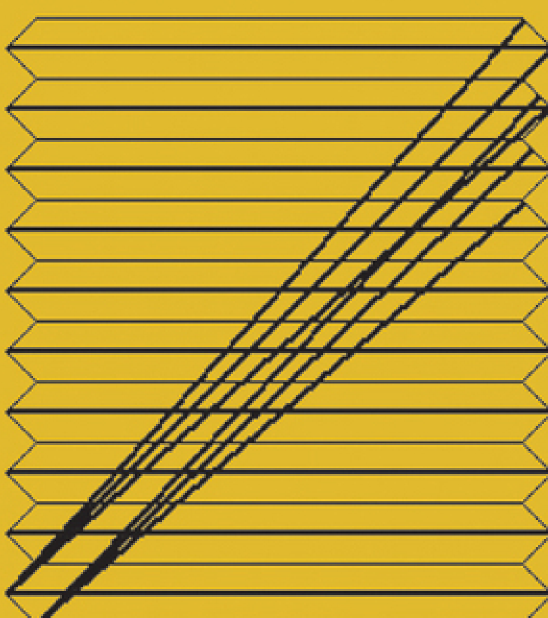
Chemical Analysis: A Series of Monographs on Analytical Chemistry and Its Applications, Mark F Vitha, Series Editor

INTERNAL REFLECTION AND ATR SPECTROSCOPY

MILAN MILOSEVIC



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AND ITS APPLICATIONS

Series Editor
MARK F. VITHA

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INTERNAL REFLECTION AND ATR SPECTROSCOPY

Milan Milosevic

MeV Technologies LLC

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To my wife and son

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PREFACE

This book attempts to provide a bridge between the topics of electromagnetic theory and spectroscopy, and in particular attenuated total reflection (ATR) spectroscopy. Electromagnetic theory is typically addressed in physics textbooks dealing with electromagnetic wave propagation in media and the reflection and refraction of the electromagnetic wave at interfaces between different media. A typical physics textbook derives Fresnel equations, mentions Brewster's angle, and total internal reflection as curiosities, and swiftly moves on to other phenomena. As far as physics textbooks are concerned, the general problem of reflection and transmission is completely solved. No new physics beyond this solution is anticipated, and as far as physics is concerned, it is dead as a research topic.

Analytical chemists, who are the primary users of spectroscopy, see the entire topic of reflection and transmission spectroscopy as a tool for finding answers about their samples. They typically concern themselves with the interpretation of spectroscopic experiments and, for their purposes, it is sufficient to assume that the absorption peaks seen in the spectra are the result of light at those frequencies being absorbed by the sample and that the absorption strength is proportional to the concentration of the absorbing substance. Analytical chemists pay only minimal attention to the physics of spectroscopic experiments. As tools, those experiments are employed to provide answers to the questions about samples that are analytical chemists' primary interest. Those cases in which analytical chemists pay any attention to the physics that underlies spectroscopy are when they encounter the so-called optical effects that interfere with the usual assumptions about the spectra such as linearity or where the features in the spectra are not consequences of light absorption by samples, but of some other phenomenon.

There is not much precedence for a book on this subject. A typical subject covered by textbooks can rely on a collection of topics that has evolved over time and distilled through many textbooks written by many authors as comprising the most appropriate set of topics for the subject. For a book attempting to cover an essentially uncovered subject, this accumulated wisdom is lacking. It is not a priori clear which topics should be addressed explicitly, which should be assumed to be in the background knowledge of the reader, and which topics should be left out as being beyond the scope of the book. Thus, the choice of topics addressed in this book reflects the preferences and fascinations of the author. In addition, the process of writing the book forced its own selection and order of topics as some were needed as prerequisites for others. Another phenomenon stepped in as well. The systematic treatment of the subject undertaken here brought up its own surprises. In following the logic of the narrative, we stumbled on some previously undescribed phenomena and effects. There was then no way of avoiding covering these phenomena, although they are not in a current vocabulary of the field.

In addition, I used the experience derived from thousands and thousands of discussions with researchers all around the world who needed specialized devices for spectroscopic measurements. Different spectroscopic measurements span a huge range of various applications of optical spectroscopy and require the choice of a spectroscopic technique most suited to a particular experiment. It was thus important to anticipate different benefits a spectroscopic technique and a particular experimental setup would have, so the most likely to succeed approach can be taken. The accumulated residue of all these discussions served as a compass for the choice of topics covered and for the assumed typical background possessed by a potential reader.

