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MOLECULAR SPECTROSCOPY

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MOLECULAR SPECTROSCOPY

PREFACE

This book is the crystallization of the lecture notes I have been compiling since 1981, the year I first taught a graduate course in spectroscopy. At the time, I was disappointed to learn that Ira N. Levine's *Molecular Spectroscopy* (John Wiley and Sons, New York, 1975) was out of print. Since then, I have made use of several excellent texts, but I felt that the time had come to mainstream the topics of condensed phase spectroscopy and time-dependent theory into the conventional introductory spectroscopy course. I wanted to write a book that would bridge tradition and innovation, that would present the necessary theoretical foundations and help students acquire the intuition needed to solve practical problems in the spectroscopy laboratory. I wanted the book to be rigorous, but not at the expense of clarity. I didn't want to follow the typical style of a foreign-language textbook, where students learn all the fine details of gender and verb conjugation, only to later visit a country where the language is spoken and find that they can't get around, having failed to learn words like "upstairs" and "outside." I wanted to write a book that would enable students to "get around" in the field.

Spectroscopy is very much the study of applied quantum mechanics. This book assumes that the reader has previously taken a one-term course in quantum mechanics, at the level of Levine's *Quantum Chemistry* (Prentice-Hall, Upper Saddle River, N.J., 1999) or P. W. Atkins' *Molecular Quantum Mechanics*, 2nd ed. (Oxford University Press, New York, 1983). Some previous exposure to statistical mechanics, as in an undergraduate physical chemistry class, will also be helpful. Chapter 1 summarizes the necessary background in these two subject areas. Even for the student with a very strong background, I recommend Chapter 1 as it will help establish some notation and recurring themes that appear throughout the book. Chapter 2 discusses both the classical and quantum mechanical theory of electromagnetic radiation, and Chapter 3 describes the electric and magnetic properties of matter on which the light-matter interaction depends. Time-dependent perturbation theory, the foundation of spectroscopic theory, is developed in Chapter 4, and in Chapter 5 I discuss the use of time-correlation functions in rotational and vibrational spectroscopy. Applications of the time-correlation function formalism are further described in Chapters 8 and 12. Chapter 6 describes the connection

between theoretical quantities, such as the electric dipole transition moment, and experimental observables, such as the intensity of absorption, emission and scattering. Chapters 7 through 12 take up specific types of spectra and applications: Chapter 7 develops atomic spectroscopy in order to introduce electronic transitions, Chapter 8 covers rotations and internal rotations, vibrational spectra are considered in Chapters 9 and 10, and molecular electronic spectroscopy is covered in Chapter 11. Chapter 12 unifies the topics of Raman and resonance Raman spectroscopy, and provides a brief introduction to nonlinear techniques. Group theory is used extensively in Chapters 10, 11, and 12, and is reviewed in Appendix C. While it is assumed that the reader has had some exposure to group theory, particularly molecular symmetry, the basic tools required for working problems are presented in Appendix C. Appendix A covers some necessary math skills and Appendix B presents some details of doing calculations in electrostatics, particularly relevant to Chapter 3. For a general review of helpful math skills, I recommend *Applied Mathematics for Physical Chemistry*, 2nd ed. (Prentice-Hall, Upper Saddle River, N. J., 1998) by James R. Barrante. I have made a strong effort to use consistent notation throughout the book, and I place great emphasis on the power as well as the limitations of approximations. A Solutions Manual for this text is available to adopting instructors (ISBN 0-13-920083-5).

In addition to the many students who helped to shape my early lecture notes and rough drafts of this book, there are many people to thank for critical reading of all or part of the manuscript. At the University of Idaho, my colleagues Phil Deutchman, Dan Edwards, Dave Marshall and Pam Shapiro reviewed chapters and contributed many suggestions. Special thanks are due to Luke Emery and Doug Daniel for critical reading of the entire book, and countless helpful comments and criticisms. The following UI graduate students used the manuscript as the text for the course and made helpful corrections and suggestions: Xuan Cao, Connor Flynn, Brian Keller, Scott Larkin, Ron Mallery, John Streiff, Robert Tolbert, Husheng Yang, Bai Yin, and Mike Wojcik. I am also indebted to my good colleagues, Frank Baglin of the University of Nevada and Nina Veas of Michelin, for careful reading and thoughtful comments on several chapters. I am very grateful to the following reviewers for their helpful suggestions: Robert R. Birge, Syracuse University; David Farrelly, Utah State University; H. Bruce Friedrich, University of Iowa; Daniel P. Gerrity, Reed College; Darla K. Graff, Los Alamos National Labs; Bruce S. Hudson, Syracuse University; Fred Northrup, Northwestern University, Thomas B. Rauchfuss, University of Illinois - Urbana/Champaign; David J. Simkin, McGill University; and Michael Trenary, University of Illinois at Chicago. I owe much to my teachers Jack Simons and Bill Guillory at the University of Utah for their inspiration. I would also like to acknowledge my editors Deirdre Cavanaugh and John Challice at Prentice-Hall for their guidance. Of course, it is customary to thank someone for doing an excellent job of typing. I only wish I could do so! Instead, I express my deepest gratitude to Robert Tolbert and John Jegla for patiently helping me in my struggle to learn L^AT_EX. This book would not have been possible without their advice. Finally, my biggest debt is to my husband, Fritz Knorr, not only for

his constant encouragement and support during the writing of this book, but more importantly for creating all the drawings. I literally could not have produced this book without him.

