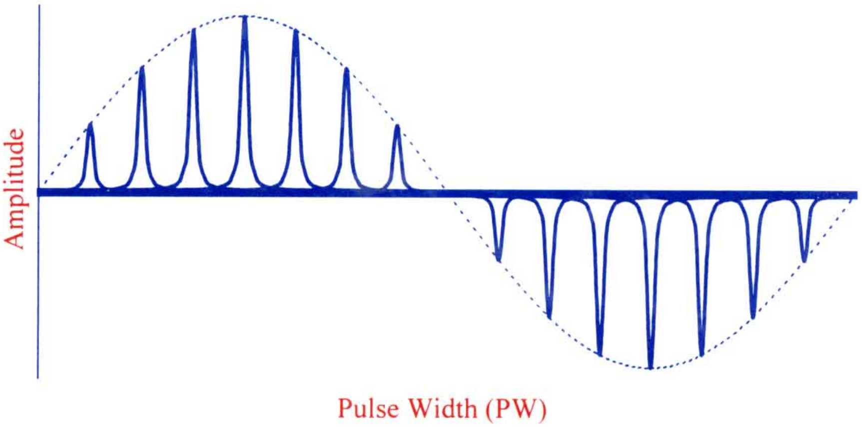
PRACTICAL SPECTROSCOPY SERIES VOLUME 21



NMR Spectroscopy Techniques

Second Edition, Revised and Expanded

edited by
Martha D. Bruch

NMR Spectroscopy Techniques

Second Edition, Revised and Expanded

Edited by
Martha D. Bruc
University of Delawar
Newark, Delawar

Marcel Dekker, Inc. New York • Basel • Hong Kong

NMR spectroscopy techniques / edited by Martha D. Bruch—2nd ed.
rev. and expanded.
p. cm. —(Practical spectroscopy; 21)
Includes index.
ISBN 0-8247-9450-8 (hardcover: alk. paper)
1. Nuclear magnetic resonance spectroscopy. I. Bruch, Martha D.
II. Series.
QD96.N8N593 1996
543'.0877—dc20 95-52707
CIP

The publisher offers discounts on this book when ordered in bulk quantities. For more information, write to Special Sales/Professional Marketing at the address below.

This book is printed on acid-free paper.

Marcel Dekker, Inc.
270 Madison Avenue, New York, New York 10016

Current printing (last digit):
10 9 8 7 6 5 4 3 2 1

PRINTED IN THE UNITED STATES OF AMERICA

NMR Spectroscopy Techniques

PRACTICAL SPECTROSCOPY

A SERIES

Edited by Edward G. Brame, Jr.

The CECON Group
Wilmington, Delaware

1. Infrared and Raman Spectroscopy (in three parts), *edited by Edward G. Brame, Jr., and Jeanette G. Grasselli*
2. X-Ray Spectrometry, *edited by H. K. Herglotz and L. S. Birks*
3. Mass Spectrometry (in two parts), *edited by Charles Merritt, Jr., and Charles N. McEwen*
4. Infrared and Raman Spectroscopy of Polymers, *H. W. Siesler and K. Holland-Moritz*
5. NMR Spectroscopy Techniques, *edited by Cecil Dybowski and Robert L. Lichter*
6. Infrared Microspectroscopy: Theory and Applications, *edited by Robert G. Messerschmidt and Matthew A. Harthcock*
7. Flow Injection Atomic Spectroscopy, *edited by Jose Luis Burguera*
8. Mass Spectrometry of Biological Materials, *edited by Charles N. McEwen and Barbara S. Larsen*
9. Field Desorption Mass Spectrometry, *László Prókai*
10. Chromatography/Fourier Transform Infrared Spectroscopy and Its Applications, *Robert White*
11. Modern NMR Techniques and Their Application in Chemistry, *edited by Alexander I. Popov and Klaas Hallenga*
12. Luminescence Techniques in Chemical and Biochemical Analysis, *edited by Willy R. G. Baeyens, Denis De Keukeleire, and Katherine Korkidis*
13. Handbook of Near-Infrared Analysis, *edited by Donald A. Burns and Emil W. Ciurczak*
14. Handbook of X-Ray Spectrometry: Methods and Techniques, *edited by René E. Van Grieken and Andrzej A. Markowicz*
15. Internal Reflection Spectroscopy: Theory and Applications, *edited by Francis M. Mirabella, Jr.*
16. Microscopic and Spectroscopic Imaging of the Chemical State, *edited by Michael D. Morris*
17. Mathematical Analysis of Spectral Orthogonality, *John H. Kalivas and Patrick M. Lang*

