagnetic radiations travel at a constant speed in vacuum which is the speed of light (c, $2.997\,924\,58 \times 10^{8}$ m s^{-1}), the frequency of IR radiations is therefore lower compared to that of the visible light, applying the formula $\upsilon = c/\lambda$ where υ = the frequency of light, c = the speed of light, and λ = the wavelength of light. This in turn means that energy associated with the IR radiations is inferior to that of the visible light and greater than that of microwaves, for instance [5–8].

Accordingly, and possessing an energy that can initiate molecular vibrations, IR radiations act by instigating recurring oscillations of the atoms' positions around their bonds, while the entire molecule is in a continual *translational* and *rotational* movement. As the position of a molecule in the space could be outlined by the three Cartesian coordinates: x, y, and z, this molecule would have three degrees of freedom (3 DoF) in terms of its motion. Consequently, and for a nonlinear molecule with N atoms, DoF = 3N. Normal modes of vibrations for such a molecule can be obtained following the exclusion of the DoF for the translational and rotational

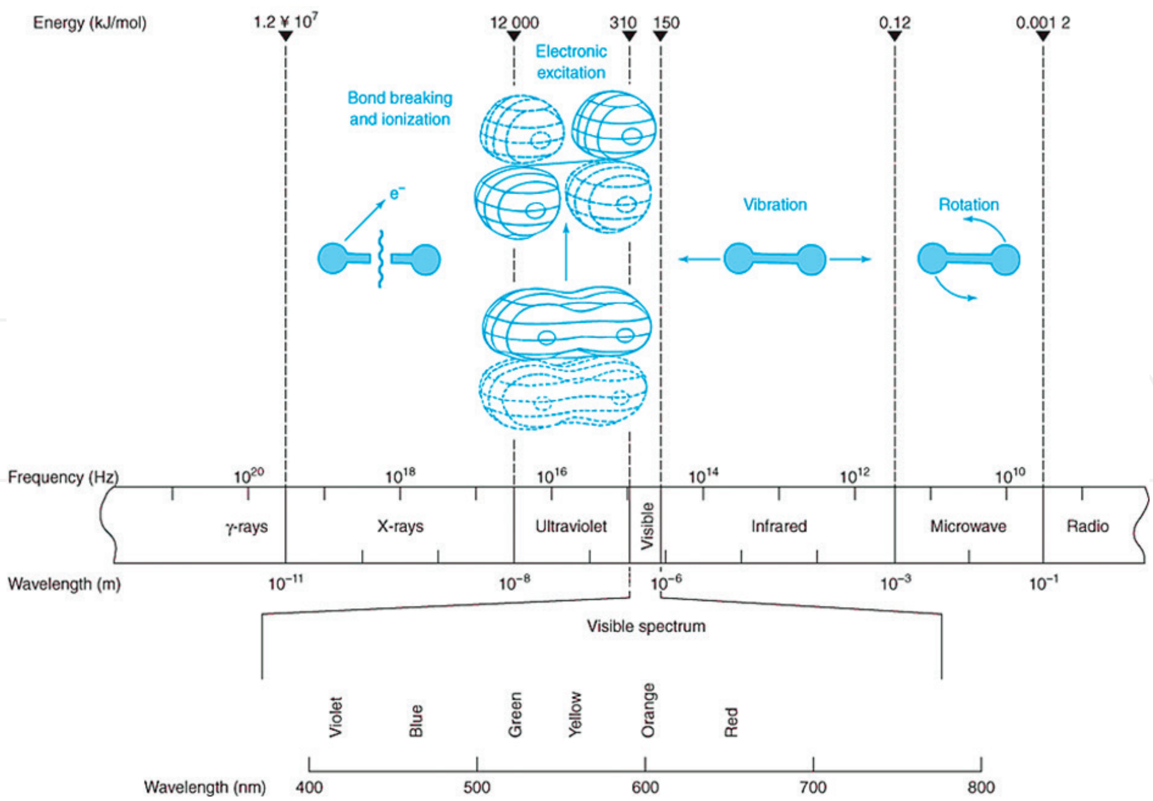

Figure 1.
Schematic portrayal of the electromagnetic spectrum, showing representative molecular processes that occur in each region [2].

motions and are equal to 3N-6. As the rotation of a linear molecule around the bond axis does not involve a change in energy and hence cannot be observed, the number of internal motions would be 3N-5 [1, 8–11].