I assumed that the reader is somewhat familiar with the basic theory of classical electrodynamics and with basic calculus. Some of the topics covered could have been left out of the book as already familiar to the reader but were included for completeness and to provide coverage of the subject with unified notation and within a single system of units.

The main character in this book is the evanescent wave. I covered the evanescent wave in many different ways, both to help the reader understand it as a physical phenomenon and to help the reader understand ATR spectroscopy, which is based on it. I initially described evanescent wave as it is described in a typical textbook on electrodynamics or physical optics. This description suffices for most of what we want to understand about the evanescent wave and ATR spectroscopy. It took almost the entire book until this conventional understanding ran into a proverbial brick wall and the received wisdom needed to be reevaluated. This happened as I covered the ATR spectroscopy of powders. It happened in the course of writing the chapter and was forced out by the need to provide clear understanding of the ATR spectroscopy of powdered media. Some of the dead ends in this effort were left in the text to help the reader appreciate the difficulties the conventional understanding was not able to resolve.

Although the evanescent wave is the main character in this book, the unsung hero that emerges from the narrative is the classical electromagnetic theory and its description of reflection, transmission, and wave propagation through media. This description remained meaningful as we pushed it to incorporate more and more phenomena that we wanted to understand. The formalism readily incorporated the description of absorbing media, the extension of internal reflection into the regime of supercritical angle of incidence, and the extension into metal optics.

In the text, the words light and electromagnetic radiation are used interchangeably. Light is any electromagnetic radiation that is manipulated by usual optical means such as lenses and mirrors. Therefore, light is any electromagnetic radiation, from far infrared (IR) (wavelength about 0.1 mm) to deep UV (wavelength about 0.1 μm), not just visible light.

A short discussion of certain aspects of actual ATR experiments was incorporated since these are of interest to the intended readers and generally belong under the topic of "optical effects." These effects fall into the gap between the subjects of physical optics and analytical chemistry and are thus rarely discussed. However, these effects, as demonstrated in the text, can cause a nonlinear response of the absorbance transform of ATR spectra even if it is assumed that for ATR, in the absence of these effects, the absorbance transformed spectrum would exhibit a linear response.

Explicit effort was made to avoid quantum mechanics in presenting the concepts and results. For the most part, it is possible to describe the subject within the formalism of classical physics. It is, of course, not possible to avoid quantum mechanics when trying to further elaborate on most of the concepts discussed in the text, but it is satisfying not to have to drag in the unintuitive murkiness of quantum physics in order to understand the physical mechanisms underlying the phenomena utilized in spectroscopy.

In discussing how the various spectral features relate to a sample or to an experimental setup, we resorted to the numerical approach. All spectra shown in the book are numerically simulated using an early prototype of the SimSpec™ software. We found numerical simulations preferable to actual spectra since, in a numerically simulated spectrum, everything is under explicit control, so it is easier to sort out which parameter, whether sample or experimental setup related, is responsible for a particular spectral feature. For instance, it would be much harder to deposit an ultrathin film of a known thickness than to simply type in the appropriate number into the software. Also, experimental parameters such as the angle of incidence or polarization are not easy to set accurately in an actual experiment, while they are set with perfect accuracy in a numerical simulation. Numerically calculated spectra are easy to study. The mathematical expressions from which these spectra are calculated involve absolute values of complex numbers. That makes them difficult to scrutinize analytically, so their behavior is hard to infer directly from their form. Thus, it should not be surprising that careful investigations of these expressions can turn new and unexpected results despite the fact that these expressions have been around for a long time.

The efforts that my wife Violet put in helping me complete this book were instrumental to the project coming to completion. She carefully read the manuscript, made many helpful comments and suggestions, and provided support, encouragement, and inspiration.

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October 2011

1 Introduction to Spectroscopy

1.1 HISTORY

Spectroscopy got its start with Newton's observation that the white light from the sun can be separated into different colors using a prism. This observation became not only foundational to the theory of light but also to the understanding of human color vision. Color vision is a crude form of spectroscopy. We can often guess on the nature of a material by its color. We can only perceive three primary colors. That makes the human eye a very crude spectrometer. However, even at this crude level, it was apparently advantageous to us, during evolutionary history, to trade higher image resolution for color vision.

