Nuclear Magnetic Resonance Spectroscopy

Second Edition

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FOREWORD

In 1980 Jiri Jonas and I wrote a review article titled "NMR in Chemistry — An Evergreen." We sought to capture in the title the continued vitality and growth of NMR spectroscopy, a never dormant field. Since its inception forty years ago NMR has been a cornucopia of exciting and extremely useful phenomena, with new and ever more powerful techniques for observing them — dipolar broadening and motional narrowing, chemical shifts, J-coupling, spin echoes, superconducting solenoids and high fields, Fourier transform methods, high resolution solid state NMR, two dimensional methods, and most recently, magnetic resonance imaging.

This book captures the always refreshing spirit of NMR today. Although billed as a second edition of Bovey's 1969 offspring, it is an accurate reflection of twenty more years of NMR — twice as big and twice as good. The chapter on experimental methods now stresses Fourier transform methods and superconducting magnets. Double resonance and spectral editing techniques are found in the chapter on coupling of nuclear spins, and an entire chapter is devoted to two-dimensional NMR and another to solids. The latest views on MR imaging, water suppression, and zero-field NMR are given in a special topics finale.

Today's seminar circuit style of learning has given new currency to Samuel Johnson's 1766 statement, "People have now-a-days got a strange opinion that everything should be taught by lectures. Now, I cannot see that lectures can do so much good as reading the books from which the lectures are taken." This is one of them.

H. S. Gutowsky

PREFACE TO THE FIRST EDITION

Following the appearance in 1959 of the first, and now classical, monograph on high resolution NMR by Pople, Schneider, and Bernstein,[1] no new comprehensive work appeared in this field for many years despite the fact that it was advancing very rapidly. Beginning in 1964, this vacuum began to be filled by an increasing flow of books of varying scope and technical level, including two annual review series. At the present time, one can no longer complain that there is a serious lack of coverage of the field, at least so far as the organic chemist is concerned.

In 1965, I published in *Chemical and Engineering News* an article describing in simplified terms the basis of high resolution NMR spectroscopy and its applications. The response to this article was large and widespread, and encouraged the idea that despite the other texts then available there was still a need which might be filled by expansion of this review to a book of moderate size, written in more or less the same spirit. This volume is the result.

This work is intended for the graduate student or research worker in industry who needs a text that is pitched at a modest, relatively nonmathematical level and that can be applied in solving problems related to the structure and behavior of organic molecules. The tone is empirical throughout; the theoretical basis of the more important effects being sketched in only lightly where it seemed to be appropriate. The text is supplemented by the following appendixes: Appendix A: Table of Nuclear Properties; Appendix B: Table of τ-Values for Selected Organic Compounds in CCl_4 Solution; Appendix C: Calculated Shielding Effects Produced by Ring Currents in a Benzene Ring; Appendix D: Calculated Spectra; Appendix E: Proton Spin-Spin Coupling Constants.

A certain degree of repetition of mathematical developments given in other texts was unavoidable. For example, no worthwhile discussion of line shapes can be given without at least some consideration of the Bloch equations (Chapters I and VII), even though they are undoubtedly more authoritatively dealt with elsewhere. In Chapter IV, the discussion of the analysis of NMR spectra omits all except the most elementary quantum mechanical background, as this is amply treated in other sources. But tables of line positions and intensities are included, as these are necessary to support the text. In addition, some 300 computer-generated line spectra are given in Appendix D. These represent a fair proportion of the simpler types of "strong-coupled" spectra with which the reader may need to deal. This feature is believed to be unique in a text, although an earlier compilation was published as a book by Wiberg and Nist in 1962,[2] using a different type of pictorial display.

No effort has been made to discuss the spectral properties of classes of organic compounds in a systematic way, as, for example, in the comprehensive texts of Emsley, Feeney, and Sutcliffe[3] and Suhr.[4] Spectra are introduced only to illustrate specific points. This is in no sense a handbook or encyclopedia of data. For this purpose, the reader may wish to consult the spectral catalogue in two volumes distributed by Varian (Palo Alto, California) or my published tables.[5]

I wish to thank Mr. F. P. Hood and Mr. J. J. Ryan for running many of the spectra and assisting in the preparation of figures; Dr. W. P. Slichter and Dr. D. W. McCall for many helpful discussions; Dr. G. V. D. Tiers for permission to reproduce the data appearing in Appendix B; Dr. S. Meiboom for critically reading the entire manuscript; and the American Chemical Society for permission to reproduce figures from the *Chemical and Engineering News* article referred to above. The calculated spectra in the text and in Appendix D were produced by means of a digital computer program devised by Dr. L. C. Snyder and Mr. R. L. Kornegay of the Bell Telephone Laboratories. Grateful acknowledgment is due them for the use of the program and for many helpful discussions concerning it.

