

CHAPTER II

THEORETICAL BACKGROUND

2.1 Fundamentals of Light Propagation

Light is by nature an electromagnetic wave produced by the vibration of an electric charge. In its simplest monochromatic form, light can be represented as polarized, oscillating electric and magnetic fields that propagate in space, as depicted in Figure 2.1 [28].

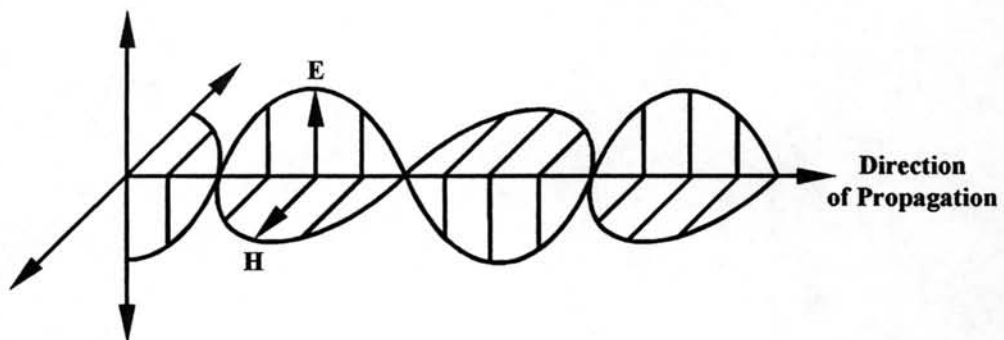


Figure 2.1 Propagation of a linearly polarized electromagnetic wave in the direction of propagation.

The electric (**E**) and magnetic (**H**) vectorial components are orthogonal to each other and to the direction of propagation. In unpolarized light, the electric component **E** is randomly oriented in an infinite number of directions, but remains always perpendicular to the direction of propagation.

When an electromagnetic radiation impinges on a matter, rays of the incident beam may be reflected, scattered, transmitted, or absorbed that depending on the experimental arrangement. The total amount of incident energy is the sum of reflected, scattered, transmitted, and absorbed light. A schematic illustration for an interaction between light and matter is illustrated in Figure 2.2. This process can be expressed by the following relationship:

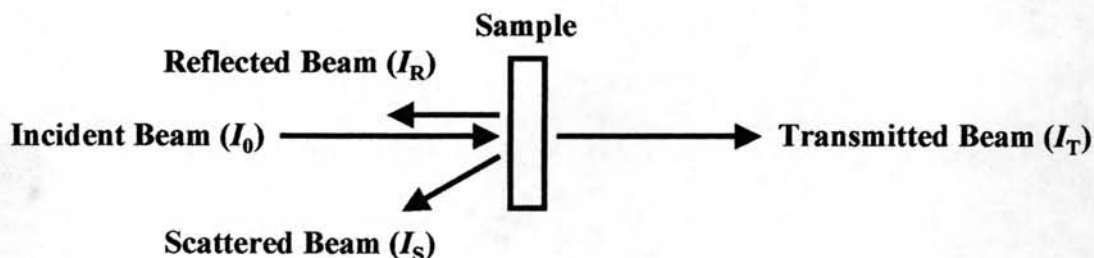


Figure 2.2 Interactions of light with matter.

$$I_0 = I_R + I_S + I_T + I_A \quad (2.1)$$

where I_0 is the intensity of the incident radiation and I_R , I_S , and I_T are the reflected, scattered, and transmitted radiations, respectively. I_A is the radiation absorbed by matter. The intensity of each radiation depends on the intensity and wavelength of the incident radiation, the optical properties of the specimen, the concentrations of species, and the geometry of the experimental setup.