In the times of Newton, the hurdle to overcome was to understand the nature of light. Newton himself proposed the so-called corpuscular theory of light with which he was able to explain all then known properties of light (i.e., the propagation of light in a straight line and the laws of reflection and refraction). Newton proposed that light consists of tiny particles (corpuscles). Huygens, a contemporary of Newton, proposed the so-called wave theory of light, in which light is a wave phenomenon like a wave on the surface of water. Using his theory, he too was able to explain all the known properties of light. To make their respective theories work, Newton and Huygens made opposite assumptions about the speed of light in optically transparent media such as water or glass. Newton needed light to go faster through such media for his theory to work. Huygens needed it to go slower.

However, what settled the dispute was not the measurement of the speed of light in transparent media; it was the observation that light can form interference patterns. Only waves can form interference patterns and that settled the dispute. Huygens won. Later, measurements of the speed of light in denser media such as water confirmed Huygens's assumption. Light was a wave phenomenon.

Internal Reflection and ATR Spectroscopy, First Edition. Milan Milosevic.

Different colors of light correspond to different wavelengths. In studying light dispersion by a glass prism, Herschel noticed that there is an invisible component of solar radiation next to red light. Thus, infrared (IR) light was discovered. Later, it was discovered that there is also an invisible component of solar radiation next to violet that was named ultraviolet (UV).

In the early nineteenth century, Fraunhofer noticed a curious phenomenon. By using a prism to disperse solar radiation, he observed tiny black lines superimposed over a continuous rainbow-colored solar spectrum. Some wavelengths in the continuous spectrum of sunlight were missing. The dark lines, later named Fraunhofer lines, were present whether he used one type of glass prism or another. The appearance of the lines was mysterious, but Fraunhofer could find them not only in the solar spectrum; he was also able to observe them in the spectra of distant stars. Following the work of Thomas Young with interference of light, Fraunhofer developed diffraction grating as a means to disperse light in a more effective way than with glass prisms. The gratings enabled spectroscopy with a much higher resolution than prisms and enabled the direct measurement of the wavelengths of light.

Fraunhofer died without knowing what caused his dark lines. It was Kirchoff, working some 30 years after Fraunhofer's death, who realized that each element or compound is associated with its own unique set of spectral lines. This was the official birth of spectroscopy as a scientific discipline. The implications of this observation were extremely important. For instance, it told us that distant stars were made from the same elements found here on Earth. We could not know that any other way with any certainty. This is a nontrivial finding about the nature of the universe. There is no a priori reason why the distant worlds, many light-years from Earth, would not be made from an entirely new type of matter, entirely different from what we are familiar with here on Earth.

Intrigued by these mysterious lines and their association with different elements, many researchers started studying spectra of flames and other light sources. It was discovered that, when heated, the atoms emit bright lines. Soon it was realized that these bright lines match some of the dark lines found in the solar spectrum. Associating lines with particular elements became the primary aim of the new science of spectroscopy. Soon people would talk about sodium lines, mercury lines, and so on.

It was also realized that the dark lines were due to absorption of light by the elements that would, when heated, emit those same lines. Soon, it became possible to analyze a spectrum of a mix of elements by sorting out the lines due to each element, that is, to analyze a mixture for its constituents. Furthermore, by observing the relative intensities of lines due to each element, it became possible to estimate the relative abundance of different elements in a mixture. This was now already true spectroscopy.

Early on, spectroscopists realized that they could substitute a photographic plate for their eyes and that they could photograph a spectrum. The spectrograph represented a permanent record of a spectrum and could be subsequently analyzed in great detail. Different spectra could be compared. Employing long exposure times allowed recording spectra from very faint sources otherwise too weak to be observed by the eye. The use of photography also extended the spectral range of spectroscopy from visible to UV and, to a more limited extent, to the IR spectral regions.

By improving the spectroscopic equipment and increasing the resolution of the spectroscopic measurement, spectroscopists soon realized that many single lines seen through the early spectroscopes were not really single and that sometimes, under high spectral resolution, a much finer structure would be revealed. They found single lines resolving into doublets, triplets, quadruplets, and so on. By the dawn of the twentieth century, a great amount of very detailed spectral information was amassed. The experimental precision with which these spectral measurements were pursued seems almost fanatical, but what propelled it was the constant stream of discoveries that accompanied it. For instance, it was discovered that some prominent lines in the sun's spectrum could not be matched by anything known on Earth. They attributed it to a new element that they aptly named helium after the Greek sun god Helios. Soon thereafter, helium was discovered on Earth.