F. A. Bovey

Murray Hill, New Jersey
October, 1968

[1] J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance." McGraw-Hill, New York, 1959.

[2] K. B. Wiberg and B. J. Nist, "The Interpretation of NMR Spectra." W. A. Benjamin, New York, 1962.

[3] J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy" (2 vols.). Pergamon Press, London, 1965.

[4] H. Suhr, "Anwendungen der Kernmagnetischen Resonanz in der Organischen Chemie." Springer, Berlin, 1965.

[5] F. A. Bovey, "NMR Data Tables for Organic Compounds," Vol. 1. Wiley (Interscience), New York, 1967.

PREFACE TO THE SECOND EDITION

Professor Gutowsky vividly portrayed in the Foreword the dramatic progress that has been made in NMR since the First Edition of this book appeared in 1969. The present book is much altered and expanded compared to its predecessor. For example an entire section is devoted to Fourier transform instruments, which were in their infancy in 1969 and then only rated a page of attention. This book contains an entire chapter on two-dimensional NMR and another chapter on high resolution NMR of solids, fields that had not yet been discovered in 1969. The Special Topics chapter deals with techniques such as water suppression, multiple quantum spectroscopy, and NMR imaging, areas that have had a tremendous impact on fields as diverse as protein structure determinations, 2D NMR, and medicine.

Although the present book is much updated, it is still intended for the same audience: the graduate student or research worker who needs a discussion at an introductory level, accompanied by a substantial collection of "real" examples, including chemical shift and *J*-coupling data. As a data storehouse, however, it does not pretend to compete with the massive collections now available, many in multivolume and computer-searchable forms. Rather, it draws attention to the types of molecules that are encountered in an academic or industrial chemistry laboratory, and makes appropriate references to these extensive compilations of NMR data when necessary.

As in the First Edition, the level is purposely kept fairly non-mathematical. In this book there are no Hamiltonians and no matrices. The goal is to convey the basic fundamentals of NMR spectroscopy in a descriptive manner so that the concepts can be readily grasped and applied by the widest number of NMR users.

This edition is accompanied by a number of appendices that have proved extremely useful to graduate students and researchers over the years. These include Appendix A: Table of Nuclear Properties; Appendix B: Calculated Proton Spectra; and Appendix C: Proton Spin-Spin

Coupling Constants. However, Appendix D: Carbon-Proton and Carbon-Carbon Spin-Spin Coupling Constants, is completely new, and is indispensable for conformational analysis and structure determinations.

Throughout the book the reader will find a mix of early, low-field NMR spectra, complete with "ringing," and new high-field, Fourier transform spectra. These old spectra convey a sense of history and are useful for pedagogical purposes, whereas the high field spectra proclaim the incredible power of modern NMR methods. In either case, care has been taken to reproduce the spectra in a clear and large format. The same is true for the chemical formulas, which form an indispensable part of this volume.

It is most important to emphasize my indebtedness to my co-authors, Dr. Lynn W. Jelinski, who contributed Chapter 2 on experimental methods and Section 9.2 (of Chapter 9) on NMR Imaging; and Dr. Peter A. Mirau, who was co-author of Chapter 6 on two-dimensional NMR and of Section 9.3 (of Chapter 9) on Solvent Suppression. Dr. Mirau also obtained important data for Chapters 4 and 5, which is acknowledged in the text. There are also many references, particularly in Chapter 4, to unpublished work of Mr. Frederic Schilling, who played a most important role in the genesis of this work. Vital also were extensive discussions of NMR phenomena with all of these persons. Thanks are also due to Mary E. Flannelly and Susan A. Tarczynski, who "text-processed" the manuscript, and to Jean O'Bryan and Menju Parikh, who assembled the book in its final camera-ready form.

Frank A. Bovey
February 18, 1988

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CHAPTER 1

FUNDAMENTAL PRINCIPLES

1.1 INTRODUCTION

In addition to charge and mass, which all nuclei have, many isotopes possess spin, or angular momentum. Since a spinning charge generates a magnetic field, there is associated with this angular momentum a magnetic moment. The magnetic properties of nuclei were first postulated by Pauli[1] to explain certain hyperfine structural features of atomic spectra. The phenomenon of nuclear magnetic resonance has long been known in molecular beams and has been effectively exploited by Rabi and his co-workers[2,3] to give much useful information concerning nuclear properties. The field of organic chemistry has for the most part been developed without any reference to these properties. Only since the discovery of nuclear magnetic resonance in bulk matter, i.e., in such substances as water and paraffin wax, by Purcell *et al.*[4] at Harvard and Bloch *et al.*[5] at Stanford has this phenomenon become of interest to the chemist.

