Cambridge University Press
052184276X - Molecular Reaction Dynamics
Raphael D. Levine
Frontmatter
More information

Molecular Reaction Dynamics

Molecular Reaction Dynamics is a brand new version of the text by Levine and Bernstein. The book delivers an updated treatment of this fundamental topic. An appreciation of how chemical reactions occur and their control is essential to chemists and to those in interdisciplinary fields such as materials and nanoscience, drug design, and astrochemistry. The first half of the book describes experimental techniques for initiating and probing reaction dynamics and the essential insights gained. The second part explores key areas including photoselective chemistry, stereochemistry, chemical reactions in real time, and chemical reaction dynamics in solutions and interfaces. Typical of the new challenges are molecular machines, enzyme action, and molecular control. With problem sets included, this book is aimed at advanced undergraduate and graduate students studying chemical reaction dynamics, as well as physical chemistry, biophysics, and materials science.

Raphael Levine is Max Born Professor of Natural Philosophy at the Hebrew University of Jerusalem and Distinguished Professor of Chemistry at the University of California, Los Angeles. He is active in the area of chemical reaction dynamics and his published scientific work has earnt the recognition of the Israel Prize and the Wolf Prize. He is a member of the Israel National Academy of Sciences and a foreign member of the National Academy of Sciences of the United States and of Academiae Europaeae.

Molecular Reaction Dynamics

Raphael D. Levine

CAMBRIDGE
UNIVERSITY PRESS

PUBLISHED BY THE PRESS SYNDICATE OF THE UNIVERSITY OF CAMBRIDGE
The Pitt Building, Trumpington Street, Cambridge, United Kingdom

CAMBRIDGE UNIVERSITY PRESS
The Edinburgh Building, Cambridge, CB2 2RU, UK
40 West 20th Street, New York, NY 10011–4211, USA
477 Williamstown Road, Port Melbourne, VIC 3207, Australia
Ruiz de Alarcón 13, 28014 Madrid, Spain
Dock House, The Waterfront, Cape Town 8001, South Africa

http://www.cambridge.org

First published 2005

Printed in the United Kingdom at the University Press, Cambridge

Typefaces Times New Roman 10/13 pt. and Universe *System* LaTeX 2$_\varepsilon$ [TB]

A catalog record for this book is available from the British Library

Library of Congress Cataloging in Publication data
Levine, Raphael D.
Molecular reaction dynamics / Raphael D. Levine.
p. cm.
Includes bibliographical references and index.
ISBN 0 521 84276 X
1. Molecular dynamics. 2. Chemical reaction, Conditions and laws of. I. Title.
QD461.L66 2004
541′.394 – dc22 2004045662

ISBN 0 521 84276 X hardback

I am grateful to the many people who, over the years, joined me
to watch the molecules dance to the tune of time.
This book is dedicated to Mira who is able to make us join the dance.

The cover illustration is by the late Israeli physical chemist and artist Jacob Wilf. Jacob was my friend and we had many scientific discussions. One result is that he has drawn several paintings depicting themes from Molecular Reaction Dynamics such as harpoon reactions, stereodynamics and cluster impact. The painting shown on the cover is titled 'surprisal analysis' and was dedicated to me by the artist. The topic of surprisal analysis is discussed in Section 6.4.2. The works of Wilf on a variety of scientific themes were exhibited at the Israel National Academy of Sciences and other Institutions. Many paintings by the late Jacob Wilf can be seen at http://jacob.wilf.org/

Contents

Preface

Molecular reaction dynamics unfolds the history of change on the molecular level. It asks what happens on the atomic length and time scales as the chemical change occurs. This book is an introduction to the field.

Molecular reaction dynamics has become an integral part of modern chemistry and is set to become a cornerstone for much of the natural sciences. This is because we need a common meeting ground extending from nanoscale solid state devices through material and interface chemistry and energy sciences to astrochemistry, drug design, and protein mechanics. For some time now the quantitative understanding on the molecular level has provided this common ground. At first, the scaffolding was the concept of the molecular structure. Once we understood the spatial organization we felt that we had an entry to real understanding. The required input was provided by the different experimental methods for structure determination and, from the theory side, by quantum chemistry and by equilibrium statistical mechanics. But now we want more: not just the static structure, we also ask how this structure can evolve in time and what we can do to control this evolution. We want to write the history of the change or, better yet, to be a conductor and orchestrate the motion. This is what this book is about.

In going from statics to dynamics we need new experimental tools and also theoretical machinery that allows for the dependence on time. This means that the stationary states that are usually the subject of an introductory quantum mechanics course have to be extended to non-stationary ones. Fairly often, classical dynamics is sufficient to describe the time evolution but there are a number of interesting exceptions. Non-equilibrium statistical mechanics is necessary to describe systems with many degrees of freedom and their far-from-equilibrium pattern formation.

Molecular reaction dynamics is not yet able to do all that has to be done. There are places where we lack understanding of the principle and not only of the details of a particular family of processes. Indeed, as we move into more complex systems the gaps in our understanding are wider than the passes. As just two examples, we do not have a complete understanding of the atmospheric chemistry of the outer planets nor can we describe how an enzyme mobilizes chemical energy to its active site. But we do have enough of the basics in place that it is a good time to stop and survey where we are, where we need more work on the foundations, and where there are whole areas that call for applications,

where different subjects need to be better connected, and what new families of processes are there to be deciphered. This book is a primer for what we already know.

