

Preface

I am a card-carrying, small-molecule spectroscopist. I like simple models and the possibility of certainty that an analysis is correct.

When I was a graduate student in William Klemperer's laboratory, I received a precious gift: I became a molecular spectroscopist. In my 40 years at MIT, my students, postdocs, and collaborators kept me focused on the crucial question: "what makes *this* experiment interesting?" Often, they provided both question and answer. I have been energized and educated by their questions, ideas, and ah-hah moments. Always, they had me saying brilliant things I did not know that I knew. But a mirror never knows the beauty it reflects. I dedicate this book to William Klemperer and *my* special sub-group of *his* scientific descendants.

Frequency-domain experimentalists observe transition frequencies and intensities. Wavefunctions are not directly observable. The challenges of spectroscopy are: (a) assign the observed transitions; (b) fit the directly sampled energy levels to a quantum mechanical model; (c) make predictions about other spectra; and most importantly, (d) capture the dynamics and dynamical mechanisms that are encoded in the spectrum. The effective Hamiltonian, \mathbf{H}^{eff} , is an essential tool for meeting all four of these challenges without license to take a peek at the wavefunction (especially its nodal structure, which is tantamount to assignment, and its time evolution, which reveals mechanism). This short book is an express user's guide for beginners who know neither the basics nor the elegant simplicity and intuition-guiding power of the models that lie beyond archival molecular constants. It is not a textbook. It is neither rigorous nor logical. My goal in writing this book is to provide a set of ideas, tools, and challenges that will ignite the ability of beginning students to see what is intuitive and memorable in molecular spectra.

The lecture format permits strong opinions, personal choices of topics, and intentionally incomplete examples. My idea is to provoke my readers to explore other examples, to create freehand figures that are qualitatively but not quantitatively correct, and to practice using tools and concepts that are derived from my idiosyncratic point of view rather than from a balanced and scholarly treatment. I have attempted to make connections between disparate topics without being burdened by lengthy justification. I have presented several of my favorite topics. My dream

is that mastery of the main topics in these eight chapters/lectures will serve the student as preparation for productive years as a spectroscopist, and will be at least as enlightening as a semester-long sojourn in a course based on a carefully integrated formal textbook.

The vast majority of citations in this book are to relevant sections of *The Spectra and Dynamics of Diatomic Molecules* [1], and to a long paper devoted to my favorite topic, effective Hamiltonians [2]. This excess of self-citation is one of the special privileges accruing to an author of lecture notes rather than a textbook.

I thank the Alexander von Humboldt Foundation for the Humboldt Research Award that gave me the opportunity to spend several months as a member of Gerard Meijer's Molecular Physics Department at the Fritz Haber Institute of the Max Planck Society in Berlin. I especially thank Gerard Meijer for inviting me into his laboratory while it was crackling with excitement, creativity, and experimental virtuosity.

I am thrilled that this book will be published as the harbinger of a new Springer book series entitled "Alexander von Humboldt Lectures," the purpose of which is to make the lectures presented by Humboldt Awardees and Humboldt Professors available to students who were unable to attend them in person. Bretislav Friedrich had the idea for this series and I thank him for talking me into putting my lectures into book form.

This book owes its existence to Peter Giunta's ingenuity, artistry, and efficiency. The text for each lecture was written longhand in Berlin and FAXed to Peter at MIT in Cambridge on the day before the lecture. Peter created a LaTeX draft, which I would proofread, mark up, and send back to Peter. Before each lecture I was able to hand out a set of notes to the class!

Cambridge, MA, USA

Robert W. Field

References

1. H. Lefebvre-Brion, R.W. Field, *The Spectra and Dynamics of Diatomic Molecules* (Elsevier, Boston, 2004)
2. R.W. Field, J. Baraban, S.H. Lipoff, A.R. Beck, Effective Hamiltonians, in *Handbook of High-Resolution Spectroscopies*, ed. by M. Quack, F. Merkt (Wiley, Oxford, 2010)

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Field, R.W.

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