However, the abundance of information generated by spectroscopy was contrasted with the total lack of understanding of how the spectra themselves are generated. People knew that light is a wave phenomenon similar to sound. The sound generated by a taut string consists of a set of characteristic frequencies. A string with a different tension or of a different length produces a sound of a different frequency. This would make it plausible that different elements would produce different sets of light frequencies. Even the fact that a taut string could be resonantly excited into vibrations by a sound of the same frequency that it would sound if struck was seen analogous to why cold atoms would absorb the same frequencies of light that they would emit when heated.

While not in itself surprising, the existence of these characteristic frequencies associated with different elements was totally stomping the scientists when they tried to understand them based on the available physical theories known collectively as classical physics. Soon, it became obvious that classical physics could not explain the observed spectra. A revolutionary new theory called quantum mechanics had to be developed to provide the explanation. The explanation, however perfect, came with an uneasy requirement to abandon common sense and to proceed into the unintuitive and forbidding world of quantum mechanics following mathematics where intuition fails.

After first providing a spectacular confirmation that the universe is filled with the same atoms and compounds that we find here on Earth, spectroscopy provided another spectacular result. Measuring spectra of distant nebulae in the first half of the twentieth century, Hubble discovered that the spectral lines of elements and compounds from those distant nebulae are shifted from their terrestrial positions toward lower frequencies (referred to as redshift since red light is the visible light with the lowest frequency). This was a puzzling discovery.

The explanation that was eventually accepted is that those distant nebulae recede from us in all directions with high speeds. The recession at high speeds shifts frequencies through what is known as Doppler effect. The effect is commonly observed when a whistling train passes by. The pitch of the whistle is higher while the train is approaching and it suddenly turns lower as the train passes by and starts moving away.

By studying how the redshift correlates with the distance from Earth, Hubble found that the farther away a nebula (today referred to as galaxy) is, the larger the redshift. This finding stood in a distinctly anti-Copernican spirit; that is, that Earth has no special place in the universe, but it was soon realized that the same is true for every point in the universe. The universe is expanding from every point in every direction. The most significant implication of that observation is that, by playing backward the movie of the expansion, we find that the entire universe came into existence in a huge "bang" some 13.7 billion years ago. Spectroscopy thus ushered the age of the big bang cosmology.

Ultraviolet and visible spectroscopy could progress by using photographic techniques to record spectra. However, IR spectroscopy could not since the sensitivity of the photographic plates to IR light greatly diminishes for the wavelengths longer than those of red light. Thus, to pursue IR spectroscopy, a new way of light detection had to be employed. Early in the twentieth century, Coblentz developed and used a thermopile detector to push spectroscopy far into the IR. He used rock salt prisms (as opposed to glass prisms, which are opaque to longer wavelengths) to disperse light and placed a thermopile detector to detect the IR light of a selected wavelength. The thermopile detector consists of a thermocouple and a voltmeter. In this way, he could read the voltage produced by the thermocouple when heated by IR light at the selected wavelength. A graph connecting the thermocouple response versus wavelength is called the spectrum. In this way, working painstakingly, Coblentz collected a large number of very high quality spectra of a great variety of compounds. The amazing specificity of the IR spectra of different compounds rivaled the specificity of atomic spectra. Coblentz soon realized that different functional groups are characterized by specific absorption peaks. Thus, for instance, the presence of a C-H group in a molecule was revealed by characteristic spectral absorptions. The same is true for the O-H and other groups. Thus, IR spectroscopy became a great tool not only to identify an unknown substance by comparing its spectra to the spectra of known compounds, but it allowed the molecular structure to be inferred from the information contained in its IR spectrum directly, just based on the known absorption bands associated with various functional groups. Coblentz's work established modern IR spectroscopy. The period following World War II saw the introduction of the first commercial IR spectrometers. They had motorized wavelength scanning and produced plots of spectra using chart plotters. Spectral collection was transformed from painstaking work taking hours to routine scans taking a few minutes each.