Considering the electromagnetic radiation when the sample is inserted between a light source and a detector, the sample absorbs a fraction of the incident radiation. In order to measure the region and amount of light being absorbed by the sample, we need to measure the ratio of transmitted (I_T) and incident (I_0) intensities of the radiation. The ratio is proportional to the transmittance of the sample. This relationship can be quantitatively related to the chemical composition of the sample by the *Beer-Lambert law* as:

$$\frac{I}{I_0} = e^{-A(\bar{\nu})} = e^{-c_2 \varepsilon(\bar{\nu}) l} \quad (2.2)$$

where $A(\bar{\nu})$ is the absorbance of the sample at a given wavenumber $\bar{\nu}$, c_2 is the concentration of the absorbing functional group, $\varepsilon(\bar{\nu})$ is the wavenumber-dependent absorption coefficient, and l is the film thickness for the infrared beam at a normal incidence to the sample surface.

The simple transmission technique involves passing infrared radiation through the sample and detecting a portion of the radiation that is transmitted. This technique provides significant information concerning molecular structures and their properties. Nevertheless, transmission mode is not applicable to surface analysis. If one requires gaining an insight understanding of the surface properties such as chemical compositions, molecular orientation, and chemical reaction, a surface sensitive technique is required. Attenuated total reflection (ATR) FT-IR spectroscopy is a good candidate for that purpose. It is not only a technique that provides the information, which directly associated to chemical composition of the sample, but also a surface sensitive sampling technique [28].

2.2 Attenuated Total Reflection Fourier Transform Spectroscopy (ATR FT- IR)

ATR is a well-known technique for measuring infrared spectra. It is a method of internal reflectance, whereas specular and diffuse reflections are methods of external reflectance. The infrared light is directed into an internal reflection element (IRE) fabricating from a high refractive index material with an angle that total internal reflections occur inside the crystal. The light exits the crystal and passes through the detector. At each reflection, part of the light called the *evanescent wave* passes the crystal interface and interacts with a sample placed in close contact with the crystal. The infrared spectrum may be collected. The IRE is normally a material with high index of refraction, such as zinc selenide (ZnSe), germanium (Ge), and diamond. The material employed as an IRE has an effect on the ATR measurement because materials of different refractive index affect the depth of penetration and the occurrence of anomalous absorption [34].

2.2.1 Snell's Law: A Principle of Light Reflection and Refraction

When an electromagnetic radiation strikes a boundary between two media with different refractive indices, refraction and reflection occur. The law that governs the reflection process requires that the angle of incidence is equal to the angle of reflection. In this case, reflection is specular. If electromagnetic radiation passes from one medium to another that has a different refractive index, a suddenly change of

beam direction takes place because of the differences in propagation velocity through the second medium. If light propagates through an incident medium with refractive index n_1 and enters a medium with refractive index n_2 (Figure 2.3), the light path will be changed and the extent of refraction is given by the following expression, known as *Snell's law* (equation 2.3):

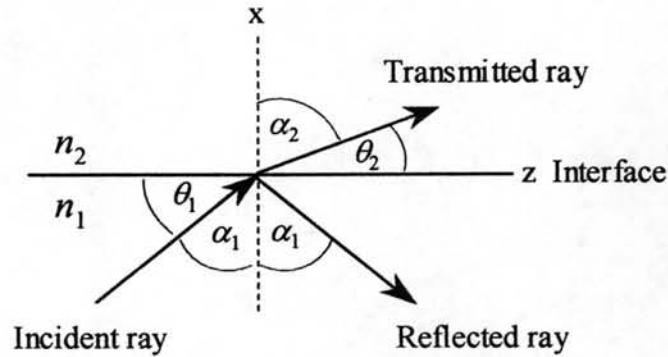


Figure 2.3 Reflection and refraction of a plane wave at a dielectric interface based on Snell's Law.

$$n_1 \sin \alpha_1 = n_2 \sin \alpha_2 \quad (2.3)$$

where α_1 and α_2 are the angles of incidence and refraction, respectively [32].

