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Preface

The last few decades have witnessed an enormous development in all branches of science devoted to studying molecules in excited states. Huge progress in laser technology has opened up completely new possibilities in both temporal and spectral domains. The achievement of femtosecond time resolution makes it possible to monitor the elementary processes that occur immediately after absorption of a photon. The use of tunable, narrowband lasers provides a means to selectively excite and follow the fate of a single molecule. Traditional divisions into separate areas of research, such as photochemistry and photophysics, are no longer valid. The same becomes true for the experimental techniques, which are getting more and more "hyphenated."

The progress in computational methods is equally impressive. Excited states of what the quantum chemists used to call "large" molecules (the size of naphthalene) can now be calculated by very sophisticated *ab initio* procedures. The calculations for yet larger molecules are limited to semiempirical methods. However, the software required for such computations is now available in user-friendly versions and can easily be installed on an average personal computer. Moreover, the development of molecular dynamics techniques makes it possible to study conformational changes in really huge molecules, such as proteins.

This stunning speed of the outgrowth of experiment and theory makes it very difficult, even for a person directly working with excited states, to keep track of all important publications, novelties and trends. Therefore, the idea of this book is to present an overview of a variety of important works performed in this field. The focus is on the conformational aspects of molecules in excited states. Obviously, a subject like that cannot be exhausted in just one volume. The intention was rather to expose the reader to the multitude of topics covered by this area. In preparing particular chapters, the authors were requested to follow two guiding principles: (i) to present the main issues related to their field of investigation and (ii) to describe the methods used to detect and study the excited-state species.

In choosing the topics, the idea was to present problems that are being heavily discussed and for which definitive solutions are still in the making. A typical example of such an issue, which is discussed in Chapter 1, is provided by various models that are put forward to explain the nature of the dual fluorescence observed in dimethylaminobenzonitrile and derivatives.

In the vast literature dealing with excited states, one can distinguish many papers that revolve about common subjects, such as (i) conformation changes accompanying photoinduced electron transfer; (ii) photochromism; (iii) photoisomerization, often involving a large-amplitude motion; (iv) intramolecular and intermolecular aspects of excited-state proton transfer; (v) photodissociation; and (vi) elementary photophysical and photochemical processes in living systems. Most of these subjects have been covered in the present volume, with the exception of photochromism (mentioned briefly in Chapter 2), on which separate books have been published recently. Photobiology was also not included explicitly, although many of the systems discussed in this volume serve as models in the studies of important photoprocesses occurring in living organisms.

The first chapter describes excited-state conformational changes that occur in molecules consisting of an electron donor and acceptor, linked by a single bond. Photoexcitation of such systems may lead to a charge transfer state for which the angle between the planes of the donor and the acceptor can be very different than in the ground state. This is a result of the competition between two factors, acting in opposite directions. On one hand, flattening of the molecule can be energetically advantageous because of increasing conjugation. On the other hand, twisting towards a fully perpendicular conformation leads to an increase of the dipole moment and is therefore helped by a polar solvent, which can further stabilize such a structure. As a result, the final conformation may be very sensitive to the environment. For the same molecule, flattening may occur in nonpolar solvents, while twisting may prevail in polar ones.

In Chapter 2, conformational aspects of excited-state proton transfer are discussed. These are of particular importance in systems in which not one, but two or more, protons are moving within the short lifetime of an excited state. In such cases, the reaction coordinate is often dominated by terms not necessarily related to proton motion, but rather by those that depict the spatial rearrangement (e.g., motion of an alcohol molecule around the excited chromophore, flattening of a dimeric structure, or a mutual rotation of proton donor and acceptor groups).

Chapter 3 describes an important, yet still relatively little-known, problem: the role played by friction between the solute and solvent molecules in chemical reactions, in particular those involving large-amplitude motion. Various theoretical models of friction are presented and compared with the experimental data. Modeling the friction, especially its frequency and spatial dependence, is a formidable task. Fortunately, it becomes feasible with the development of ultrafast spectral techniques and computational procedures.

Chapter 4 is devoted to exciplexes and other excited-state complexes. Mechanisms of their formation and decay are discussed, as well as the geometric and electronic structure. This chapter also contains a brief introduction to the Marcus theory of electron transfer—in particular, to the notion of "inverted region," a concept that is able to explain a phenomenon rather unusual for an ordinary chemist—a decrease of the reaction rate with the increasing driving force for the process. Another uncommon process presented in this chapter is the "harpooning mechanism," in which the photoinduced electron transfer is a prerequisite for a conformation change. Interestingly, this represents, in a way, a negative of the mechanism described in Chapter 2, by which a conformational process prepares the stage for a proton transfer reaction.

Chapter 5 is devoted to one of the basic problems in organic photochemistry: To what extent does the ground-state distribution of different conformers influence the outcome of a photochemical reaction? Experimental and theoretical procedures are described that allow one to determine the characteristics of each of the rotamers present both in the ground and excited states. The authors start from the classical "NEER principle," which postulates nonequilibration of excited rotamers. A direct consequence of this rule is that the products of a photochemical transformation are determined by the ground-state equilibria. Systems that obey the NEER principle are presented along with those that do not.

The NEER principle is also critically discussed, extended, and reformulated in Chapter 6, which is devoted to theoretical studies of excited-state conformational properties. The authors show that the ground-state distribution of conformers determines the accessibility of excited-state decay channels, which, in turn, is crucial for the fate of an excited molecule. A fundamental role in the photophysics is played by the geometry of conical intersections—extremely efficient channels for photochemistry and radiationless deactivation. It is remarkable how well the position of the conical intersection can be calculated, nowadays even for large molecules.

The structural and kinetic aspects of the excited state are closely related. In this volume, the emphasis is rather on the former, although in many places the latter also receive due attention. The book is not intended to describe in detail the experimental and theoretical techniques used for conformational studies. Still, the reader will find descriptions of many experimental approaches in Chapters 1–5, whereas Chapter 6 presents the principles underlying calculations of ground- and excited-state minima, transition states, and conical intersections.

The resulting volume is dedicated to audiences consisting of physical and organic chemists, photobiologists, and material science specialists. It is the hope of the editor that the ideas presented in this book may stimulate further activity in the fascinating area of conformational studies of excited molecules.

Jacek Waluk

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