Early spectroscopy was almost exclusively transmission spectroscopy. Some reflection spectroscopy was pursued within the research community interested in optical properties of metals and within the mirror making community, which needed a way to properly characterize its offerings. Reflection spectroscopy was also of interest for crystallography. However, it was not until the advent of attenuated total reflection (ATR) spectroscopy that a spectroscopic technique other than transmission spectroscopy was routinely used. Attenuated total reflection spectroscopy is an unlikely spectroscopic technique. It is based on the phenomenon of total internal reflection that has been known for a long time and has even been discussed by Newton in his *Opticks*. During total internal reflection, a special type of electromagnetic wave called the evanescent wave is formed on the other side of the reflecting interface. An absorbing material brought into contact with the totally reflecting interface absorbs some of the intensity of the evanescent wave and the intensity of the reflected light is thus attenuated with respect to the incoming intensity—hence, the name ATR spectroscopy. In many respects, ATR spectra resemble transmission spectra. That helped ease the acceptance of ATR spectroscopy by the IR spectroscopy community. Attenuated total reflection spectroscopy was proposed in 1959–1960 independently by Harrick and Fahrenfort.

Fahrenfort approached ATR from the single reflection side. Harrick approached it from the multiple reflection side.

Standard commercial spectrometers are built for transmission measurements so reflection measurements could not be done with these spectrometers. Researchers in the field had to design and build their own devices that allowed them to use ATR spectroscopy in their existing spectrometers. Some of the first commercial ATR accessories for use in the existing commercial spectrometers were made by Wilks, enabling anybody with an IR spectrometer to use ATR spectroscopy. Multiple reflection ATR spectroscopy initially took hold. Multiple internal reflection elements became available in a number of standardized sizes and were offered by multiple vendors. The popular ATR materials included germanium, KRS-5 (thalium bromoiodide), silicon, ZnSe, and ZnS. The initial rationale for using multiple reflection ATR was that the absorbance produced in ATR spectroscopy is very weak and that the only practical way to reach a good signal/noise (S/N) of a measurement was to use multiple reflections.

The second half of 1980s saw the wholesale replacement of older grating-based spectrometers with new Fourier transform infrared (FTIR) spectrometers. This replacement drastically increased spectrometer performance, enabling much higher S/N measurements. This rekindled the interest in single reflection ATR spectroscopy. Starting in the early 1990s, the interest in single reflection ATR spectroscopy got a further boost from the interest in ATR microsampling. Microsampling single reflection ATR spectroscopy soon became the dominant spectroscopic technique in IR spectroscopy. This trend was further stimulated by the introduction of diamond as the ATR material. The mechanical strength, abrasion resistance, chemical inertness, and great optical characteristics of diamond propelled diamond single reflection ATR spectroscopy into a nearly universal spectroscopic technique. A broad range of sample types, from hard solids to liquids to powders, can all be readily analyzed using a single diamond ATR accessory.

1.2 DEFINITION OF TRANSMITTANCE AND REFLECTANCE

Transmittance and reflectance are quantities measured in a spectrometric experiment. A spectrometric experiment consists of a light source, a discriminator to separate contributions from different frequencies (or wavelengths) of light, and a detector. The setup may also include suitable optics to guide light from the source to the detector.

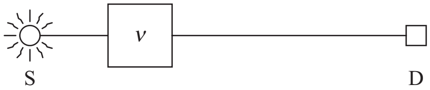

Figure 1.1 Schematic representation of a spectrometric experiment. Source S sends light of all frequencies through the monochromator, which selects only light of frequency v to proceed to detector D.

The source emits light of different frequencies. The light then goes through the discriminator. The simplest type of discriminator is a prism that splits light into different frequencies (or wavelengths) and allows one frequency at a time to reach the detector. This type of discriminator is called a monochromator. One can also use an optical grating instead of a prism to split white light into its constituent frequencies. An array of detectors could be used instead of a single detector, and all the frequencies (wavelengths) of light could be detected simultaneously. Yet another way to discriminate different frequencies is to modulate each frequency of light with a different frequency as it is done with a scanning Michelson interferometer, to record the signal as a function of the modulation parameter, and subsequently, to transform mathematically the recorded signal into a spectrum. A spectrum of a source is a graph that shows how much power is emitted by the source at different frequencies (wavelengths) of light. Acquiring a spectrum is the goal of a spectrometric experiment.

A spectrometer, shown schematically in Figure 1.1, is a device specifically developed to collect spectra. Every spectrometer consists of a wavelength discriminator and a detector. Most also incorporate a source of light. In addition, there is a lot of control electronics. The light source is usually a hot body that emits light such as a bulb, but it could also be an LED, a laser, plasma, and so on. Or the source could be external to the spectrometer as it is for spectrometers attached to astronomical telescopes used to acquire spectra of distant stars. If the sample itself is the source of light that is analyzed by the spectrometric experiment, then the resulting spectrum is called emission spectrum. As we are interested in ATR spectroscopy, we are not going to cover emission spectroscopy here. We always assume that a source is integral to the spectrometer and that the spectra collected are those of the integral source modified by the presence of the sample. It is important that the source emits light throughout the spectral region of interest and that the light output is stable; that is, it does not fluctuate with time.