2.2.2 The Evanescent Field at Total Internal Reflection

The total internal reflection (TIR) phenomenon occurs when light traveling in an optically dense medium strikes the boundary of a second medium with a relatively lower refractive index, at a certain angle greater than the critical angle. Based upon the definition of angles in Figure 2.4, the critical angle with respect to the normal of a dielectric interface (θ_c) is defined by Eq. 2.2. Under this circumstance, the refracted angle α_2 equals 90° , indicating that no light beam emerges on the opposite side of the optically rarer medium. Therefore, only light incident on a high-index prism at angles exceeding the critical angle will be totally reflected.

$$\theta_c = \sin^{-1}(n_2/n_1) \quad (2.4)$$

Total internal reflection spectroscopy is the technique of recording the optical spectrum of a sample material that is in contact with an optically denser medium. The wavelength dependence of the reflectivity of this interface is measured by introducing light into the denser medium. In this technique the reflectivity is a measure of the interaction of the electric field with the material and the resulting spectrum is also a characteristic of the material [30, 36].

2.2.3 Internal Reflective Element (IRE)

IREs must have a high refractive index and are transparent throughout the mid-infrared region. IREs must also withstand physical and chemical contact with samples. Recently, Zinc selenide (ZnSe) and germanium are commonly used for macro and micro IRE. The internal reflection is a convenient method for infrared chemical analysis on the micro or nanoscale. Although, in principle the large prism such as hemisphere IRE can be used, but the location of the sample on the micrometer-sized area cannot be characterized. Thus the micro IRE has been developed. An advantage of small IREs is used in attachments for analyzing milligram or microgram of sample quantities and the simplicity of sampling small area on macro samples. Another advantage is that the good contact between IRE and the sample can be achieved. Because of the applied force, the smaller the area of contact can make the higher the pressure on the sample [1].

2.3 ATR Spectral Intensity

When electromagnetic radiation traveling within a denser medium (IRE) impinges at the interface with a rarer medium of lower refractive index (i.e., a sample) at an angle of incidence greater than the critical angle, a strong evanescent field is generated at the interface. The evanescent field is strongest at the interface and decay exponentially as a function of the distance into the rarer medium. If the rarer medium is absorbing at the coupled frequency, the intensity of the reflected radiation becomes smaller than that of the incident radiation. The magnitude of reflection loss (or absorption) is proportional to the product between the imaginary part to the complex dielectric constant and the evanescent field amplitude.

Table 2.1 Properties of materials used for IREs [1].

Material	Refractive index n at 1000 cm^{-1}	Maximum use (Temperature ($^{\circ}\text{C}$))	Hardness (Kg mm^{-1})	Useful range for ATR (cm^{-1})
Diamond	2.39	550	8820	4200-200
Silicon	3.42	300	1150	8300-1500, 360-120
Zinc Selenide	2.43	325	20	20000-650
Germanium	4.02	100	780	5500-830

The absorbance $A(\theta, \nu)$ can be expressed in term of the experimental conditions and material characteristics as follows:

$$A(\theta, \nu) = \frac{2\pi\nu}{\ln(10) n_{\text{IRE}} \cos\theta} n_{\text{sample}}(\nu) k_{\text{sample}}(\nu) d_p(\theta, \nu) \langle E_0^2(\theta, \nu) \rangle \quad (2.5)$$

where θ is the angle of incidence, ν is the frequency of the incident radiation (i.e., in wavenumber unit), n_{sample} and k_{sample} , respectively, are the refractive index and the absorption index of the sample, $d_p(\theta, \nu)$ is the penetration depth, and $\langle E_0^2(\theta, \nu) \rangle$ is the *mean square evanescent electric field* (MSEvF) at the IRE/sample interface. The penetration depth, defined as the distance at which the MSEvF decays to $1/e$ of that at the interface, is given in terms of experimental conditions and material characteristics as follows [37]:

$$d_p = \frac{\lambda}{2\pi n_{\text{IRE}} [\sin^2 \theta - (n_{\text{sample}}(\nu) / n_{\text{IRE}})^2]^{1/2}} \quad (2.6)$$

For FT-IR practical work, it is often convenient to express frequency in terms of wavenumber, the penetration depth decreases when wavenumber increases. This also leads to a decrease of relative band intensities in the ATR spectrum with increasing wavenumber. Furthermore, the changing of the angles of incident effect the

penetration depth. If the angle of incident is increased, the penetration depth will be decreased and the spectral intensity will be decreased. The greater penetration depth implies the greater distance from surface of the sample where chemical information can be observed by ATR technique [1].