By and large, vibrational spectroscopy is the communal label given to describe measurements involving both infrared (IR) and Raman spectroscopy (RS). As an approach, vibrational spectroscopy is used to measure *molecular* vibrations resulting from absorption of light/photons. Therefore, absorption of energy, E, that matches the vibration frequency, υ, would trigger molecular vibration because of the change in the dipole moment. Both techniques give spectral sketches that express the chemical temperament of a sample.

Two main modes of vibrations are commonly known; *stretching* (where the distance between the two atoms and hence the bond length are affected) and *bending* (where the slant between the two bonds is altered). Further classification of the types of motions would include two stretching modes: *symmetric* (where the two atoms *simultaneously* move toward and away from the central atom) and *anti-symmetric* (where one of the atoms move toward the central atom, while the second moves away from the central atom). Bending vibrations include four types of motions; *rocking* (the two atoms moving in-plane either clockwise or anti-clockwise), *scissoring* (also in-plane, both atoms are simultaneously moving either toward each other or away from each other), *wagging* (out-of-plane, where both atoms simultaneously move like a V sign back and forth), and *twisting* (out-of-plane, where one atom moves forward while the other moves backward), **Figure 2** [10].

Overall, occurrence of vibration of a particular mode, rather than another, is influenced by quite a few considerations. In general, the *mode of vibration* itself is one of the considerations, e.g., bending needs less energy compared to stretching and hence is more feasible. Another concern is the *bond strength*, where a single bond is weaker compared to a double bond, which in turn is weaker than a triple

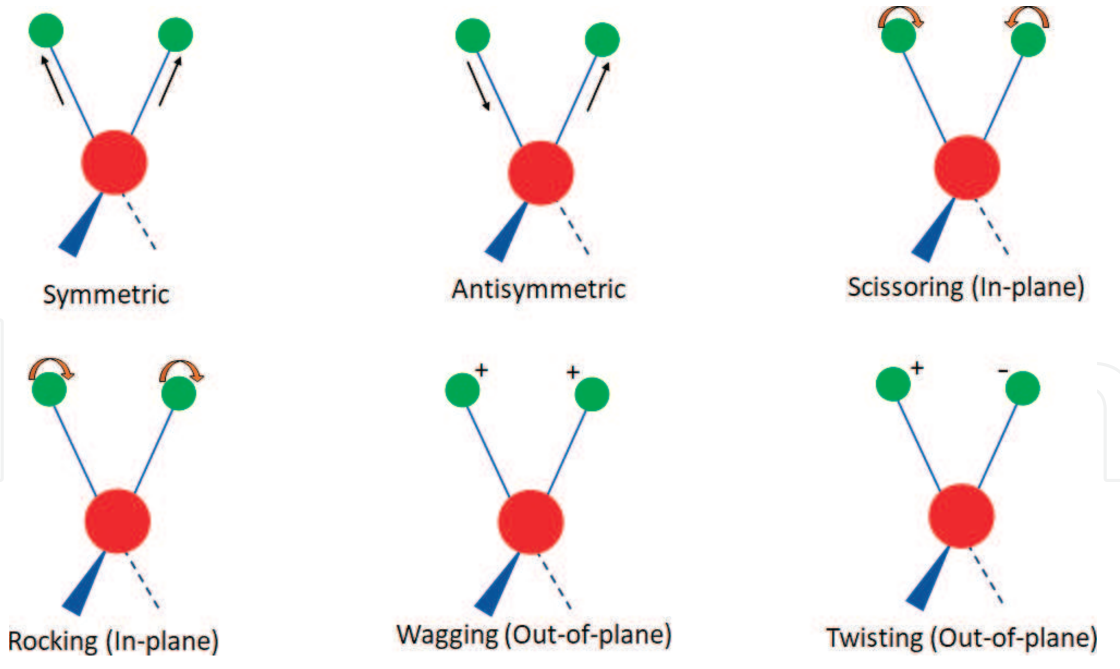

Figure 2.
Modes of molecular vibration.

bond. Therefore, a single bond needs less energy and appears at a lower wavenumber (ῦ). Mass of the atoms is another consideration, where heavier atoms would vibrate more slowly compared to the light atoms.

2. Advances in IR spectroscopy

Before introducing the reader to the instrumentations and sampling techniques used in the IR region and their impact on the advances in the field of IR spectroscopy, it is crucial to first present the zones of IR.

