Preface

The world we live in is filled with molecules. Starting with oxygen and nitrogen in the atmosphere, water, carbon dioxide, and ammonia are all molecules. Furthermore, plants and animals are all composed of molecules. In the field of chemistry, which is regarded as science for molecules, it has been one of the most important and long-lasting fundamental issues to know the geometrical structure of a variety of molecular species around us.

Roughly speaking, there are two major methods to investigate the geometrical structure of molecules in the gas phase. One is molecular spectroscopy and the other is gas electron diffraction. In molecular spectroscopy, molecules are irradiated with light or electric waves, and a diagram called a spectrum is measured. In the diagram, rich information regarding the dynamics of electrons within a molecule, the vibrational motion of nuclei within a molecule, and the overall rotational motion of a molecule are encoded. Specifically, from the spectrum related with the rotational motion of molecules, we can derive information which is directly connected to the geometrical structure of molecules.

Therefore, it can be described that the most central issue in the field of molecular spectroscopy is to know how we can extract information concerning molecular motion from an observed spectrum. If we regard a spectrum as a secret code, the issue is nothing but decoding the code and developing the methodology on the decoding procedure. In order to decode the spectrum and to derive information of molecules properly, we need to realize that molecules are described by quantum mechanics.

In the present textbook, we learn that the motion of electrons in a molecule, molecular vibration, and molecular rotation are all "quantized" and that the consequence of the quantization appears vividly in the spectrum. Furthermore, we understand how we can determine the geometrical structure of molecules, and simultaneously we appreciate the fundamentals of quantum mechanics of molecules.

On the other hand, in the gas electron diffraction experiment, we irradiate molecules with an electron beam which is accelerated to a very high speed. Though the electron beam is a beam of electrons, each of which is a particle, it has the character of waves. Consequently, the beam is scattered by more than one nuclei within a molecule, and the scattering waves interfere with each other. This means that the information about the distances among the nuclei is recorded in an observed interference pattern. In the present textbook, we understand the fundamental mechanism of the scattering of electrons by a molecule on the basis of quantum mechanics, and in addition, we learn how the geometrical structure of molecules is determined from such an electron diffraction image.

By reading this textbook, readers can understand that the two most direct procedures to determine the geometrical structure of molecules are an analysis of a rotational spectrum and that of a gas electron diffraction image, and that the information obtained from a vibrational spectrum is a prerequisite for their analyses. And the readers can find an answer to the fundamental question, "What does the determination of the geometrical structure of molecules really mean?" through the understanding of the difference in the physical meaning of the molecular structure determined by molecular spectroscopy and that of the molecular structure determined by gas electron diffraction. When the readers study quantum mechanics, a variety of examples related with molecules introduced in the present textbook should be certainly helpful to appreciate the value of quantum mechanics.

I would like to note here that the kind cooperation I received from many people enabled me to write this textbook. First of all, I would like to thank Prof. Tadamasa Shida (Kanagawa Institute of Technology) and Prof. Koji Kaya (Institute for Molecular Science, Emeritus Professor of Keio University) for giving me the opportunity to write this textbook and for the helpful advice they offered regarding its contents.

Prof. Toshihiro Ogawa (Japan Aerospace Exploration Agency, Emeritus Professor of the University of Tokyo) and Prof. Yutaka Kondo (The University of Tokyo) kindly pointed me to some important references and documents on an infrared emission spectrum of the Earth that had been recorded by a satellite, which is referred to in Chap. 1. Prof. Ogawa's guidance was invaluable as I wrote on the absorption of infrared light by molecules in the atmosphere, and he gave me his kind permission to print the unpublished spectra, shown as Figs. 1.5 and 1.7 in Chap. 1.

Valuable comments and kind guidance were also given to me by Prof. Yasuki Endo (The University of Tokyo) and Prof. Satoshi Yamamoto (The University of Tokyo) on the references on the spectra of interstellar molecules, by Prof. Kazuo Tachibana (The University of Tokyo) on the photoabsorption of organic molecules, by Prof. Haruki Niwa (University of Electro-Communications) on bioluminescence, and by Dr. Tadaaki Tani (Fujifilm Co.) on photosencitizing dyes used in color photograph films. My thanks also go to Prof. Noriaki Kaifu (National Astronomical Observatory of Japan), who gave me kind permission to include his spectra of interstellar molecules. Prof. Kozo Kuchitsu (Josai University, Emeritus Professor of the University of Tokyo) also gave me his kind permission to use his electron diffraction photographs, and offered some valuable comments on the contents of Chap. 1. I would like to mention here that some of the materials dealt with in this textbook are based on my research results obtained when I was a graduate student in Prof. Kuchitsu's research group, and those obtained when I was a staff member of the research group of Prof. Soji Tsuchiya (now Waseda University, Emeritus Professor of the University of Tokyo).

I am indebted to the members of my research group, Ms. Kyoko Doi, Mr. Motoyuki Watanabe, Mr. Taiki Asano, Mr. Tomoya Okino, Ms. Aya Kaijiri, and Ms.

