THEORY OF MOLECULAR RELAXATION

Applications in Chemistry and Biology

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A Wiley-Interscience Publication

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THEORY OF MOLECULAR RELAXATION

Applications in Chemistry and Biology

To
My Parents
My Wife, Margareta
My Brother, Douglas

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PREFACE

Approximately two years ago, when I first contemplated the writing of this book, I thought that a concise description of the quantum statistical techniques in the treatment of relaxation processes would be timely. As a result of many recent efforts on the quantum-statistical mechanical treatment of rate processes, solutions to some of the traditional problems in chemistry have now become well-established. A number of these solutions are now suitable for introduction into standard physical chemistry textbooks. In spite of this, most chemistry students are unfamiliar with the basic techniques involved. These techniques include second quantization, operator algebra, the basic notion of irreversible thermodynamics, and linear-response theory. Unfamiliarity breeds an unjustified fear of these simple, but elegant, techniques, and fear leads to the usual blocks to conceptual thinking.

That such mental blocks can be removed is demonstrated by a simple experiment which I performed during my recent visit to Taiwan at the National Tsing Hua University. There I was asked to give a series of twenty-four lectures on photochemical relaxation phenomena. During the course of these lectures, I was able to begin, literally, "from scratch" in eventually arriving at the derivation of some recent theoretical results obtained by my associates and myself. These results had just appeared or were scheduled to appear in the *Journal of Chemical Physics*. Starting with a general phenomenological description of relaxation in chemistry and physics, I proceeded to outline the basic notion of the Born-Oppenheimer adiabatic approximation. This was followed by a description of Onsager's formulation of irreversible thermodynamics in the so-called quasi-thermodynamic approximation. Next, I used Kubo's linear-response theory to calculate the rate constants for specific relaxation processes. To facilitate the calculations, I introduced the techniques of second quantization and operator algebra. I ended the series of lectures by obtaining the final expressions for intramolecular electronic relaxation processes in large

molecules, and by conveying to the class the fact that the difficulties associated with the application of these techniques actually do not go beyond those associated with the understanding of the simple harmonic oscillators!

This book is not intended to be a standard treatise that provides an encyclopedic overview of the entire subject of relaxation phenomena. Nor is it intended to be a mere pedagogic account of standard theory. Instead, it is written with the hope of communicating to the reader a certain approach to scientific research. In this sense, the book offers a central "plot." First, questions are raised regarding the interpretations of some frequently observed phenomena in terms of existing theories. To answer these questions our attention is turned to the fundamental principles of quantum statistical mechanics. We then proceed to apply the formal results by (a) making specific model calculations that allow a physical interpretation of the abstract theory and (b) choosing specific experimental situations to which the model calculations are applicable. Once the theoretical concepts are well grounded by the quantitative comparison of theory and experiment in terms of these model calculations, we then venture into more complex phenomena. The rigorous theory can then be applied to provide a set of qualitative guidelines upon which to base our interpretations.

A central purpose of the book is to integrate formal theory with experiment in varying degrees of approximation. Earlier chapters deal with an exposition of standard material. As the basic theory becomes fully developed, the text undergoes a shift in direction and delves into selected areas of current research. In the evolution from pedagogy to new developments, three recurring points of emphasis are made; (1) the intimate relationship between the dynamical and structural properties of matter, (2) the importance of keeping the set of postulates to an irreducible minimum, and (3) the consistency of postulates and consequences in the hypothetico-deductive procedure.

Part One of this book is based on the series of Tsing Hua lectures, which were also given as part of an introductory statistical mechanics course to a group of second-year graduate students at Purdue University during the fall of 1973. The same material was again presented in a series of twenty lectures to a group of research workers at the University of Lyons, France during the spring of 1975. The many interactions with these three groups of students and colleagues have proved to be most valuable.

Part Two of this book provides an account of a group of selected applications of the relaxation theory to problems that are of current interest. This account is heavily biased toward the research work of my collaborators and myself. Regretably, an adequate summary of many

outstanding contributions cannot be attempted because of the limitations of space and time. It is hoped that these limitations do not severely diminish the usefulness of the book. A comprehensive review of the vast areas in molecular relaxation is manifestly impossible between the covers of a single volume. Even so, I have attempted to provide a coherent view of research work in five distinct areas of current interest: radiationless relaxation in large molecules, relaxation of rare earth ions in crystals, activated rate processes in condensed media, intramolecular rearrangement reactions in carbonium ions, and photosynthesis. I believe that the approach taken here can be readily extended to other areas of endeavor.