2.1 Zones of the IR region

Three main zones can be identified in the IR region:

i. The far-IR (FIR, 400–10 cm^{-1}, 25–300 μm)

ii. The mid-IR (MIR, 4000–400 cm^{-1}, 2.5–25 μm)

iii. The near-IR (NIR, 14,000–4000 cm^{-1}, 0.7–2.5 μm)

Ranges given between parentheses are identified on the wavenumber (ῦ) and wavelength (λ) scales, respectively, **Figure 3** [12]. It is noteworthy to mention that different schemes for the IR division exist depending on the application. For example, a sensor response division scheme classifies the IR region into five zones instead of the three shown above depending on the detector's sensitivity [13–15]. Some classifications add a region of long-wave IR (LWIR) or thermal IR (TIR: 8–15 μm).

The MIR region can be further divided into the *fingerprint* region (400–1400 cm^{-1}) and the *functional groups*' region (1400–4000 cm^{-1}). For that reason, the MIR region is the most commonly used where most compounds would have a *signature* absorption/emission in this region.

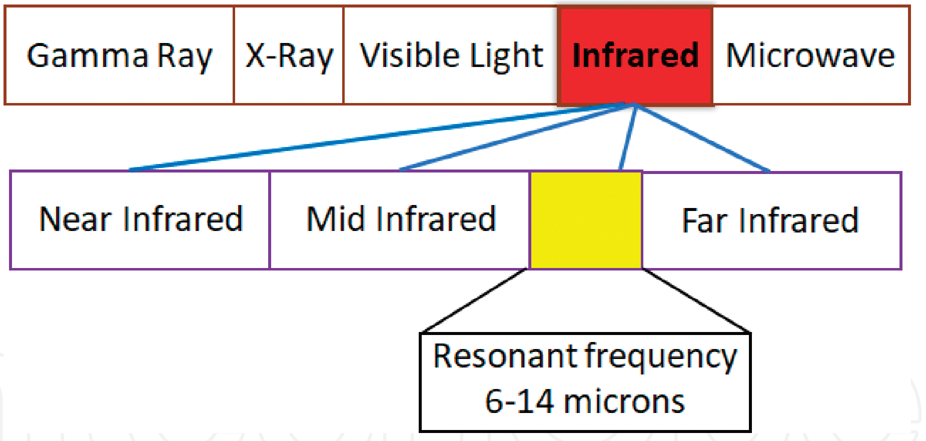

Figure 3.
Section from the electromagnetic spectrum showing regions of IR. The diagram is replicated from https://en.wikipedia.org/wiki/Far_infrared#/media/File:Electromagnetic_Far_Infrared.jpg.

Absorption in the NIR region is an outcome of two major processes: *molecular overtones* and *combinations.* For simplification, an *overtone* is a frequency that is higher than the fundamental frequency (lowest frequency). Both frequencies (overtone + fundamental) are known as *harmonic partials*. In simpler words, each fundamental frequency will generate a succession of absorptions at integer multiples of this frequency, and a molecule experiencing an overtone is the one getting excited from the ground state to the second excited state [16]. Consequently, NIR absorptions need higher energy than a fundamental, and few overtones can be observed in this region. On the contrary to overtones arising from a group of fundamental absorptions, combinations, appearing because of the allocation of energy between two or more fundamental MIR bands that get excited simultaneously, are largely seen. Therefore, the NIR region is basically a region of broad peaks with limited use (except for bulk materials keeping in mind that NIR can penetrate much further compared to MIR). Thus, application of multivariate calibration techniques would resolve the complexity of the spectra and help extracting the needed information [16]. Yet, it is noteworthy to mention that each of the three regions (mid-, near-, and far-) has significant applications in different fields as will be seen in the subsequent sections.

2.2 Instrumentations and sampling techniques

In general, this field has seen a major progress especially after grating was first introduced in 1823, and after the first commercial IR spectrometer came to the scene. The conventional IR spectrophotometer, first introduced in the 1940s, was a dispersive instrument. Rudimentary parts of this instrument were *a radiation source*, *a monochromator*, and *a detector,* most frequently in a double-beam setup. Monochromator, the dispersive device, serves to separate the broad spectrum of IR radiations into a continuous sequence of IR bands with resolved frequencies. These instruments work by tracing only a sole frequency at a time. Consequently, a whole spectrum needs a long time to be recorded [6–8, 17, 18]. It was in the 1960s when Fourier transform (FT) instruments came to the scene. The key difference between FT and dispersive instruments was the presence of *interferometers*. The output of the FT-IR instrument is then called an *interferogram.* FT-IR instruments, though were intended to extend the use of IR, had limited applications and were used only for advanced research. This was mainly because of the expensive component electronics and the need for supercomputers to record the generated data. However, after the microelectronic revolution, the capabilities and availability of these instruments have been greatly improved. In addition to the noticeable speed in acquiring spectra, improved signal to noise ratio, high resolution, accuracy, and reproducibility, FT-IR offers two major pluses over the classical dispersive instruments [6–8, 17–20]:

i. Multiplex plus: where all frequencies fall on the detector in unison. Therefore, each resolution component is grasped continually, creating a multifaceted spectrum.

ii. Throughput plus: the presence of gratings and prisms in a dispersive instrument and the need for an ingress slit would decrease the amount of light reaching the detector. Quite the reverse, an interferometer has a large orifice that in turn increases the output.

Samples to be measured with FT-IR or dispersive instruments (*transmission techniques*) need a prior treatment. A solid sample is mixed with potassium bromide, packed together into a compressed disc, and inserted into the pathway of radiation. Liquid samples are placed in special holders or mounted on the surface of a KBR disc. Other sampling techniques, e.g., *reflectance techniques*, however, permit IR radiations to be applied on a larger assortment of sample forms without additional treatment. As their name implies, radiations in these techniques are *reflected* from the sample surface rather than being *transmitted* through it. Reflections might be *total internal, specular,* or *diffuse.* Details on speculations of each technique can be summarized as follows and as shown in **Figure 4**:

i. Total reflection IR or attenuated total reflectance IR (ATR-IR): where light undergoes several internal reflections when passed through an ATR crystal of high refractive index (RI), which in turn is in contact with the sample. The resultant evanescent wave spreads to the sample and infiltrates to a depth that is dependent on a variety of controls such as light wavelength, RI of the crystal and the medium being examined, and incidence angle. An ATR crystal might be made of *Diamond*, *Zinc Selenide (ZnSe), Germanium (Ge), or Silicon (Si).* The resulting spectrum is analogous to that produced by dispersive instruments especially for thin films [21, 22]. ATR-IR is suitable for a variety of sample forms with no or minimal need for sample preparation. Yet, ATR-IR is less sensitive compared to transmission-based techniques.

ii. Specular reflection IR spectroscopy (SRS): also known as external reflection IR occurs when light is reflected from a specular surface (mirror-like) at a well-defined angle that is equal to the angle of incidence of IR radiation. Analogous to ATR-IR, thin films' reflectance spectra are like the transmission spectra and are identified as a reflection-absorption mode. For ultrathin films (monomolecular layers), however, using a grazing incidence mode is needed where the path of radiation becomes parallel to the metal surface augmenting the absorption intensity. In general, coupling of an IR spectrophotometer with an optical microscope is known as FT-IR microscopy. Collection of the specular reflection spectrum is performed using such a setup and is commonly known as micro FT-IR [8, 19, 22–24].

iii. Diffuse reflectance spectroscopy (DRS): this is a combination between internal and external reflections and originates from rough surfaces *(powders)* reflecting light in different directions. Having diffuse reflectance exploited in IR FT spectroscopy is known as DRIFTs [8, 25].

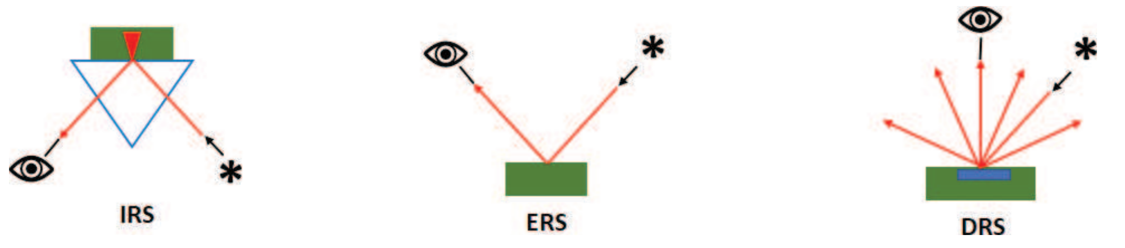

Figure 4.
FT-IR reflection modes.