2.4 Limitations of ATR FT-IR

For ATR analysis, any sample that comes into contact with the IRE can be analyzed. Thus, the uniform sample-IRE contact is of a greater concern. With traditional ATR spectroscopy (macro methods), it is desirable to achieve contact over the entire IRE surface (approximately 5×5 mm.). While this requirement is easily achieved with liquid samples, obtaining good contact with solid samples will be difficult. Moreover, a large contact area also results in an average molecular information over a large sampling area. The changing of molecular information in small area cannot investigate.

2.5 FT-IR Microspectroscopy

Infrared microspectroscopy could be defined as the coupling of a microscope to an infrared spectrometer. Infrared microscope is generally designed with two paths from the sample to the detector: transmission and reflection. In the transmission mode, the infrared light passes through the sample and is collected by a second infrared objective that re-collimates the beam and sends it to the infrared detector. In reflection mode, the infrared light reflects off the sample and passes back through the illuminating objective. Moreover, the microscope contains one or more apertures used for defining the sample area of interest. Infrared microspectroscopy provides the capability to collect spectrum on a small area (as small as about 10 μm in diameter).

2.5.1 External Reflection (Specular Reflection) Techniques

Specular reflection is the front-surface (Fresnel) reflection from the exterior surface of a material. The simple rule for specular reflection is that the angle of reflection equals the angle of incidence. For most organic samples, only about 5 to 10

% of the energy is reflected. Because specular reflection is a relatively weak process for dielectric materials, the sample should have a level, lustrous surface, and a large area should be analyzed to achieve high S/N spectra.

For different energies of incident radiation produce specular reflection spectra that are different from normal transmission spectra. The changes of the energy of incident radiation or reflectivity are the results of the superposition of two optical parameters: the refractive index and the extinction coefficient. In spectral regions of strong absorption, the refractive index of the sample will decrease at wavenumbers just higher than the maximum absorption and will increase dramatically while passing through the band. This combination of the refractive-index component with the extinction coefficient k forms the distinctive specular-reflection spectrum. The mathematical relationship called the *Kramers-Kronig (KK) transformation* calculates the dispersion $[n(\nu')]$ and the extinction coefficient spectrum $[k(\nu')]$ from specular data. This is expressed by:

$$n(\nu') = n_x + \int_{-x}^{+x} \frac{k(\nu')\nu}{\nu^2 - \nu'^2} d\nu \quad (2.7)$$

where n is the index of refraction at frequency ν' , n_x is the index of refraction at frequency $\rightarrow 0$, ν' is the frequency, ν is the frequency of maximum absorption, and k is the extinction coefficient.

The KK transformation can be calculated with most data-processing programs, making specular reflection a more desirable analytical measurement. In specular-reflection spectra, the KK transform will be most accurate when the S/N is high, there is no diffuse reflection or scattering, and the interference from water vapor and CO₂ are low. Nevertheless, the sample is a good specular reflector or it is not; its ability to reflect is determined by its physical condition, refractive index, and absorption [31-32].

