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Lasers and Chemical Change

With 245 Figures

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הַזֹּרְעִים בְּדִמְעָה בְּרִנָּה יִקְצֹרוּ׃

תהלים, קכו׃ה

Those who sow in tears shall reap in joy

(Psalms, 126 : 5)

Preface

Lasers and chemical change is the study of radiation and molecules in disequilibrium. The distinguishing feature of such systems is the extreme departure from thermal equilibrium: the radiation is usually confined to a narrow frequency range, is well collimated, and is far brighter than black body radiation; the chemical composition and also the distribution of molecules over their different energy states are often markedly displaced from that expected at equilibrium. Such systems can be used as a source of laser radiation and, reversedly, lasers can rapidly and selectively displace molecular systems from equilibrium. The subsequent evolution of the initially prepared state can then be monitored - again using lasers.

One purpose of this book is to introduce the concepts required to discuss systems of radiation and molecules in disequilibrium. These include the physics of (laser) radiation and of radiation-matter interaction and molecular structure and spectroscopy. Excellent textbooks of these topics are available and our survey (in Chap.3) is only intended to accent the essential points, with special reference to atomic and molecular radiation physics. Considerably more attention is given to the topic of disequilibrium in chemical systems (Chap.2). In particular we consider both inter- and intramolecular dynamics with special reference to energy requirements and energy disposal in chemical reactions and to what goes on in between - intramolecular energy migration. Disequilibrium in macroscopic systems and their temporal evolution is then discussed in terms of the underlying molecular events. The discussion throughout is in terms of a thermodynamiclike formulation motivated by information theoretic considerations and is illustrated by examples drawn from current studies. The principles of the design of such experiments, the experimental setups as used in practice, and the nature and interpretation of typical results are discussed in detail in Chaps.4 and 5.

Lasers and chemical change is primarily the study of the phenomena of interconversion of radiant and chemical energy. Exoergic chemical reactions can be employed to generate laser radiation and lasers can be used to induce

and to interrogate chemical reactions. The first chapter is an introduction of these two broad classes of phenomena (which are then treated in more detail in Chaps.4 and 5). It also serves to motivate the need for the theoretical concepts introduced in Chaps.2 and 3. The first chapter is self-contained, but many details are glossed over. The basic phenomena and the essential interpretation can however be found there.

Large sections of Chaps.4 and 5 are devoted to case studies. Attention is given to the experimental arrangements with special reference to the more commonly used techniques. Chapters 4 and 5 describe the practice of chemical lasers and laser-induced chemistry, including the blending of experimental studies and theoretical interpretation.

The material in Chap.1 is suitable for inclusion in advanced undergraduate physical chemistry courses. The other chapters are for the graduate level. It is however our intention and hope that they will also prove useful to the specialist. The selection of topics and their relative emphasis reflect not only our judgment but also our expertise and research interests, the overall progress in the field, and the availability of other sources. In particular, laser-induced processes in condensed phases (solutions, matrices, mixed crystals) and in biological systems are not covered. We have not tried to be exhaustive and the list of references is by no means complete and is only meant to offer an access to the literature. We have tried to offer an integrated picture, to emphasize chemical reactions and chemical lasers, to draw attention to the complexities and the promises associated with the use of larger molecules, and to stress the theme of disequilibrium on both the microscopic and macroscopic levels.

The rapid progress in this field has been made possible by the elegant and probing experiments and the incisive interpretation carried out by many of our colleagues. Inspection of the contents of this volume demonstrates the magnitude of our debt to them. Our own work has been supported by the U.S. Air Force Office of Scientific Research, the U.S.-Israel Binational Science Foundation, the Israel Academy of Sciences and Humanities, the "Bundesministerium für Forschung und Technologie", and the "Max Planck Gesellschaft zur Förderung der Wissenschaften e.V.". We also wish to thank Dr. M.J. Berry for his involvement during the initial stages of this project and Dr. H.K.V. Lotsch of Springer-Verlag for his constant advice and for not giving up hope. Last but not least, we are very grateful to our families for their continuous encouragement and support.

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