

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

INTERNAL REFLECTION AND ATR SPECTROSCOPY

MILAN MILOSEVIC



 **WILEY**

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INTERNAL REFLECTION AND ATR SPECTROSCOPY

Milan Milosevic

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To my wife and son

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