18. Laser Spectroscopy: Techniques and Applications, *E. Roland Menzel*
19. Practical Guide to Infrared Microspectroscopy, *edited by Howard J. Humecki*
20. Quantitative X-ray Spectrometry: Second Edition, *Ron Jenkins, R. W. Gould, and Dale Gedcke*
21. NMR Spectroscopy Techniques: Second Edition, Revised and Expanded, *edited by Martha D. Bruch*
22. Spectrophotometric Reactions, *Irena Němcová, Ludmila Čermáková, and Jiří Gasparič*

ADDITIONAL VOLUMES IN PREPARATION

Preface

Nuclear magnetic resonance (NMR) spectroscopy has undergone an explosion in the last two decades; it is now one of the most widely used analytical tools. Furthermore, many laboratories are now equipped with sophisticated NMR instrumentation capable of performing a variety of powerful experiments in a straightforward manner. However, much of the power afforded by these capabilities is often not exploited because the average user does not have the knowledge required to perform these experiments. In addition, there is a common misconception that *all* analytical problems can be solved by NMR. The purpose of this book is to provide an overview of the strengths and weaknesses of various NMR techniques so that researchers can make informed decisions regarding which, if any, NMR experiments should be performed to address the problem at hand.

The contributors were chosen because of their expertise in various areas of NMR spectroscopy. The goal is to provide practical, not theoretical, information regarding the performance and interpretation of NMR experiments.

Not every NMR technique is discussed; the chapters are intended to cover the most commonly used NMR methods. The references provide experimental details for each method.

This book should be suitable for anyone with some knowledge of NMR who wishes to learn more about a given technique. It is ideal for a graduate student or technician who wishes to gain insights into the practical aspects of NMR spectroscopy techniques. However, it is also suitable for experienced researchers who want to learn about NMR techniques with which they have no prior experience.

Martha D. Bruch

Contributors

Navin Bansal, Ph.D. Department of Radiology and Graduate Program in Biomedical Engineering, University of Texas Southwestern Medical Center at Dallas, Dallas, Texas

Anita J. Brandolini, Ph.D. Edison Research Laboratory, Mobil Chemical Company, Edison, New Jersey

Martha D. Bruch, Ph.D. Department of Chemistry and Biochemistry, University of Delaware, Newark, Delaware

Cecil Dybowski, Ph.D. Department of Chemistry and Biochemistry, University of Delaware, Newark, Delaware

Lynn W. Jelinski, Ph.D. Center for Advanced Technology—Biotechnology, Cornell University, Ithaca, New York

Cynthia K. McClure, Ph.D. Department of Chemistry and Biochemistry, Montana State University, Bozeman, Montana

Michael T. Melchior, Ph.D. Research and Engineering Department, Corporate Research Laboratories, Exxon, Clinton Township, New Jersey

Josep Rizo, Ph.D. Department of Pharmacology, University of Texas Southwestern Medical Center at Dallas, Dallas, Texas

Viswanathan Seshan, B. Tech. Graduate Program in Biomedical Engineering, University of Texas Southwestern Medical Center at Dallas, Dallas, Texas

Daniel D. Traficante, Ph.D. NMR Concepts and Department of Chemistry, University of Rhode Island, Kingston, Rhode Island