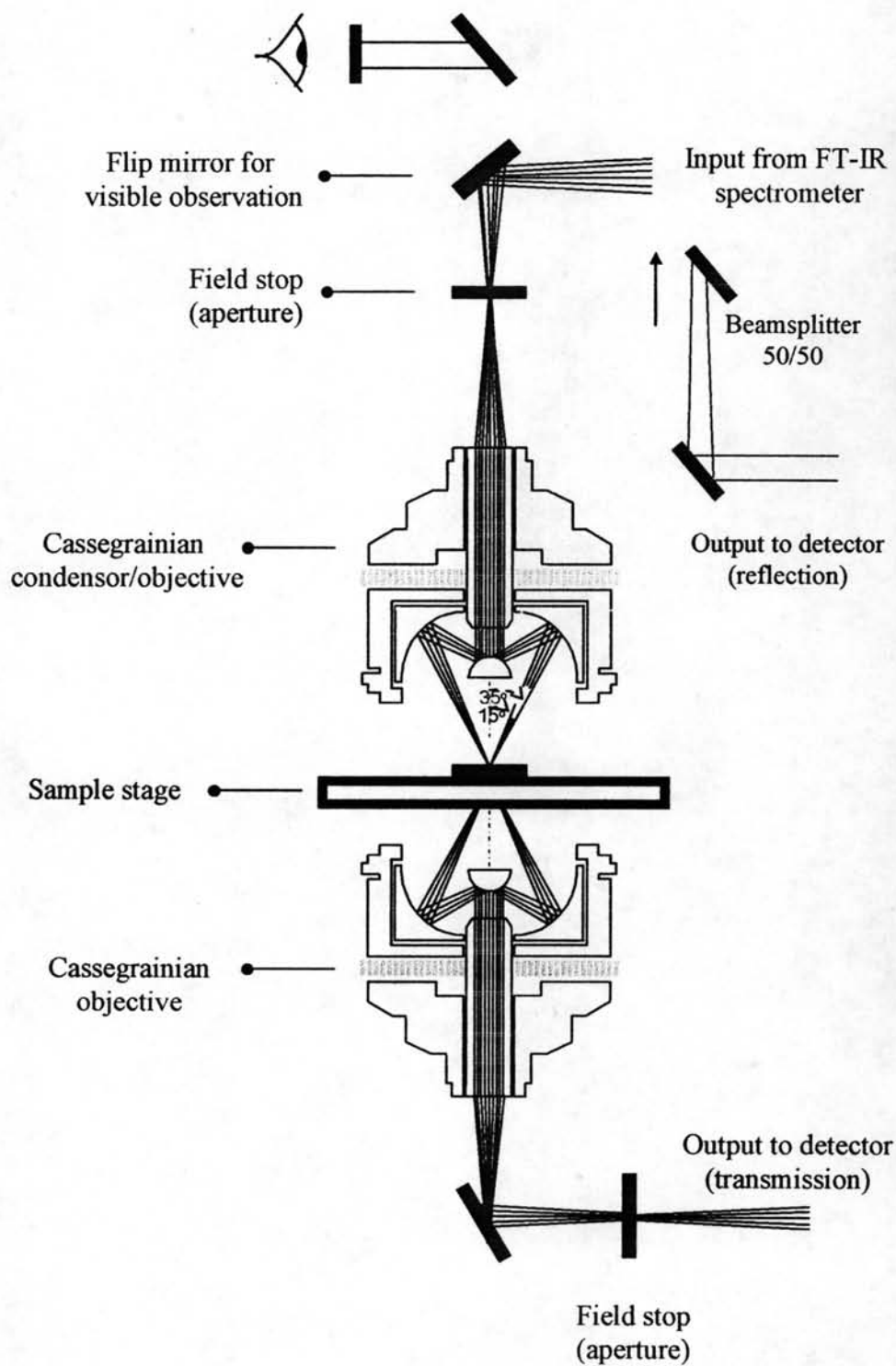


Figure 2.4 Optical diagram of an infrared microscope.

2.5.2 ATR FT-IR Microspectroscopy

ATR FT-IR microspectroscopy, the infrared radiation is coupling via infrared objective onto the IRE. The infrared radiations pass into the IRE where they are internally reflected and collected in reflection mode. In order to probe the sample, the IRE must be in contact with it. This way, the light is normally reflected inside of the IRE and is absorbed by the sample, where the penetration depth of the light is on the order of the wavelength.

The developments of IRE employed various size of IRE from macro to micro-size. The ATR FT-IR microspectroscopy has an advantage over the other infrared microspectroscopy techniques where the IRE is small in size (μ IRE). The infrared radiation can only be absorbed by the material in contact with the IRE.

The infrared absorption spectrum of molecular compounds contain bands associated with specific functional groups. The plot of the variation of such absorption band intensities over the entire area of the sample can be considered to be a chemical map of the sample. Recently, such chemical mapping or functional group imaging on a microscopic level using Fourier transform infrared spectroscopy has become popular. Fourier transform infrared spectroscopy has become a powerful tool for analysis of microscopic contaminants in chemical systems and for the characterization of inhomogeneous materials on a microscopic scale. The ability of FT-IR microimaging can be used to produce complementary information along with other established imaging techniques, such as electron microscopy [1, 31].