I am grateful to Professor Marvin M. Miller (Purdue), who has made important contributions to Chapter 5 and who is primarily responsible for the discussion on cooperative radiationless relaxation. I am thankful to Professors Dennis J. Diestler (Purdue) and Karl F. Freed (Chicago) for their contributions in the development of the activated rate process theory described in Chapter 7, and for their continuous collaboration and discussions throughout the entire course of this work. To these three valued colleagues I owe much of my understanding of the fundamental approach to molecular relaxation. I also wish to acknowledge the various contributions of my research associates, particularly those of Drs. Howard V. Lauer, Steven L. Naberhuis, and William A. Wassam. These contributions form the basis for a number of discussions in Chapters 5, 6, and 7.

A comprehensive assessment of the long-standing controversy over the nonclassical carbonium ion question is given in Chapter 8. My interest in the chemistry of carbonium ions was triggered by a stimulating talk by Professor George A. Olah (Case Western) given on April 16, 1974 at Purdue University. My appreciation of the intricacies of this research area has been catalysed by the extensive discussions and communications with Professors James H. Brewster (Purdue), Herbert C. Brown (Purdue), Gerhard L. Closs (Chicago), Martin Saunders (Yale), and Charles F. Wilcox (Cornell).

During the preparation of this book, I was unexpectedly led to an interesting model for the primary light reaction in photosynthesis. I have greatly benefited from numerous exhaustive and largely critical comments on many aspects of this model by Professor Gerhard L. Closs, Dr. Joseph J. Katz (Argonne National Laboratory), Professor Kenneth Sauer (Berkeley), and two or three anonymous referees who repeatedly recommended rejection of various versions of my papers on photosynthesis. These comments were mostly concerned with an apparent conflict between my model and several existing interpretations. Without these comments, it would have been difficult for me to arrive at a consistent view of the observed experimental behavior of chlorophyll interactions

detailed in Chapter 9. In numerous critical stages of the development of the photosynthesis theory, I had frequently called on the help of Professors James H. Brewster, Herbert C. Brown, and William A. Cramer (Purdue), sometimes at rather unconventional hours of the day or night. To these colleagues and their families, I extend a deep sense of gratitude—and apology for the inconvenience that I must have caused.

The bulk of this book was written during the first six months of the academic year 1973–1974. The unwavering moral support of a number of my colleagues at Purdue University have alleviated the occasional trials and frustrations of effort. In this respect, I am particularly grateful to Professor Herbert C. Brown, who has provided me with a sense of balance and a certain perspective on the philosophy of science. The book was completed during the fall of 1974 when I was a Visiting Professor at the University of Chicago. I am thankful to Professor Stuart A. Rice (Chicago) for a thorough reading of the entire manuscript and for a number of critical suggestions that have significantly influenced the final outcome of this book. The latest developments in the photosynthesis theory have been brightened by the numerous interactions with Professor Richard A. Dilley (Purdue) and Martin D. Kamen (Southern California), and by the experimental work of Dr. Vaughn J. Koester (Purdue). In May and June of 1975, these developments have been presented and extensively discussed in colloquia sponsored by the State University of Leyden, Holland, and by the French Physical Society in Lyons. They have been incorporated into Chapter 9 in the galley proofs.

In addition to the above-mentioned individuals, I have been stimulated and encouraged by a large number of friends and colleagues in institutions where I have been asked to lecture during the preparation of this book. The many vigorous discussions which have followed my talks on photosynthesis and spectroscopic relaxation phenomena have inevitably modified and contributed to many details of the theory. In particular, I would like to mention Mrs. Francoise Gaume of the University of Lyons; Dr. James R. Norris of Argonne National Laboratory; Professor Howard Reiss of the University of California, Los Angeles; Professors Govindjee, Lawrence R. Faulkner, and Rudolph A. Marcus of the University of Illinois; Professors Hua Chang, Shiu-Shien Shu, and Sung-Mao Wang of the National Tsing Hua University; Drs. James D. McElroy, Frank A. Stillinger, and Peter M. Rentzepis of Bell Telephone Laboratories; Professor G. Wilse Robinson of California Institute of Technology; Professor John C. Wright of the University of Wisconsin; Professors Sighart F. Fischer and Paul A. Loach of Northwestern University; Professors Peter Yates and George Burns of the University of Toronto; Professors Peter Langhoff, Attila Szabo, and A. SanPietro of the University of Indiana; and

Dr. Arnold Hoff, Professors L. N. M. Duysens and J. van derWaals of the State University at Leyden, the Netherlands.