Misato Yarumura, who have kindly read through my drafts a number of times to help ensure the readability of the text while keeping its scientific rigorousness. Dr. Akiyoshi Hishikawa, Dr. Kennosuke Hoshina, and Dr. Ryuji Itakura have given me their valuable comments on the scientific content throughout the book. Mr. Takashi Amano also gave me some valuable comments on the discussions in Chaps. 2 and 3, and Ms. Keiko Kato on the topic of Chap. 4. I am also indebted to Dr. Kennosuke Hoshina for carefully checking over the numerical calculations in the text and for helping me with the illustrations of gas electron diffraction, and to Mr. Tokuei Sako and Mr. Takashi Amano for their help on the figures explaining vibrational wave functions in Chap. 2.

As my thanks go out to all of these people whose cooperation and support have been invaluable to me as I wrote this book, I would like to also express my sincere gratitude to the members of the editorial department of Iwanami Publishing Co. for their heartfelt efforts and valuable support in editing this book.

Last but not least, I would like to thank my mother, Kiyoko Yamanouchi, who passed away at the end of last year, for her presence and the comments she gave me after reading through a part of the text.

I am dedicating this volume to my wife Yuko, whose constant moral support and understanding have been indispensable as I kept on writing on weekends and holidays, and to my two daughters, Aki and Nao, who I hope may grow up to read this textbook in the future and give me their impressions and comments.

Tokyo, Japan Kaoru Yamanouchi
August 2001

Preface to the English Edition

It surprises me to note that it has now been ten years since I first published this textbook. To my gratitude, it was welcomed by university professors and researchers in Japan not only in the field of physical chemistry but also in physics, as a concise textbook that teaches students fundamental ideas of quantum mechanics through discussions of how geometrical structures of molecules are determined. I have since been using this textbook in my lecture course entitled Quantum Chemistry I at the University of Tokyo, for undergraduate science course students in the second semester of their second year.

Readers can learn about "a particle in a box" in Chap. 1, "harmonic oscillators" in Chap. 2, "angular momenta" in Chap. 3, and "the scattering theory and Schrödinger's equation for radial motion" in Chap. 4. Topics such as electronic transitions in dye molecules, molecular vibration, molecular rotation, and electron scattering by molecule will make it easy to grasp how useful it is to learn quantum mechanics. Reading this textbook, students may realize that quantum mechanics is indispensable in explaining a variety of phenomena occurring around us in our daily life.

Because of this feature, I have decided to call the English edition of this textbook "Quantum Mechanics of Molecular Structures," instead of "Determination of Molecular Structure," which would be a direct translation of the original title in Japanese.

I started my career as a scientist by studying microwave molecular spectroscopy and gas electron diffraction. Even now, I can very clearly remember how much it excited me to know how precisely I could determine the internuclear distances and bond angles of molecules by applying these two methods. Later, I started exploring more dynamical aspects of molecules, such as chemical bond breaking and rearrangement processes induced by light. In recent years, my major concerns have been responses of atoms and molecules to intense laser fields,[1] and my discussions

[1] See, for example, "K. Yamanouchi et al. eds., Progress in Ultrafast Intense Laser Science I–VIII, (2006)–(2011)" and "K. Yamanouchi ed., Lectures in Ultrafast Intense Laser Science I (2011)," in Springer's Series in Chemical Physics.

with colleagues involve how to investigate ultrafast atomic and molecular processes in the femtosecond and attosecond[2] time domains.

These topics may be seen as more advanced than those previously investigated in the field of structural chemistry, where microwave molecular spectroscopy and gas electron diffraction were used. Nevertheless, I am reminded of how important it is to have concrete knowledge and understanding of how molecules rotate and vibrate in the frontier research field.

Through the interactions between matter and ultrashort intense laser light, we can generate light in the wide wavelength range spanning from terahertz (THz) radiation to soft-X ray. Interestingly, we have learned that the THz radiation can be used as an ideal light source for high-resolution rotational spectroscopy through which transitions between high-J rotational levels of molecules in the gas phase can be measured with a high-resolution, as an extension of microwave molecular spectroscopy to a higher frequency domain. We have also recently investigated electron scattering processes in the presence of an ultrashort light field, which is called laser-assisted electron scattering, and found that it can be used as an ultrashort camera shutter for probing dynamical motions of molecules by gas electron diffraction. Thus, we can see that the classical and established research fields of molecular spectroscopy and gas electron diffraction are now being revisited and are pushing forward the frontiers of research.

I hope that this English edition of my textbook will be used worldwide in teaching undergraduate courses in universities, so that science course students can comprehend the quantum mechanical images of molecules around us. I also hope it will prove helpful in research scenes as a concise guidebook for molecular spectroscopy and gas electron diffraction.

I would like to thank Dr. Norio Takemoto, a former graduate student in my research group, for his help in revising some parts of the text in Chap. 2 in the Japanese edition, and Ms. Chie Sakuta for helping me edit this English edition. My thanks also go to Dr. Claus Ascheron, Physics Editor of Springer-Verlag at Heidelberg, for his kind support.

Tokyo, Japan Kaoru Yamanouchi
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[2]1 femtosecond is 10^{-15} s and 1 attosecond is 10^{-18} second.

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