2.5.3 Principles of ATR FT-IR Mapping

Infrared microspectroscopy are generally collected as individual spectrum, or part of a line or area map. For infrared microscope systems, the latter mode is automated with software control and a motorized microscope stage. A sampling area of the map was selected through the built-in infrared objective. The radiation from the infrared objective is focused on the IRE located on a motorized x-y stage of the microscope. The infrared radiations pass into the IRE where they are internally

reflected and directed to detector in reflection mode. The x-y motion of the sample stage is controlled by the computer. The variable aperture that is part of the microscope determines the area of the sample. With the sampling area thus predetermined by the use of the variable aperture, a series of infrared spectra of the sample under studying are recorded by x-y translation of the sample stage.

The computer that is part of the FT-IR data system keeps tracking of the spectra recorded and their corresponding x-y coordinates. It is a relatively simple for the producing the functional group images. These images are produced by displaying or plotting the infrared band intensities in the recorded spectra as a function of the x-y coordinates. The infrared bands under consideration can be selected based on their functional group. Alternatively, images of infrared absorption band ratios, or the results of quantitative analysis based on the infrared spectra, could also be produced. These images can be presented in the form of three-dimension image wire frame or contour plots using commercially available software packages. Chemometric techniques such as factor analysis, principle component regression analysis, partial least squares analysis, and Gram-Schmidtorthogonalization procedure can be used to enhance the information content in the images [31, 34].

2.5.4 ATR FT-IR Microspectroscopy using Diamond μ IRE and Ge μ IRE

Natural diamond is hardness known material. The high refractive index diamond can be employed as an IRE. Moreover, the IRE is transparent in the mid-infrared region. Diamond has three major absorption bands in the mid-infrared region, namely **one-phonon** ($1400\text{-}900\text{ cm}^{-1}$), **two-phonon** ($2650\text{-}1500\text{ cm}^{-1}$), and **three-phonon** ($3900\text{-}2650\text{ cm}^{-1}$) absorptions. The absorption magnitude in the one-phonon region depends strongly on the concentration of nitrogen impurities. Although the two-phonon region is always over-absorbing, it has little effect on the analysis of organic materials since most of the materials do not absorb in this region. The three-phonon absorption imposed insignificant interference on the absorption of the materials.

