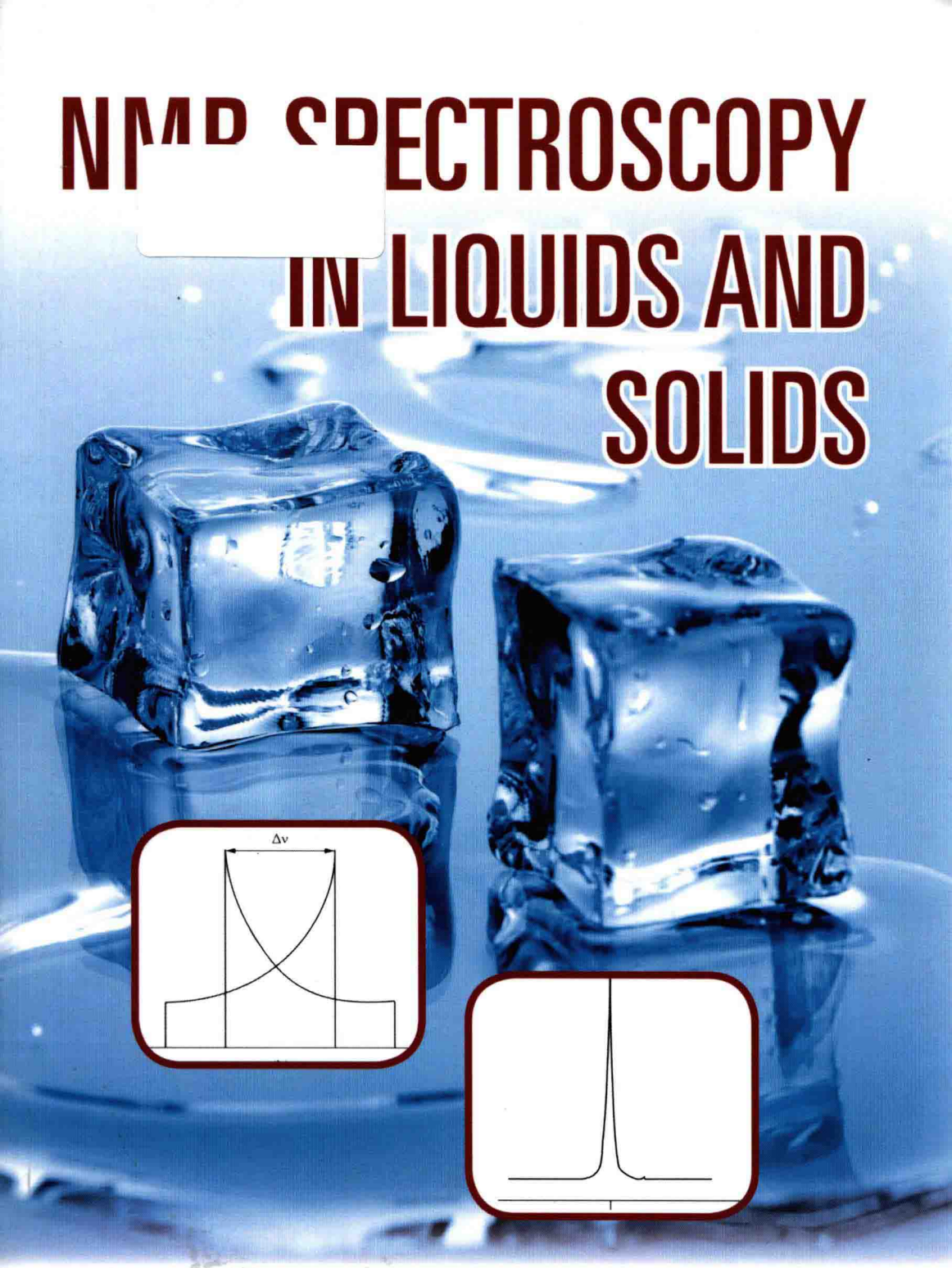
NMR SPECTROSCOPY IN LIQUIDS AND SOLIDS



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Preface

This book is intended for those who are just beginning research activity in chemistry, biochemistry, geochemistry, chemical engineering, or other science and wish to use NMR as the main research method for investigating solutions and the solid state. This text is not a reference book with a great number of tables and NMR data that can be found elsewhere in the literature; however, it does cover basic NMR concepts that must be understood to perform NMR experiments on liquid and solid samples and to interpret the data collected to determine structures and molecular dynamics. The book has been written by an expert who began his research career using iron permanent electromagnets and continuous-wave irradiation, later moving on to superconducting electromagnets with pulsing NMR. Many NMR experiments mentioned in this text have been taken from the author's own experience, including studies of inorganic and organic molecules in solutions and molecular aggregates and materials in the solid state.

What is new and different in this book?

