Fundamentals of Laser Spectroscopy for Atoms and Diatomic Molecules

For the engineer or scientist using spectroscopic laser diagnostics to investigate gas-phase media or plasmas, this book is an excellent resource for gaining a deeper understanding of the physics of radiative transitions. While a background in quantum mechanics is beneficial to the reader, the book presents a comprehensive review of the relevant aspects of the field, extensively covering atomic and molecular structure alongside radiative transitions.

The author employs effective Hamiltonians and Hund's case (a) basis wavefunctions to develop the energy level structure of diatomic molecules. These techniques also form the basis for treating radiative transitions in diatomic molecules. Recent advancements in quantum chemistry, enabling readers to calculate absolute single-photon and Raman transition strengths, are also presented.

Illustrated with detailed example calculations of molecular structure and transition rates, this self-contained reference for spectroscopic data analysis will appeal to professionals in mechanical, aerospace, and chemical engineering, and in applied physics and chemistry.

Robert P. Lucht is the Bailey Distinguished Professor at Purdue University. His research projects range from the physics of emerging laser techniques to applications of laser diagnostics in practical combustion devices such as gas turbines. Professor Lucht is a fellow of Optica, AIAA, ASME, and the Combustion Institute. He also received the AIAA Aerodynamic Measurement Technology Award.

“This is an excellent and essential book for anyone seeking a detailed understanding of the fundamental physics pertaining to absorption, emission, and Raman spectroscopy of diatomic molecules. It is a must-have for laser spectroscopists studying the gas phase.”

Christopher Goldenstein, Purdue University

“This book presents a thorough foundation for both linear and nonlinear spectroscopy of atoms and diatomic molecules, including examples relevant to combustion science and high-temperature gas physics. The author develops both classical and semiclassical quantum models that describe atomic and molecular spectral properties and interactions with electric fields and lasers. The detailed derivations provide deep insight into the underlying mechanisms. At each step, the author makes the connection between derived expressions and relevant applications, reflecting his long leadership in the development and application of advanced spectroscopic methods. This book serves as a welcome benchmark for the community.”

Richard B. Miles, Texas A&M University

“Here is an invaluable resource for graduate students and researchers wishing to study the fundamental theory and finer details of gas-phase laser spectroscopy. It describes atomic and molecular structure, the physics behind matter and laser radiation interaction, and the theory of specific spectroscopic techniques, all in one comprehensive, in-depth text.”

Chloe E. Dedic, University of Virginia

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Dedicated to my late parents Alta and George Lucht

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Preface

Spectroscopic laser diagnostics have been applied to the study of flames, plasmas, and fluid dynamics for over 50 years, and there have been many books that summarize the application of laser diagnostics in these systems. In books such as *Laser Diagnostics for Combustion Temperature and Species* by Alan C. Eckbreth, different laser techniques are discussed, including some discussion of the physics of interaction of the laser with atomic and molecular resonances.

The focus of this book is the physics of radiative transitions for gas-phase spectroscopic diagnostics. The idea for this book grew out of my own experience in trying to educate myself in the physics of radiative transitions. As an undergraduate at Purdue University, I wrote a report entitled "Fundamentals of Absorption Spectroscopy for Selected Diatomic Flame Radicals," with Richard Peterson and my late advisor Normand Laurendeau as coauthors. This was my first exposure to the literature of spectroscopic transitions and was a tremendous learning experience for me. It also turned out that it was useful for others in the combustion diagnostics community, which was a very young and expanding community at that time.

The book begins in Chapter 1 with a discussion of the energy and interactions of a classical electric dipole; this includes a discussion of the interaction of a classical dipole with a monochromatic laser field – to introduce the concepts of absorption and stimulated emission – and the radiation emitted by an oscillating dipole – to introduce the concept of spontaneous emission. Chapter 2 contains an introduction to atomic structure, and essential quantum mechanical concepts are introduced in a discussion of the structure of atomic hydrogen. Most significantly, the quantum treatment of angular momentum is discussed, and *3j* symbols and the Wigner-Eckart theorem are introduced. The structure of diatomic molecules is discussed in Chapter 3. The treatment of energy levels in diatomic molecules is based on the effective Hamiltonian method featuring the use of Hund's case (a) basis wavefunctions. Electric dipole resonance transitions in atoms are discussed in Chapter 4, and the Wigner–Eckart theorem is applied. Electric dipole resonance transitions in diatomic molecules are covered in Chapter 5. The treatment of electronic transitions in diatomic molecules again features the use of Hund's case (a) basis wavefunctions. Tables of rotational line strengths are developed in a different kind of format incorporating the weighting coefficients for the different Hund's case (a) basis wavefunctions. Herman–Wallis effects for electronic transitions are discussed in detail and incorporate Rydberg–Klein–Rees (RKR) calculations of vibration–rotation wavefunctions and quantum chemistry calculations of the dependence of the electronic transition moment on internuclear separation. The physics of absorption and emission processes is discussed in Chapter 6. Detailed example problems are included at the conclusions of Chapters 6, 7, and 8. The focus of Chapter 7 is Raman spectroscopy. Placzek polarizability theory is developed using irreducible spherical tensors. Following a similar approach to Chapter 5, Herman–Wallis effects for Raman transitions are discussed in detail and incorporate RKR calculations of vibration–rotation wavefunctions and quantum chemistry calculations of the dependence of the Raman polarizability on internuclear separation. Finally, in Chapter 8 the third-order nonlinear coherent anti-Stokes Raman scattering (CARS) susceptibility is derived in detail. The physics of both nanosecond and femtosecond CARS is discussed.

I would like to acknowledge the support of my wife Martha and my two daughters Kimberly and Heather during the rather lengthy process of writing this book. I would like to thank my graduate advisors Donald Sweeney and the late Normand Laurendeau for introducing me to the fascinating field of laser spectroscopy. My colleagues Drs. Roger Farrow and Larry Rahn at Sandia National Laboratories introduced me to the absorbing world of nonlinear optics in general and CARS in particular. I would also like to thank my numerous graduate students who have made my academic career such a pleasure. I would like to thank in particular my PhD students Robert Hancock, Ken Bertagnolli, Mark Woodmansee, Steve Green, Fred Schauer, Terrence Meyer, Joel Kuehner, Tom Reichardt, Sean Kearney, Robert Foglesong, Sukesh Roy, Rodolfo Barron-Jimenez, Ning Chai, Waruna Kulatilaka, Aman Satija, Mathew Thariyan, Warren Lamont, Daniel Richardson, Carson Slabaugh, Gurneesh Jatana, Alfredo Tuesta, Clare Dennis, Levi Thomas, Neil Rodrigues, Mingming Gu, Will Senior, Ziqiao Chang, and Ben Murdock. These students worked with me on the theory, development, and application of advanced laser spectroscopic techniques, such as CARS spectroscopy, laser-induced fluorescence (LIF) spectroscopy, and polarization spectroscopy; this research forms the motivation for the material presented in this book. I would especially like to thank Ziqiao Chang and Will Senior for proofreading the final version of the manuscript.