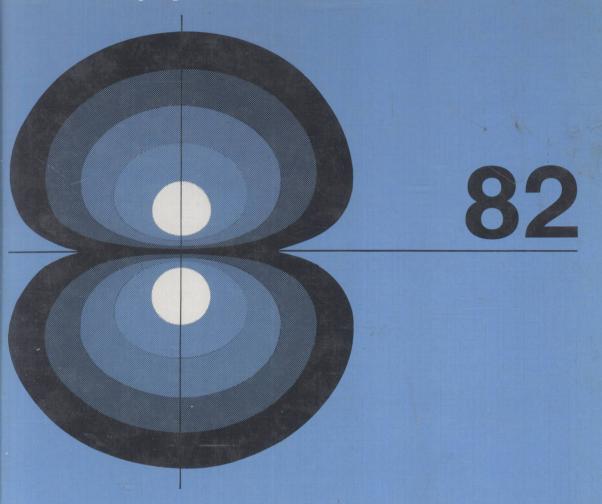
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# DYNAMICS OF EXCITED MOLECULES

Edited by

#### **KOZO KUCHITSU**

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#### PREFACE

This book has emerged from a joint research project, "Dynamics of Excited Molecules", undertaken by about 50 molecular scientists in various institutions in Japan. This project was organized under the sponsorship of the Ministry of Education, Science and Culture of Japan in the category called "Grants-in-Aid for Scientific Research on Priority Areas", in the period of April 1987 – March 1990, with one extra year for completion of publication.

The principal aims of our activities under this project were as follows:

- 1. To produce and identify new chemical species in vibronically (or vibrationally) excited states and to obtain accurate and detailed information on their fundamental properties such as their geometric and electronic structures and their potential energy surfaces.
- 2. To understand the dynamical processes of excited chemical species such as intramolecular and intermolecular energy transfer, dissociation, ionization, and chemical reactions.
- 3. To open new fields of research which utilize the dynamical properties of excited species.
- 4. To develop new experimental and theoretical methods to explore the frontiers of this field of research.

This project resulted in a large number of original papers. The organizing committee of this project, composed of Professors Eizi Hirota, Mitsuo Ito, Soji Tsuchiya and myself, started planning, as one of the essential activities of this project, publication of an integrated collection of reviews to be complementary to publication of original papers. We aimed at an overall review of this exciting field of molecular science by careful selection of key subjects and suitable authors from the members of our joint project. We asked them to highlight the important problems in their fields, based on their own achievements made in relation to this joint project, and to set the stage for future research. We hope that this volume will be useful to many scientists and engineers throughout the world.

I am grateful to Elsevier Science B.V. for their kind editorial advice and assistance and to Drs. Y. Ozaki and K. Horiai, Josai University, Mr. A. Hayashida, Mr. J. Kobayashi and Mrs. K. Adachi, Nagaoka University of Technology, for their technical help in the preparation of the camera-ready manuscripts.

Kozo Kuchitsu

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### Chapter 1

# Dynamics of Excited Molecules. An Introduction

Kozo Kuchitsu and Soji Tsuchiya

#### 1. Introduction

This volume contains a number of review articles on the dynamics of molecules in excited electronic and vibrational states, investigated mainly by spectroscopic experiments. One of the highlights of these articles is to present the recent development of various spectroscopic techniques and their applications to studies of the structures and dynamics of molecular species in the gas phase, condensed phases, and intermediate phases such as intermolecular complexes and atomic or molecular clusters. The target chemical species range from diatomics to relatively complicated aromatics, many of them being nonrigid or short—lived molecules, radicals, and positive or negative molecular ions. In many instances the states in question are vibrationally highly excited, predissociative, or autoionizing. The physical and chemical properties of many of these chemical species, particularly their excited states, and sometimes even the species themselves had been postulated or predicted for decades, but their exact details had remained essentially unexplored.

The advances in modern techniques of chemical physics, particularly laser spectroscopy and quantum—theoretical calculations, have provided accurate and detailed information on the structure and dynamic behavior of excited molecules and their roles in intermolecular interactions and chemical reactions. Extensive studies are being made to give direct answers to the following crucial problems of reaction dynamics:

- 1. How does a reactant molecule acquire the activation energy?
- 2. How is this activation energy distributed among the various degrees of freedom of the activated molecule?
- 3. What is the structure of the activated molecule, and how does it change as it passes across the transition state?
- 4. How does the rate of reaction depend on the quantum states of the reactant?