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Finally, I should like to mention my wife, Margareta, but not because she has encouraged me in my work. On the contrary, she has on numerous occasions succeeded in making me spend glorious days in total oblivion of science. Her interest and faith has made possible the writing of this book.

FRANCIS K. FONG

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The sources of illustrations that had been taken from earlier publications are listed as follows: Figs. 6.1–6.5, F. K. Fong, S. L. Naberhuis, and M. M. Miller, *J. Chem. Phys.* **56**, 4020 (1972); Figs. 5.2, 6.6–6.9, F. K. Fong and W. A. Wassam, *J. Chem. Phys.* **58**, 957 (1973); Figs. 6.13–6.17, H. V. Lauer and F. K. Fong, *J. Chem. Phys.* **60**, 274 (1974); Figs. 6.18–6.28, F. K. Fong, H. V. Lauer, C. R. Chilver, and M. M. Miller, *J. Chem. Phys.* **63**, 366 (1975); Figs. 7.5, 7.6, F. K. Fong, *Phys. Rev.* **187**, 1099 (1969); Figs. 7.7, 7.8, R. H. Heist and F. K. Fong, *Phys. Rev.* **B1**, 2970 (1970); Fig. 7.9, F. K. Fong and D. J. Diestler, *J. Chem. Phys.* **57**, 4953 (1972); Fig. 7.14, K. F. Freed and F. K. Fong, *J. Chem. Phys.* (in press 1975); Figs. 7.11, 8.1, 8.3, F. K. Fong, *J. Am. Chem. Soc.* **96**, 7638 (1974); Figs. 9.1–9.4, J. C. Wright, D. J. Zulacha, H. V. Lauer, D. E. Cox, and F. K. Fong, *J. Appl. Phys.* **44**, 781 (1973); Figs. 9.5–9.8, D. J. Zalucha, J. C. Wright, and F. K. Fong, *J. Chem. Phys.* **59**, 997 (1973); Figs. 9.10, 9.15, F. K. Fong, *Proc. Nat. Acad. Sci.* USA **71**, 3692 (1974); Figs. 9.11, 9.12*a*, F. K. Fong, *J. Theoret. Biol.* **46**, 407 (1974); Figs. 9.12*b*, 9.14, F. K. Fong, *Appl. Phys.* **6**, 151 (1975).

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THEORY

Chapter One
INTRODUCTION

A system in thermodynamic equilibrium gives the appearance of rest, because all its measurable properties are time independent. When an external disturbance is introduced, the system becomes displaced from the initial equilibrium conditions. This displacement gives rise to measurable relaxation effects that are manifestations of the molecular properties of the macroscopic system.

Since by postulate entropy is maximized when the system is at equilibrium, it follows that the act of relaxation or regression toward equilibrium must be driven by the tendency of a nonequilibrium system toward entropy maximization. In principle, therefore, it should be possible to treat all relaxation phenomena in terms of the time evolution of the appropriate entropy function. In this respect, the theory of relaxation may be constructed in terms of two related but distinctly different formalisms: (1) the macroscopic description of irreversible thermodynamics and (2) the molecular description of quantum statistical mechanics.

This book is primarily concerned with the molecular approach. In this approach our goal is twofold. First, we find an expression that relates the macroscopic rate constant for a given relaxation process to the appropriate molecular Hamiltonian. We then proceed to evaluate this expression in order to cast it in a form amenable to experimental verification. In equilibrium statistical thermodynamics, the macroscopic observables are related to molecular properties through partition functions. In the present case, as we shall see in the following development, the time-dependent observables of nonequilibrium systems can be interpreted in terms of molecular behavior via time-correlation functions.

In this chapter a phenomenological description of the problem of molecular relaxation is given. Two specific examples, dielectric relaxation and internal radiationless relaxation, are described. The concept of the participation of vibrational degrees of freedom is introduced. Two historical developments (one by Debye and the other by Eyring), which have exerted strong influences on the study of relaxation, are reviewed. This review provides the background for our present approach to relaxation.

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