

Preface

The title of this book is borrowed, slightly modified, from Gerhard Herzberg, whose scholarship, vision, and generosity pervade and enrich the field of Molecular Spectroscopy. We dedicate this book to his memory.

By adding the word “dynamics” to the title Herzberg chose for his book, and by putting it on an equal footing with “spectra”, we express our belief that there is no fundamental difference between frequency and time domain spectra, no advantage in insight from an eigenstate vs. a wavepacket picture. There is profound complementarity. Herzberg taught us about the patterns that are likely to be found in a spectrum, how to use these patterns to make secure assignments, and how to build models that reproduce the measurements to the precision of the experiment. But patterns are made to be broken, and the breaking of standard patterns is the key to perceiving those dynamical features that demand explanation.

No spectrum, no matter how simple, is dynamics-free. No dynamical process, no matter how complex, fails to reveal its essential characteristics in one or a series of well designed spectroscopic experiments. The essential unity of spectrum and dynamics, of patterns of eigenstates and dynamical mechanisms, of simple few-level perturbations and multi-continua photofragmentation processes is the subject of this book.

The foundation for this book is “Perturbations in the Spectra of Diatomic Molecules.” We hope that the spectroscopic community will find this book to be more than a corrected and 50% expanded version of the 1986 text. The focus is no longer on perturbations *per se*, but rather on all spectra of diatomic molecules, perturbed and regular, frequency domain and time domain. By putting the word “perturbations” in its title, we misleadingly narrowed the apparent scope of the previous book. In addition, we artificially restricted the treatment of intramolecular dynamics to *simple* decay processes such as predissociation, autoionization, and collision induced transitions. In modern experiments, femtosecond laser pulses create coherent superpositions of eigenstates, called *wavepackets*. The time evolution of a wavepacket is simultaneously more complicated than a single exponential decay yet more easily visualized, as ball-and-spring motions, than the equivalent information contained in a collection of level spacings and transition intensities in a frequency domain spectrum.

A frequency domain spectrum is a group of transitions between discrete energy eigenstates or between discrete states and continuum states. What is surprising and beautiful is the wealth of information about intramolecular motions contained in such a set of transitions. Eigenstates

are *stationary* states, but they encode *dynamics* in subtle and often unexpected ways. Continua are dynamical entities, but in many ways they are modeled using the same terminology, concepts, and techniques as discrete eigenstates. Spectroscopic access to a continuum typically derives from an initially highly localized, perfectly know-able, and experiment-specific “pluck”. This pluck and the mechanism of the ensuing dynamics are well described by the same basis states and coupling matrix elements as are used to represent the discrete and continuum eigenstates.

The spectra of diatomic molecules are neither as simple as one might naively expect nor as complex as one might believe is warranted for a many-body system. Small molecules may not be very smart, but they have one big advantage over experimentalists and theorists, they know their Hamiltonian!

This book is written for experimentalists by a theorist and for theorists by an experimentalist. We present the models and concepts needed by theorists to understand the spectroscopic language spoken by molecules as translated by experimentalists and the tools and terminology needed by experimentalists to communicate with both molecules and theorists.

Molecules are complex, many-body systems. But, especially for a short time after a specific, experimentalist-designed, localized excitation is created, the evolution of the excitation in the molecule is simple, mechanistic, visualizable, and describable, not stochastic, statistical, or chaotic. The vast majority of inter-particle and inter-state interactions negligibly affect the early time intramolecular dynamics.

The experimentally achievable localized excitations are typically described by one of the zero-order basis states (see Section 3.2), which are eigenstates of a part of the total molecular Hamiltonian. Localization can be in a part of the molecule or, more abstractly, in “state space”. The localized excitations are often described by extremely bad quantum numbers. The evolution of initially localized excitations is often more complex and fascinating than an exponential decay into a nondescript bath or continuum in which all memory of the nature of the initial excitation is monotonically lost. The terms in the effective Hamiltonian that give birth to esoteric details of a spectrum, such as fine structure, lambda doubling, quantum interference effects (both lineshapes and transition intensity patterns), and spectroscopic perturbations, are the factors that control the evolution of an initially localized excitation. These factors convey causality and mechanism rather than mere spectral complexity.

An effective Hamiltonian contains all of the control parameters needed to describe a spectrum and any conceivable time domain experiment, not just the specific experiment by which these control parameters were determined. This is our unique message to the time-domain community. There

exists a century of insights into relationships between observables, into ways to create, describe, and interrogate the post-preparation evolution of a localized excitation, and into the energy and intensity patterns on which unique assignments of a spectrum are based. Semi-classical theory provides a link between Quantum Mechanics, where information about motion and causality is non-transparently embedded in a time-independent Hamiltonian matrix, and Classical Mechanics, where motion is directly observed and observations of motion reveal the specific and spatially localized forces that influence that motion. It is always possible and often informative to convert a quantum mechanical effective Hamiltonian (in which all of the control parameters are determined by a fit to a spectrum) to a classical mechanical effective Hamiltonian (see Section 9.4.13).