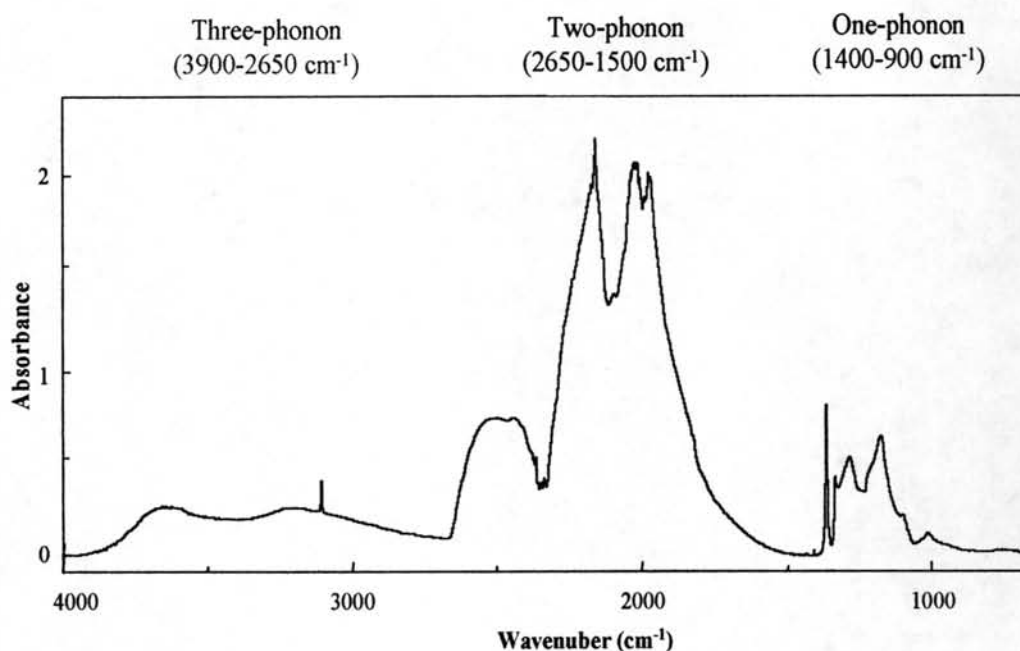


Figure 2.5 Transflectance spectra of round brilliant cut natural diamond.

Principle of Light that Entering the Diamond μ IRE

In principle, a gem quality diamond was cut and polished in such a proportion that the number of total internal reflections (TIR) within the diamond is maximized through the carefully faceting processes with respect to refractive index, cut shape, and cut proportion. However, the cut proportion is sometimes compromised by carat weight of the diamond. The number of TIRs within a faceted diamond depends strongly on the angle and position light enters the diamond. This phenomenon is due to the dispersion of light associated with traveling distance and the number of TIRs. Due to its relatively high refractive index ($n_{\text{Diamond}} = 2.417$), the evanescent field generated at the interface between a diamond and a material of lower refractive index can be exploited for the physiochemical characterization as that in the conventional IRE (i.e., germanium and zinc selenide). To collect an ATR spectrum using a gem quality round brilliant cut diamond IRE, the infrared radiation from a 15X Schwarzschild-Cassegrain infrared objective of an infrared microscope is coupled into and is collected from the table facet under a normal incidence. Examples of ray tracings inside a faceted diamond with a Tolkowsky's recommended cut proportion

are shown in Figure. 2.7. According to the traveling path of the coupled radiation, the re-emerging radiation from the table facet is defined as the *transflected radiation* [36].

Due to the complex surfaces of the faceted diamond and the divergence of the coupled radiations, the radiations impinge the table facet with different angles and/or positions undergo different traveling paths inside the diamond. The coupled radiation undergoes total internal reflection at the pavilion facet can be utilized for ATR FT-IR spectral acquisition of a material.

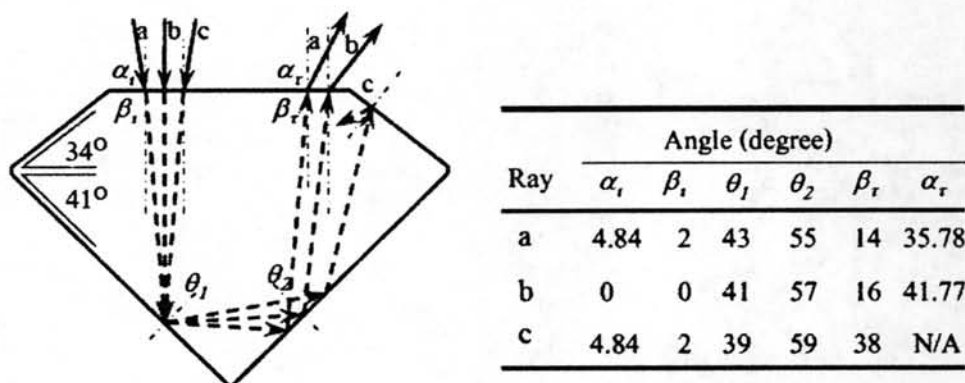


Figure 2.6 Ray tracing of the coupled radiations within the faceted diamond. Angle of reflection and refractions defined with respect to the direction normal are summarized.

Principle of Light that Entering the Ge μ IRE

The optical design of the objective, the focused radiation contains rays with angles of incidence ranging from 15° to 35° . By coupling this focused radiation into specially designed IREs made of high refractive index materials and by making the angle of incidence at the sampling surface greater than the critical angle, a spectral acquisition under the ATR FT-IR condition can be realized [31].