1. Presents current understanding and applications of solution and solid-state NMR techniques
2. Combines and formulates common principles for NMR experiments in gases, liquids, and solids
3. Pays considerable attention to nuclear relaxation, from the phenomenon itself to applications in solutions and solids
4. Formulates general strategies for studies and demonstrates how to choose the appropriate experiment, what methods and pulse sequences are suitable for particular situations, and how to assign signals in the NMR spectra of simple and complex molecular systems

The book is organized into ten chapters that include numerous illustrations and recommended literature. Chapters 1 to 4 cover the basic principles, and Chapters 5 to 10 describe NMR applications. These chapters have been written in such a way that they can be presented as ten lectures for NMR spectroscopy courses aimed at undergraduate and postgraduate students or young researchers at colleges and universities. Only minimal knowledge of physics and quantum mechanics is assumed.

Introduction

Nuclear magnetic resonance (NMR) is a powerful instrumental method that rapidly and adequately handles a large number of scientific and applied tasks on both the molecular and atomic levels. Because a NMR signal can be detected in gases, solutions, liquids, and solids, including crystals and amorphous homogeneous or heterogeneous systems, this method can be successfully applied in physics, chemistry, food chemistry, biochemistry, geochemistry, biology, geology, archeology, pharmaceuticals, and materials science fields. Moreover, an interesting version of NMR, magnetic resonance imaging (MRI), has become a reliable diagnostic tool in both human and veterinary science and medicine, particularly for research into the brain. MRI is also applicable to the study of materials chemistry.

The modern arsenal of NMR methods and techniques is extremely large. Due to the increasing complexity of objects involved in NMR studies, this arsenal is constantly growing and being modified. Over its 70-year history, NMR research has stimulated the development of new scientific fields. Successes in radiofrequency technology from 1952 to 1953 led to the appearance of the first commercial NMR spectrometers, which strongly impacted research in chemistry, biochemistry, and biology. In turn, the synthesis and study of complex objects, such as biochemical molecular systems and complex inorganic/organic molecular aggregates, required the availability of more powerful NMR instrumentation offering better spectral resolution and sensitivity. Such improvements would have been impossible in the absence of innovations in magnet technology that created stronger and stronger homogeneous magnetic fields. In addition, the development of computers capable of very fast Fourier transform (FFT) processing has resulted in the routine use of two-, three-, or four-dimensional NMR spectroscopy for structural analyses in solutions and solids to assign signals in the NMR spectra of complex molecular systems.

Due to the impressive development of NMR techniques, NMR applications are expanding from molecular and low-temperature physics to archeology, where, for example, the natural destruction of wood is the focus of researchers. In spite of such developments, it is obvious that without a deep understanding of NMR and nuclear relaxation their successful application cannot be guaranteed. Moreover, such an understanding cannot be gained by any computer search (such as Google, for example), a popular approach among students and young researchers. Searches such as these can provide only fragmented knowledge.

With regard to the history of NMR,[1] after the first successful observation of NMR signals in gases occurred in 1937, C.J. Gorter attempted to detect resonances in the condensed phase in order to detect lithium nuclei in crystalline LiF and protons in crystalline potassium alum. Similar experiments had been performed on ^{19}F nuclei in the crystal solid KF but no NMR signals were found. Today, it is known that the nuclei were invisible due to the exclusively long relaxation times in the very

pure crystals. Relaxation times are still an issue for NMR beginners, as the behavior of nuclei in NMR experiments is time dependent, and their relaxation times strongly affect the NMR data obtained.

In contrast, due to the relatively short relaxation times of protons in paraffin wax and water, researchers Purcell and Bloch reported the first NMR signals in the condensed phase in 1945. These experiments led to the application of NMR as an analytical method. Later, Blombergen, Purcell, and Pound[2] formulated the theory of nuclear relaxation now referred to as the BPP theory. It should be noted that the BPP theory is valid for all states of matter—solids, liquids, or gases—where the dipole–dipole internuclear interactions govern nuclear relaxation via molecular motions. Extremely low-temperature relaxation measurements performed in solid H_2 at a temperature of 1 K have emphasized the importance of such motions in the dipole–dipole relaxation process. It should be noted that further reconsiderations of nuclear relaxation processes have led to only small additions to the relaxation theory first published in 1948.

The rate and the character of molecular motions strongly change upon going from liquids to solids. This factor affects the experimental conditions required for the detection of NMR signals. Ice demonstrates the principal differences in NMR experiments on liquids and solids. The line width of the ^1H resonance in liquid water is very small (<1 Hz), whereas the resonance of solid water broadens up to ~10^5 Hz due to strong dipolar proton–proton coupling against a background of very slow molecular motions. It is obvious that different technical solutions are needed to detect NMR signals in solids.

Despite the first early successes in understanding the relaxation behavior of nuclei in liquids and solids, the relaxation mechanism in crystal solids, such as CaF_2, remained unclear. In 1949, Bloembergen[3] reported on the nature of ^{19}F relaxation, termed *spin diffusion*. This relaxation occurs via energy diffusion from nuclear spins to paramagnetic centers present in the crystal as impurities, and it can be effective for the strong dipolar coupling ^{19}F–^{19}F.