As was the original (1974) intention, this book seeks to describe why a particular experiment was carried out, what we have learned, what concepts are necessary to describe and understand the experiment, and how we move forward. The problems that follow each chapter provide additional applications and illustrations. A concept that is much more prominent in the present version of the book is *coherence*, and we bring it in as soon as possible. Much recent progress has come through the outstanding development of computational means. These include not only the ability to compute the forces between atoms at realistic accuracy, but also the computation of the (classical or quantal) motion subject to these forces and the ability to visualize the resulting dynamics. Our debt to these developments will be clear throughout the book, but what we will be concerned with is what we have learned rather than how to implement a computation. The need for visualization arose not only because of the increasing concern with more complex systems, but also because of the technological ability to achieve a time resolution sufficient to probe intramolecular motions. Instead of just imagining how the reaction unfolds in time, we can directly image the transformation experimentally. In a different dimension, the experimental ability to image the distribution of the products of the reaction in space has a major impact. We are almost ready to be able to image in both space and time. Another key initiative is the bold forays into dynamics in the condensed phase and interfaces. The integration of our understanding of gas phase, isolated collision dynamics and of dynamical proceedings dressed by their environment is already making promising progress. Because the chemical change is localized in space and time we can often think of a change in a complex system as a reaction center "solvated" by the rest of the system. Therefore, issues similar to dynamics in the condensed phase arise in the need for rational drug design or the understanding and development of molecular machines and other applications where the molecules are large.

This book is based on my class notes at the Hebrew University of Jerusalem and at the University of California, Los Angeles. The level is that of senior undergraduate or graduate students. The prerequisite is a class in chemical kinetics. Some familiarity with spectroscopy and with statistical mechanics is beneficial but not essential, and introductory material is provided where necessary. The scope of the book is more than can be covered in a lecture course of one semester. The first six chapters develop the tools and illustrate their applications. The examples are usually simple ones that can be used to make the point. The development in these chapters is linear, there are sections that can be skipped, but the order of topics is sequential. There are people who will want to get as quickly as possible to Chapter 5. This is understandable, but I recommend first to go at least through Sections 2.1, 2.2, and 2.3. In the following six chapters the text is arranged

around applications where each chapter has a common theme. This part of the book offers a choice of material because the different chapters are almost, but not quite, independent of one another. Starred sections take you away from the main line of development.* There are endnotes that provide more details and also cite original sources for the results quoted. References to review-type articles are provided to enable further reading. (A complete bibliography, with titles, is at the very end of the book.) Revision problems with hints follow each chapter. Some of these problems are easy but others are not.*

* Both in class and in writing I use too many footnotes. I hope that it does not distract you too much.

Acknowledgments

The text is a completely rewritten version of Levine and Bernstein, *Molecular Reaction Dynamics* (1974). In this task I have received indispensable advice and encouragement from R. N. Zare (Stanford) and J. L. Kinsey (Rice). I am very grateful to them and at the same time I wish to clearly state that all remaining shortcomings in presentation and coverage are entirely my responsibility. Chapter 10, on stereodynamics, plainly shows my indebtedness to Richard Zare. As I was writing, Tamar Raz was preparing an abbreviated version of the text, in Hebrew, for distance learning by senior undergraduates of the Open University of Israel. The feedback from Tamar has been essential. I also acknowledge the critical help of Micha Asscher, Michal Ben-Nun, Richard Bersohn, Eleanor Campbell, Mervin Hanson, Robert Gordon, Mark Marshall, Izhack Oref, Eliyahu Pollak, Françoise Remacle, Sanford Ruhman, Benjamin Schwartz, Tamar Seideman, and Yehuda Zeiri. They have read and commented on one or more chapters and did their very best to help me make the text clearer and more accurate. Here, too, I bear complete responsibility for the final version. I have profited from detailed information communicated to me by Stephen Bradforth, David Chandler, Wilson Ho, Kendal Houk, Todd Martinez, Gilbert Nathanson, Gabor Somorjai, and Steven Stolte. Graduate students Hadas Amiezer, Ayelet Gross, and Dan Steinitz have each helped in essential ways. Many colleagues and students have provided additional insights and advice. Mrs E. Guez has followed the evolution of this book from its addressograph plates typed in 1972.

I have tried to make sure that proper reference is provided for specific results cited in the text. I recognize that I have probably failed fully to do so, and I apologize beforehand. I would be grateful to anyone putting me right on this, as well as on any other aspect. I welcome comments (rafi@fh.huji.ac.il).

This book would not have been possible without the many years of fruitful collaboration with the late Richard Bernstein.

I thank the US Air Force Office of Scientific Research, the Volkswagen Foundation, the United States–Israel Binational Science Foundation, the German–Israeli Binational Science Foundation, the James Franck Program, and the Humboldt Foundation for the support of my work on molecular reaction dynamics. Directly and indirectly this support was critical to my being able to write this book.