The hemispherical dome of the miniature cone-shaped Ge IRE facilitates the coupling of the focused radiation traveling into the IRE by minimizes the reflection loss at the air/Ge interface. If a nearly perfect coupling was assumed, the radiation

transmitted through the air/Ge interface of the dome and impinged the Ge/air interface of the tip without a significant change in the angle of incidence). To ensure a good contact, the circular tip of the IRE was made a hemispherical surface. Since the contact area is small ($\sim 100 \mu\text{m}$ or less than in diameter), a good contact was achieved with a minimal force exert on the tip. For the Ge μIRE ($n_{\text{Ge}} = 4.0$), the critical angle for the total internal reflection (TIR) at the interface with air ($n_{\text{air}} = 1.0$) and an organic medium ($n_{\text{organic}} = 1.5$), respectively, are 14.48° and 22.02° . As the results, parts of the coupled radiation can be employed for ATR FT-IR investigation of a material having an optical contact with the tip of the miniature IRE. To eliminate interference from the internal reflection associated with the radiation having an angle of incidence smaller than the critical angle, an opaque circular adhesive tape was placed on the center of the hemispherical dome. Due to an effective condensation of the coupled radiation and an efficient light-matter interaction under the ATR condition at the tip of the IRE, ATR FT-IR spectra of a small specimen or a small area can be acquired with superb spectral quality.

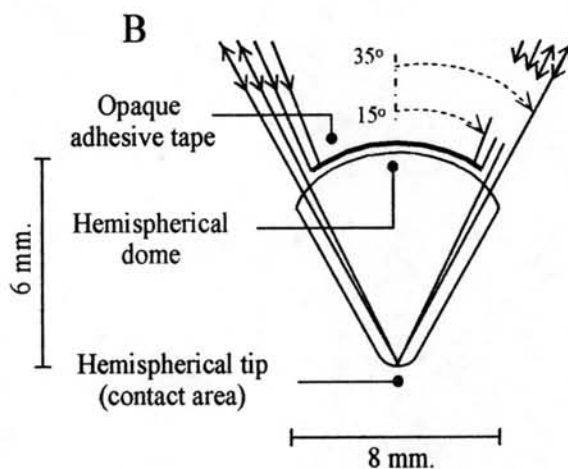


Figure 2.7 Schematic illustration of ray tracing within the infrared objective focused radiation traveling within the diamond μIRE .

2.6 Quantitative IR Spectroscopy of Polymer

IR spectroscopy is routinely employed to estimate an identity and the concentration of absorbing species in multicomponent systems. The standard approach is to measure the spectral series of mixtures, as well as using simultaneous equations to extract the desired information associated with concentration. There are four different cases of spectral problems in the analysis of multi-component systems. In the first case that all of components in the system are known and calibration data are available, classical least-square method is appropriate for determining quantities of each component. When a proper calibration method is carried out, this approach yields quantitative data for mixtures with high accuracy. In the second situation, the spectra of components are unknown but concentrations of components of interest are known, uses of a cross-correlation procedure are needed. In the third situation, when none of any components are known, factor analysis can be applied very well. Factor analysis method provides a lower limit to the number of linear-independent components presenting in a mixture, and estimates the spectra when low numbers of components are presented. Finally, to quantify a number of known components in a presence of a variable background of unknowns is the most difficult situation. In an attempt to handle such a problem, method of rank annihilation has been developed. When there is only one known component, an amount of the component can be determined by iteratively subtracting it from the observed data until the rank of the remaining matrix is reduced by one.

The quantitative relationship between a concentration (c) of a component in a sample and its absorbance (A) is given by the *Bouguer-Beer law* as follows:

$$A = abc = \log I_0 / I \quad (2.8)$$

where I_0 / I is termed for transmittance. The constant a is an absorptivity, and b is thickness. Logarithms to the base 10 are ordinarily used, and a factor of 2.303 is incorporated into the constant a . This law assumes photometric linearity and accuracy of the spectrometer. Traditionally, constructing a calibration curve of absorbance of an analytical frequency versus the concentration can carry out quantitatively purpose by measuring the concentration of an unknown sample in either term of the

absorbance peak or the absorbance area. When two components are involved, absorbance measurements at two frequencies are necessary to estimate the individual concentrations. This method can be extended for systems with more components as well [33].