Chapters 1 and 9 are entirely new. Chapter 1 is an abbreviated users guide to the techniques used to record and assign spectra. It is an extremely condensed and idiosyncratically selective overview of important spectroscopic instrumentation, tools, and techniques. Chapter 9 is intended as a bridge between the frequency and time domain communities and also as an opening of a window onto molecules larger than diatomic molecules, in which the ideas and tools developed to describe dynamics in small molecules can be fruitfully applied to the mechanistic understanding of dynamics in larger molecules. Section 9.4 is almost entirely devoted to vibrational dynamics in polyatomic molecules. We illustrate the interconnectedness of molecular structure parameters and coupling constants through examples of effective Hamiltonian based matrix element scaling rules, opposite limiting cases in which two parameters play complementary case-preserving and case-destroying roles, and approximate partitionings of the structure and dynamics of the entire molecule into those of weakly interacting subsystems.

Chapters 2-8 are significantly revised, corrected, and expanded (by 150 pages) versions of Chapters 1-7 of "Perturbations in the Spectra of Diatomic Molecules". The most substantial additions to these chapters are: the treatment of Hund's cases in Section 3.2.1; the expansion of Chapters 7 and 8, previously restricted to Predissociation and Autoionization, to include direct photofragmentation processes and photofragment angular distributions (Sections 7.1, 7.2, 8.1, and 8.10-13); and new Sections in Chapter 6 dealing with one-color multiphoton spectroscopy (Section 6.1.2), interference effects in two-photon transition amplitudes (with substantial input from Michael Hippler, Section 6.1.2.2), F_1 vs. F_2 interference effects in the predissociation of $^2\Sigma$ states, the effect of a strong magnetic field on Rydberg states (with substantial input from Dolorès Gauyacq, Section 6.5.4), and an updated and expanded section dealing with the relationship between perturbations ("doorway states") and collisional transfer between electronic states (with

substantial input from Paul Dagdigian, Section 6.5.5). Pattern forming rotational quantum numbers and their use in assigning complex spectra, are discussed in Sections 3.2.1.2 and 6.3.3. Least squares and robust estimator fitting methods are compared in Section 4.4.1.4. The errors in the old Section 5.1.1 (now Section 6.1.1) on the interrelationships between factors related to transition intensities have been corrected. Section 3.3.5 is an introduction to electromagnetic field dressed potential curves. Schemes for coherent control of photofragment branching are introduced in Section 8.13.

Rydberg states have emerged as a major area of experimental and theoretical activity in the fifty years since Herzberg's book "The Spectra of Diatomic Molecules" was published. Therefore many of the examples in Chapters 3, 6, 7, and 8 deal with Rydberg states. Scattering theory (Multi-Channel Quantum Defect Theory, MQDT) is more appropriate than effective Hamiltonian theory to deal with interacting continuum states and the essential breakdown of the Born-Oppenheimer approximation when the Rydberg electron is far from the molecular ion-core. However, scattering theory is outside of the scope of this book, thus the treatment of MQDT in this book (Section 8.9) is only at an introductory level.

Hélène Lefebvre-Brion thanks Prof. Hajime Katô (Kobe, Japan), Prof. Alejandro Palma (Puebla, Mexico), Dr. Brenton Lewis (Canberra, Australia) and Prof. Nimrod Moiseyev (Haifa, Israel) for their hospitality during some weeks during which she has been able to work on this book. She thanks Dr. Brenton Lewis for an invitation to present a series of lectures to the Fifth Summer School on the Structure and Spectroscopy of Molecules in Canberra, Australia during January 1992. This was an opportunity for her to work on revising and extending the material in "Perturbations in the Spectra of Diatomic Molecules" for the present new book. She thanks for their answers to her questions on specific points, Drs. Alberto Beswick, Markus Drescher, Eric Charron, Claudina Cossart-Magos, Daniel Cossart, Gustav Gerber, Robert Gordon, Christian Jungen, Robert Le Roy, Frédéric Merkt, Georges Raşeev, François Rostas, Annick Suzor-Weiner, and Oleg Vasyutinskii. She realizes and regrets that many additional interesting papers concerning photodissociation and photoionization have not been referenced.

Robert Field thanks Richard F. Barrow, Thomas H. Bergeman, Padraic Burns, Daniel Cossart, Stephen L. Coy, F. Fleming Crim, Matthew P. Jacobson, Caroline C. Jarrold, David M. Jonas, Christian Jungen, Apostolos Kalamos, Michael E. Kellman, James L. Kinsey, William Klemperer, Roland Lefebvre, Robert H. Lipson, Anthony J. Merer, Frédéric Merkt, David C. Oertel, Stephen T. Pratt, Joëlle and François Rostas, Robert J. Silbey, Adam H. Steeves, Patrick H. Vaccaro, and James K. G. Wat-

son for advice and criticism. Thomas H. Bergeman, Kyle L. Bittinger, Daniel Cossart, Michael E. Kellman, Olli Launila, and Michael D. Morse provided or generated figures. Daniel Cossart, Stephen L. Coy, Paul J. Dagdigian, Dolorès Gauyacq, and Michael Hippler generously provided substantial text. Robert Field is grateful for hospitality while writing sections of this book to Hai-Lung Dai (University of Pennsylvania), Hajime Katô (Kobe University), James L. Kinsey (Rice University), Stephen R. Leone (while at JILA in Boulder, Colorado), Li Li (Tsinghua University, Beijing), Frédéric Merkt (ETH Zürich), Joëlle Rostas (Laboratoire Photo-physique Moléculaire), Timothy C. Steimle (Arizona State University), Guy Taïeb (Laboratoire Photophysique Moléculaire), Soji Tsuchiya (University of Tokyo), and Kaoru Yamanouchi (University of Tokyo).