The early classical work mentioned above and the later discovery of chemical shifts and spin–spin coupling illustrate important features of NMR: The NMR spectra recorded in liquids and solids show a number of distinguished nuclei in structurally different molecules and/or groups and even their mutual dispositions, whereas nuclear relaxation opens the way to describing molecular dynamics ranging from isotropic or anisotropic reorientations in liquids to phase transitions in rigid solids. These unique features make NMR a powerful analytical method.

The diverse NMR experiments on liquids or solids can be represented by the general scheme shown in Figure I.1. Here, each step, from the preparation of samples to interpretations and conclusions, is equally important. Actions taken at each step can result in errors, experimental or interpretational, because modern NMR spectrometers are complex multiple-pulse devices that operate with low or very high magnetic fields, up to 21.14 T. The modern tendency is to aim for full automation in the performance of experiments, including sample changes and even interpretation of the spectra. It should be noted that such automation exemplifies a black-box approach that can be successful for the routine analysis of reaction mixtures or large series of similar compounds. However, such an approach is quite ineffective in a research laboratory, where precise determination of new structures is an important part of studies. In

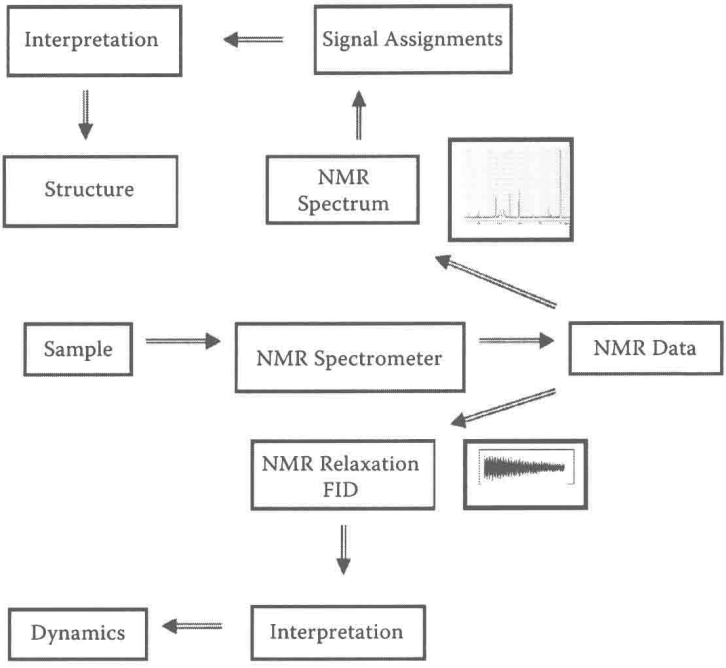

FIGURE I.1 General scheme of NMR experiments performed on solutions and solids to probe their structure and dynamics.

addition, artifact phenomena can appear in NMR experiments, further complicating their interpretation. Their recognition again requires at least minimal understanding of the physical aspects of NMR. Finally, it should be emphasized that NMR experiments resulting in NMR spectra or time-dependent data are revealing only the behavior of nuclear spins and their ensembles in the magnetic field, not groups of atoms and molecules or more complex aggregates. Understanding their nature is a product of our interpretations based on experience and numerous spectral structural relationships.

This book is compressed to ten chapters to minimize its volume. The first three chapters consider the theoretical basis of NMR spectroscopy, the theory of NMR relaxation, and the practice of relaxation measurements. Chapter 4 discusses the general aspects of molecular dynamics and their relationships with NMR. NMR spectroscopy and relaxation studies in solutions are addressed in Chapters 5 and 6, and Chapter 7 considers special issues of NMR in solutions. Chapter 8 leads into the solid-state portion of the book by introducing the general principles and strategies involved in solid-state NMR studies and provides examples of applications of relaxation for the determination of molecular dynamics in diamagnetic solids. Chapter 10 concludes with a discussion on special issues of solid-state NMR, including NMR and NMR relaxation in paramagnetic solids, an area requiring additional knowledge. Finally, the chapters are accompanied by references and recommended literature for further reading.

The book is addressed to undergraduate students, NMR beginners, and young scientists who are planning to work or are already working in the various fields of chemistry, biochemistry, biology, pharmaceutical sciences, and materials science. It provides an introduction to the general concepts of NMR and the principles of its applications, including how to perform adequate NMR experiments and how to interpret the NMR data collected in liquids and solids to characterize molecule systems in terms of their structure and dynamics.

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Author

Vladimir I. Bakhmutov, PhD, works in the Department of Chemistry at Texas A&M University. The 330 scientific articles and 5 books that he has written and published document his outstanding contributions to chemical physics research. Dr. Bakhmutov's research interests include extensive applications of solution and solid-state NMR techniques for chemistry, molecular physics, and materials science. NMR relaxation in liquids and solids applied for structural and dynamic studies is also an area of interest. Dr. Bakhmutov has been granted visiting professorships by Zurich University, Switzerland; Bourgogne University, Dijon, France; Rennes University, France; CINVESTAV, Mexico; and Iberdrola, Zaragosa, Spain.

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