For the sake of conceptual clarity, let us assume that for frequency discrimination, we are using a monochromator, a black box with input and output ports for light and a knob with a dial that allows the selection of the output wavelength. On one side comes in white light from the source, on the other side goes out light of a selected frequency (or wavelength).

A detector is a device that converts the power of incoming light into voltage. The voltage is then digitized; that is, the analog electrical signal is converted into a number. The number representing light intensity is then stored for further manipulation.

Now we can see the process of collecting a spectrum as turning the knob on the monochromator to a starting frequency and recording the intensity, moving the monochromator to the next frequency and recording the intensity and so forth until the spectral region of interest has been covered. The result is a spectrum, that is, a series of pairs of numbers in the form (frequency, intensity). We can thus collect a spectrum of the spectrometer's source $I_0(\nu)$. Imagine that we now put a sample into the beam and collect the spectrum of light from the spectrometer's source that has transmitted through the sample $I_S(\nu)$. The ratio

$$T(\nu) = \frac{I_S(\nu)}{I_0(\nu)} \tag{1.1}$$

is called the transmittance of the sample. Note an important characteristic of the thus defined transmittance. The spectrum $I(\nu)$ is the detector's response associated with the intensity of light of frequency ν. The voltage the detector puts out depends on a number of factors such as source intensity, detector area, sensitivity, spectral response, amplifier gain, and so on. Usually, a spectrum is recorded in arbitrary units. However, it is important for the detector signal to be proportional to light intensity. If it is, we say that the detector has a linear response. Thus, as we take the ratio (Eq. 1.1), all other factors cancel out and the result is the ratio of the light intensities with the sample and without the sample in the beam. All the factors related to the source, monochromator, detector, preamplifier, and so on, cancel out. The transmittance thus recorded is entirely a property of the sample itself. This is of fundamental importance. What it says is that the same transmittance of the sample would have been recorded if we had a different source instead of the original one, or a different monochromator, or a different detector. The spectrum measured, at least in principle, depends only on the sample and not the spectrometer used for the measurement. In practice, of course, this is not automatically the case, and a lot of ingenuity has to be expended on the design and manufacture of spectrometers to ensure that this is indeed true. We will come back to investigate this topic in more detail.

From definition (Eq. 1.1), we conclude that the transmittance of a sample is always a quantity smaller than one (i.e., 100%). This is so because, as light impinges on the sample, it partially reflects back from the sample, or the portion of light intensity that entered the sample can be absorbed by the sample. Both processes reduce the intensity of light on the detector as compared to the light intensity that would reach the detector had the sample not been in the beam. Therefore, the numerator in Equation 1.1 is always smaller than the denominator, and the transmittance is always less than, or at most, equal to one.

Instead of being interested in light that transmits through the sample, we could be interested in light $I_R(\nu)$ that reflects from the sample. In this case, we define the reflectance of a sample in analogy with the definition of the transmittance (Eq. 1.1); that is,

$$R(\nu) = \frac{I_R(\nu)}{I_0(\nu)}. \tag{1.2}$$

Again, we expect I_R to be always smaller than I_0. This is so because only a portion of light that was incoming onto the sample could have been reflected from it. Thus, reflectance is always less than one. It is also independent of the source of light used. If the sample does not absorb light of a particular frequency, the incoming light could be either transmitted through the sample or reflected from it. This means that for a nonabsorbing sample,

$$R(\nu) + T(\nu) = 1.$$

For an absorbing sample, we can define the quantity $A_b(\nu) = I_A/I_0$, where I_A is the intensity of light absorbed by the sample. This quantity is not called absorbance, although this would seem natural in analogy with the definitions of transmittance and reflectance. The reason for this is that the term absorbance has been historically attached to another quantity. Nevertheless, the quantity A_b completes the selection of quantities describing the interaction of a sample with light. Incident light can either be reflected from the sample, transmitted through it, or become absorbed by the sample; that is,

$$I_0(\nu) = I_A(\nu) + I_R(\nu) + I_T(\nu).$$

Consequently,

$$R(\nu) + T(\nu) + A_b(\nu) = 1$$