3. Data treatment in IR spectroscopy

Chemical data encompassed in the MIR spectra exist in peak positions, peak intensities, and peak shape. Therefore, while spectra from MIR can be easily interpreted and information can be easily extracted, the spectra obtained from NIR, however and as previously mentioned, have the absorption bands from the overtones and combinations of fundamental MIR bands and therefore need special treatment to resolve this overlapping. Analysis of data from NIR implementing multivariate data analysis or chemometrics would be a suitable approach. With the advances in data sciences, coupling of IR spectroscopy to chemometrics serves to combine the advantages of both in terms of time, effort, and multicomponent analysis. Application of a certain chemometric method in NIR data analysis would depend greatly on whether the performed analysis is qualitative or quantitative. In general, three approaches are used to examine data from NIR [26–30]:

i. Arithmetic data pre-processing: this approach helps diminution of the impact of side data and keeps the focus on the main data in a spectrum. Normalization, derivatization, and smoothing are common techniques.

ii. Classification techniques: mainly used for data obtained from qualitative analysis where samples are congregated based on their spectra. Classification might be *unsupervised* where only the spectra are known for the researcher and no other information is available, or *supervised pattern recognition* where a prior knowledge of samples' categories exists, and spectroscopists would create a classification model then evaluate this model by comparing the predicted values to the actual ones [26, 31, 32]. Principle component analysis (PCA) is a common unsupervised classification approach, while partial least squares discriminant analysis (PLSDA) is a classical supervised classification technique [28, 30].

iii. Regression methods: used mainly in quantitative analysis. Common approaches include principle component regression (PCR), multi-linear regression (MLR), partial-least squares (PLS), artificial neural network (ANN), and support vector machines (SVMs) [28].

4. What the reader will get from the next chapters

Sampling techniques such as FT-IR and ATR-IR have served in the expansion of IR applications to a variety of matrices. As an established technique that is readily available for researchers and being a cost-effective and non-destructive approach, IR spectroscopy has a realm of applications in different fields. Food analysis, nanoparticle synthesis and characterization, medicine, drug synthesis and analysis, etc. are among the applications. Yet, being insensitive, and with questionable selectivity, applications of IR are still in a need for further development.

In this introductory chapter, the author (editor) tried to shed light on the fundamentals of IR spectroscopy, advances introduced to the field with the introduction of new sampling techniques, and the common approaches of data analysis. In the following interesting chapters, one can see the IR applications in different fields disclosing themselves to the readers. Authors of every chapter have tried their best to reveal the underlying concepts associated with any of the mentioned applications. The shown assembly of the seven chapters would provide the readers with insights on

- MIR laser spectroscopy sources, especially those applicable in the 3–4 μm wavelength range, e.g., quantum cascade lasers (QCLs).

- Impact of QCLs on the existing spectroscopic schemes. Readers will see the influence of these sources on MIR applications such as detection of weapons of massive destruction, e.g., high explosives (HEs) and biological threats, as well as the analysis of pharmaceutical blends.

- Difficulties encountered in the application of MIR to an industrial environment, e.g. trace gas detection, leak detection, gas emission and monitoring of air quality, and what are the solutions available.

- The competency of FT-IR spectroscopy and micro-spectroscopy in the biomedical research area, with a capability to depict and spot serious health problems, e.g. obesity. Readers will see that FT-IR, employing ATR as a sampling mode and coupled to chemometrics, has greatly impacted the power of IR spectroscopy in terms of detection limits, early-stage detection of disease-induced changes, and inevitability of the obtained results.

- Challenges associated with VIS-NIR applications, with a sample application—such as a non-destructive approach—for assessing quality parameters of fruits and the consequent impact on their nutritional value and the economy at the far end.

- IR spectroscopic studies (reflection-absorption IR spectroscopy) of radiation-stimulated processes of adsorption, radiolysis of hydrocarbons on metal surfaces, and radiation hydrogenation of these surfaces.

- Impact of using IR in developing an ideal catalyst and efficient catalysis process, which in turn would help developing more efficient processes via reduction of energy consumption and the generation of by-products. Readers would get the sequence of such a process through the examples given, e.g., Fischer-Tropsch synthesis, ethylene oligomerization, aniline synthesis, and dehydration of aldoximes to nitriles.

- Coupling of multivariate analysis techniques to both MIR and NIR routines and its influence on the discrimination power, limits of detection and quantification, and data clustering is almost discussed in every chapter.

Finally, I think readers will find this book informative as well as interesting and probably inspiring for further advances in the field. I, therefore, invite the readers to go through the following chapters and see the different applications of IR spectroscopy.

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