This book owes its existence to Peter Giunta's determination, ingenuity, and artistry. Long before either H. Lefebvre-Brion or R. Field had the courage to imagine embarking on such an undertaking, Peter Giunta began preparing, in LaTeX, a corrected edition of "Perturbations in the Spectra of Diatomic Molecules".

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From the Preface to “Perturbations in the Spectra of Diatomic Molecules”

(Chapter numbering revised to be consistent with the present numbering.)

Examined in sufficient detail, the spectrum of every diatomic molecule is full of surprises. These surprises or “perturbations” can be at least as interesting as the vast expanses of textbook spectra lying between the surprises. Perturbations are more than spectroscopic esoterica. We hope that our discussion of perturbations provides a useful and unified view of diatomic molecular structure. This is a book about the spectra of diatomic molecules, warts and all.

This book is for graduate students just beginning research, for theorists curious about what experimentalists actually measure, for experimentalists bewildered by theory, and for potential users of spectroscopic data in need of a user’s guide. We have minimized recourse to abstract and elegant treatments (e.g., spherical tensors) wherever a simpler one (e.g., ladder operators) would suffice. We have worked through many examples rather than attempt to provide formulas and literature examples for all conceivable cases.

Chapters 2, 3, and 5 form the core of this book. Perturbations are defined and simple procedures for evaluating matrix elements of angular momentum operators are presented in Chapter 2. Chapter 3 deals with the troublesome terms in the molecular Hamiltonian that are responsible for perturbations. Particular attention is devoted to the reduction of matrix elements to separately evaluable rotational, vibrational, and electronic factors. Whenever possible the electronic factor is reduced to one- and two-electron orbital matrix elements. The magnitudes and physical interpretations of matrix elements are discussed in Chapter 5. In Chapter 4 the process of reducing spectra to molecular constants and the difficulty of relating empirical-parameters to terms in the exact molecular Hamiltonian are described. Transition intensities, especially quantum mechanical interference effects, are discussed in Chapter 6. Also included in Chapter 6 are examples of experiments that illustrate, sample, or utilize perturbation effects. The phenomena of predissociation and autoionization are forms of perturbation and are discussed in Chapters 7 and 8.

We want to thank the following experts who have helped us by reading and criticizing portions of the manuscript: M. Alexander, R.F. Barrow, N. Bessis, M. Broyer, L. Brus, M. Chergui, M. Child, D.L. Cooper, K. Dressler, C. Effantin, D. Gauyacq, A. Giusti-Suzor, R.A. Gottscho, G. Gouédard, M.

Graff, C. Green, J. T. Hougen, B. J. Howard, P. Houston, Ch. Jungen, A. Lagerqvist, C. Linton, S. McDonald, E. Miescher, J. Norman, S. Novick, I. Renhorn, J. Rostas, J. Schamps, H. Schweda, S. J. Silvers, J. Thoman, A. Tramer, P. Vaccaro, and J. F. Wyart. The errors and opacities that remain are ours, not theirs. We have not attempted to cite all relevant references; we apologize for our probably numerous failures to discuss the first and/or most important examples of phenomena, interpretations, and techniques. This book could never have been produced without the artistry of Mr. J. Lefèvre and the skillful and energetic word processing of Virginia Siggia, Kay Garcia, and Sarah M. Moore.

RWF is grateful to the Laboratoire de Photophysique Moléculaire of the Université de Paris–Sud for a visiting professorship in 1981, to S. Novick and B. Kohler of Wesleyan University and R.J. Saykally of the University of California, Berkeley, for their hospitality, and to project MAC of MIT for a grant of computer time. A NATO international travel grant greatly accelerated and enriched the process of preparing this book. RWF owes his fascination with molecules to W.A. Klemperer and the late H.P. Broida.

HLB has been greatly stimulated by many discussions with the experimentalists in the groups led by S. Leach (Orsay) and J. d’Incan (Lyon). Their numerous questions led her and Leach to organize the French meetings of the GESEM,* which provided an opportunity to develop some of the material included in this book. HLB is also grateful to the late A. Kastler, who invited her to lecture at the International Winter College in 1973 in Trieste. The lecture notes written for this purpose were the first draft for some sections of this book. Finally, her interest in perturbations goes back to a problem presented to her in 1963 by E. Miescher. This was the starting point for a fruitful and pleasant scientific exchange that is still underway. This is why this book is dedicated to E. Miescher.

*Groupe d’Etudes de Spectroscopie Electronique Moléculaire (1969–1979).