I continue to welcome comments and suggestions from readers. Throughout the chapters that follow, you will notice that I chose to use the first person plural. Who are “we?” We are the author and the reader together. It is my strong hope that the reader will follow along with me when *we* consider a topic, and when *we* show that something is true. As an active participant in uncovering the working formulas of spectroscopy, readers will surely discover a few new tricks of their own. In this way, *we* make contributions to future developments in spectroscopy.

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INTRODUCTION AND REVIEW

1.1 Historical Perspective

Spectroscopy is about light and matter and how they interact with one another. The fundamental properties of both light and matter evade our human senses, and so there is a long history to the questions: What is light and what is matter? Studies of the two have often been interwoven, with spectroscopy playing an important role in the emergence and validation of quantum theory in the early twentieth century. Max Planck's analysis of the emission spectrum of a blackbody radiator established the value of his eponymous constant, setting in motion a revolution that drastically altered our picture of the microscopic world. The line spectra of atoms, though they had been employed for chemical analysis since the late 1800s, couldn't be explained by classical physics. Why should gases in flames and discharge tubes emit only certain spectral wavelengths, while the emission spectrum of a heated body is a continuous distribution? Niels Bohr's theory of the spectrum of the hydrogen atom recognized the results of Rutherford's experiments, which revealed previously unexpected details of the atom: a dense, positively charged nucleus surrounded by the diffuse negative charge of the electrons. In Bohr's atom the electrons revolve around the nucleus in precise paths like the orbits of planets around the sun, a picture that continues to serve as a popular cartoon representation of the atom. Though the picture is conceptually wrong, the theory based on it is in complete agreement with the observed wavelengths of hydrogen! Modern quantum theory smeared the sharp orbits of Bohr's hydrogen atom into probability distributions, and successfully reproduced the observed spectral transition frequencies. Observations of electron emission by irradiated metals led to Einstein's theory of photons as packets of light energy, after many hundreds of years of debate on the wave-particle nature of light. Experiments (such as electron diffraction by crystals) and theory (the Schrödinger equation and the Heisenberg uncertainty principle) gave rise to the idea that matter, like light, has wave-like as well as particle-like properties. Quantum theory and Einstein's concept of photons converge in our modern microscopic view of spectroscopy. Matter emits or absorbs light (photons) by undergoing

transitions between quantized energy levels. This relatively recent idea rests on the foundation built by philosophers and scientists who considered the nature of light since ancient times. The technology of recording spectra is far older than the quantum mechanical theories for interpretation of spectra.

Ref. [1] gives an excellent historical account of investigations that led to our present understanding of electromagnetic radiation. Lenses and mirrors date back to before the common era, and the ancient Greeks included questions about the nature of light in their philosophical discourses. In 1666, Isaac Newton measured the spectrum of the sun by means of a prism. He speculated that the seven colors he observed (red, orange, yellow, green, blue, indigo, and violet) were somehow analogous to the seven notes of the musical scale. It is interesting that the frequency of violet light is a little less than twice that of red, so we see just less than an octave of this spectrum. We now know that the human eye can discern millions of colors [2] and that the wavelengths spanned by electromagnetic radiation extend indefinitely beyond the boundaries of vision. Newton was a proponent of the corpuscular view of light, a theory that held that light was a stream of particles bombarding the viewer. His contemporary, Christian Huygens, proposed a wave theory and showed how the concept could account for refraction and reflection. Newton had considerable influence, and the corpuscular theory dominated the scene for a long time after his death. (Its proponents may have been more zealous than Newton himself had been.) Just a few years after the discovery of the infrared and ultraviolet ranges of the spectrum, Thomas Young in 1802 made the connection between wavelength and color. Young also investigated the phenomenon that is now known as polarization. A. J. Fresnel made contributions to the emerging wave theory as well, and equations describing the polarization dependence of reflection at a boundary bear his name [1].

The nineteenth century saw many developments in the analysis of spectral lines. Fraunhofer repeated Newton's measurement of the solar spectrum in 1814, using a narrow slit rather than a circular aperture to admit the light onto the prism. The resolution of this experiment was sufficient to reveal a number of dark lines, wavelengths where the solar emission was missing. Numerous "Fraunhofer lines" are now assigned, thanks to the work of Bunsen, Ångström, and others. They originate from the reabsorption of sunlight by cooler atoms and ions in the outer atmosphere of the sun and that of the earth. In 1859, Kirchhoff demonstrated that two of these dark lines occur at the wavelengths of the yellow emission of hot sodium atoms. This helped to establish the notion that absorption and emission wavelengths of atoms coincide. Fraunhofer made further contributions by fabricating the first diffraction gratings, by wrapping fine silver wires around two parallel screws, and later by etching glass with diamond. By 1885 it was firmly established that elements have characteristic spectral wavelengths. The very discovery of the element helium in 1868 was made by analyzing the wavelengths of the solar spectrum.

The wave theory of light attracted many proponents in the nineteenth century, but it posed problems when light waves were compared to waves in matter, such as sound, which require a medium for support. How could light travel in a vacuum?