Roderick E. Wasylishen, Ph.D. Department of Chemistry, Dalhousie University, Halifax, Nova Scotia, Canada

NMR Spectroscopy Techniques

Contents

1

NMR Concepts

Daniel D. Traficante

University of Rhode Island
Kingston, Rhode Island

Nuclear magnetic resonance (NMR) rapidly became one of the most powerful analytical techniques, used in many different fields of chemistry. Not only has its importance been demonstrated in chemistry and physics, but the usefulness of NMR imaging has rapidly spread throughout the world of medicine. This chapter attempts to lay the foundation of NMR concepts, with the intention of providing a background sufficient for understanding the underlying principles embodied in the subsequent chapters of this volume.

1.1 NUCLEAR MAGNETIC MOMENTS AND THEIR PROPERTIES

1.1.1 Spin Quantum Number, Nuclear Angular Momentum, and Magnetic Quantum Number

Quantum mechanics predicts that the *maximum observable component* ($\rho_{\max}$) of the *nuclear angular momentum* (ρ_0) can have values that are only an integer number of half-multiples of modified Plank's constant $\hbar$, where $\hbar$ equals $h/(2\pi)$.

Table 1.1 Nuclear Spins Associated with Even or Odd Mass and Atomic Numbers

Mass number	Atomic number	Nuclear spin (I)
Odd	Even or odd	$\frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \ldots$
Even	Even	0
Even	Odd	1,2,3, . . .

$$\rho_{\mathbf{max}} = n \cdot \frac{1}{2} \cdot \hbar, \quad n = 0, 1, 2, 3 \ldots \tag{1a}$$

$$\rho_{\max} = I\hbar \tag{1b}$$

Equation (1b) is obtained from Eq. (1a) by letting $I = n \cdot \frac{1}{2}$, where I is called the *spin quantum number*. Only some nuclei possess the property of spin. Table 1.1 shows that a nucleus does not have spin if its mass number and atomic number are both even.

Because $\rho_{\max}$ in Eq. (1a) represents the *maximum* component of the angular momentum, I in Eq. (1b) represents the *maximum* value of the component of spin. However, *it is found that in a collection of like nuclei there are* $2I + 1$ distinct states in which the components have values equal to $-I$, $(-I + 1)$, $(-I + 2)$, . . . $(I - 2)$, $(I - 1)$, I. These values are called the *magnetic quantum numbers*, *m*. In other words, m is the complete set of values, but I is the maximum value in the set: $I = m_{\max}$. Then, analogous to Eq. (1b), the observable components of ρ are

$$\rho_i = m_i\hbar \tag{2}$$

which are shown in Table 1.2. In this table, the maximum component is $I\hbar$ because I is the maximum component of the spin.

Table 1.2 Values of the Components of the Angular Momentum (ρ) and Magnetic Quantum Numbers (m) in Terms of the Spin Quantum Number (I)

I (Must be in integral values of $\frac{1}{2}$)	$2I + 1$ (Total number of states)	Components of ρ (These must remain between the maximum values $-I$ and I)	m (Magnetic quantum numbers)
$\frac{1}{2}$	2	$-I, I$	$-\frac{1}{2}, \frac{1}{2}$
1	3	$-I, 0, I$	$-1, 0, 1$
$\frac{3}{2}$	4	$-I, -(I-1), (I-1), I$	$-\frac{3}{2}, -\frac{1}{2}, \frac{1}{2}, \frac{3}{2}$
2	5	$-I, -(I-1), 0, (I-1), I$	$-2, -1, 0, 1, 2$

1.1.2 Nuclear Magnetic Moment

Many descriptions of the nuclear magnetic moment (μ) begin by depicting the nucleus as a tiny, positively charged sphere spinning around its axis. Then, according to the familiar rules of electrodynamics in classical physics, the moving electric field creates a magnetic field—the nuclear magnetic moment. The nucleus is imagined to be a tiny magnet with north and south poles. According to classical physics, the angular momentum L of a sphere with radius R, mass m, and spinning with angular velocity ω is

$$L = \frac{2}{5} R^2 m\omega \tag{3}$$

However, the electron has a spin of $\frac{1}{2}$, but all experimental evidence to date indicates that an electron is a point particle with no spatial extent, i.e., $R = 0$. According to the above description, then, an electron should not have an angular momentum nor a magnetic moment, and EPR experiments should not be possible. Furthermore, $m = 0$ for a photon, but its spin is 1. A neutron has no net change (hence, no moving electric field), yet it has a magnetic moment! For an excellent and very readable historical account of the development of the concept of spin, see Ref. 1.

Once nuclear angular momentum has been successfully defined, we may proceed to the concept of a nuclear magnetic moment. All experimental evidence concerning the magnetic properties of nuclei is consistent with the hypothesis that the magnetic moment μ is proportional to and parallel to the angular momentum vector ρ. Hence, we may now define a *maximum* observable *component* of the magnetic moment ($\mu_{\max}$) in terms of $\rho_{\max}$.

$$\mu_{\max} \propto \rho_{\max} \tag{4}$$

$$\mu_{\max} = \gamma\rho_{\max} \tag{5}$$

In Eq. (5), γ is the constant of proportionality and is called the *magnetogyric ratio* because it equals μ (magneto) divided by ρ (gyric). It is sometimes, less appropriately, called the *gyromagnetic ratio.* From Eq. (5) we may now write

$$\mu_i = \gamma\rho_i \tag{6}$$

and, from Eq. (2),

$$\mu_i = \gamma m_i \hbar \tag{7}$$

Similarly, Eqs. (1b) and (5) can be combined to give

$$\mu_{\max} = \gamma I \hbar \tag{8}$$

Dividing Eq. (7) by Eq. (8) yields

$$\mu_i = \frac{m_i \mu_{\max}}{I} \tag{9}$$

In most books and articles, $\rho_{\max}$, $\mu_{\max}$, μ_i, and m_i are represented simply by ρ, μ, μ_z, and m, respectively, and these symbols will be used throughout this chapter.

1.1.3 Interaction Between Two Conventional Magnets

As shown in Figure 1.1, if two magnets, A and B, are placed on a frictionless surface such that their like poles face each other, there will be a force of repulsion that pushes them apart. Conversely, if their opposite poles face each other, there will be a force of attraction that pulls them together. Figure 1.1A represents the high energy state (E_h) relative to the state in which only one magnet is present, or, when the two magnets are infinitely far apart, $E_0 = 0$. The force of repulsion that pushes the two magnets apart depends on the strengths of the two magnets H_A and H_B, and this force is represented by the energy of the higher state.

$$E_h = H_A H_B \tag{10a}$$

Figure 1.1B depicts the low energy state E_l:

$$E_l = -H_A H_B \tag{10b}$$

The difference between these two energy states ΔE is the amount of energy required to turn over magnet B in Fig. 1.1B and place it in the position shown in Figure 1.1A:

$$\Delta E = E_h - E_l = 2H_A H_B \tag{11}$$

Suppose now that a collection of small compasses (magnets B) are placed on a table in the Earth's magnetic field (magnet A). Further, suppose that the magnetic fields of the compasses (H_B) are very weak compared to the Earth's field (H_A), i.e., $H_A \gg H_B$, and that the compasses are placed far enough apart so that the magnetic field of one compass does not affect that of another. If the table is not disturbed, all of the compasses will align themselves and point toward the north pole. However, if the table is shaken, some of the compasses will receive enough energy [Eq. (11)] to turn from their low energy states and point toward the south pole. If the table is shaken only slightly, only a few of the compasses will turn over; but if shaken vigorously, many will receive enough energy to turn. Note that some of those that have turned to face the south pole will turn again to face the north pole. Finally, if the table is shaken infinitely vigorously, the number pointing to the south pole will equal the number pointing north.