1.2 NUCLEAR SPIN

According to a basic principle of quantum mechanics, the maximum experimentally observable component of the angular momentum of a nucleus possessing a spin (or of any particle or system having angular momentum) is a half-integral or integral multiple of $h/2\pi$, where h is Planck's constant. This maximum component is I, which is called the spin quantum number or simply "the spin." Each nuclear ground state is characterized by just one value of I. If $I = 0$, the nucleus has no magnetic moment. If I is not zero, the nucleus will possess a magnetic moment μ, which is always taken as parallel to the angular momentum vector. The permitted values of the vector moment along any chosen axis are described by means of a set of magnetic quantum numbers m given by the series

$$m = I, (I-1), \ (I-2) \ldots, -I \qquad (1.1)$$

Thus, if I is 1/2, the possible magnetic quantum numbers are +1/2 and −1/2. If I is 1, m may take on the values 1, 0, −1, and so on. In general, then, there are $2I + 1$ possible orientations or states of the nucleus. In the absence of a magnetic field, these states all have the same energy. In the presence of a uniform magnetic field B_0, they correspond to states of different potential energy. For nuclei for which I is 1/2, the two possible values of m, $+1/2$ and $-1/2$, describe states in which the nuclear moment is aligned with and against the field B_0, respectively, the latter state being of higher energy. The detection of transitions of magnetic nuclei (often themselves referred to as "spins") between the states is made possible by the nuclear magnetic resonance phenomenon.

The magnitudes of nuclear magnetic moments are often specified in terms of the ratio of the magnetic moment and angular momentum, or *magnetogyric ratio* γ, defined as

$$\gamma = \frac{2\pi\mu}{Ih} \tag{1.2}$$

A spinning spherical particle with mass M and charge e uniformly spread over its surface can be shown to give rise to a magnetic moment $eh/4\pi Mc$, where c is the velocity of light. For a particle with the charge, mass, and spin of the proton, the moment should be 5.0505×10^{-27} joules/tesla (JT^{-1})* (5.0505×10^{-24} erg-gauss^{-1} in cgs units) on this model. Actually, this approximation is not a good one even for the proton, which is observed to have a magnetic moment about 2.79 times as great as the oversimplified model predicts. No simple model can predict or explain the actual magnetic moments of nuclei. However, the predicted moment for the proton serves as a useful unit for expressing nuclear moments and is known as the ***nuclear magneton***; it is the analog of the Bohr magneton for electron spin. Observed nuclear moments can be specified in terms of the nuclear magneton by

$$\mu = g\,\frac{ehI}{4\pi M_p c} \tag{1.3}$$

where M_p is the proton mass and g is an empirical parameter called the nuclear g factor. In units of nuclear magnetons, then

$$\mu = gI \tag{1.4}$$

In Table 1.1 and in Appendix A, nuclear moments are expressed in these units. It will be noted that some nuclei have negative moments. This is of

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* Magnetic field strengths are expressed in kgauss or tesla T; 10 kgauss = 1T.

TABLE 1.1

Nuclei of Major Interest to NMR Spectroscopists

Isotope	Abundance (%)	Z	Spin	μ[a]	$\gamma \times 10^{-8}$[b]	Relative[c] sensitivity	ν_0 at 1T (MHz)
^{1}H	99.9844	1	1/2	2.7927	2.6752	1.000	42.577
^{2}H	0.0156	1	1	0.8574	0.4107	0.00964	6.536
^{10}B	18.83	5	3	1.8006	0.2875	0.0199	4.575
^{11}B	81.17	5	3/2	2.6880	0.8583	0.165	13.660
^{13}C	1.108	6	1/2	0.7022	0.6726	0.0159	10.705
^{14}N	99.635	7	1	0.4036	0.1933	0.00101	3.076
^{15}N	0.365	7	1/2	−0.2830	−0.2711	0.00104	4.315
^{19}F	100	9	1/2	2.6273	2.5167	0.834	40.055
^{29}Si	4.70	14	1/2	−0.5548	−0.5316	0.0785	8.460
^{31}P	100	15	1/2	1.1305	1.0829	0.0664	17.235

[a] Magnetic moment in units of the nuclear magneton, $eh/(4\mu M_p c)$.

[b] Magnetogyric ratio in SI units.

[c] For equal numbers of nuclei at constant field.

some practical significance to NMR spectroscopists, as we shall see in Chapter 4, Section 4.4.4.2. Its theoretical meaning will be evident a little later. It should also be noted that the neutron, with no net charge, has a substantial magnetic moment. This is a particularly striking illustration of the failure of simple models to predict μ. Clearly, the neutron must contain separated charges (at least a part of the time) even though its total charge is zero.

Although magnetic moments cannot be predicted exactly, there are useful empirical rules relating the mass number A and atomic number Z to the nuclear spin properties:

1. If both the mass number A and the atomic number Z are even, $I = 0$.
2. If A is odd and Z is odd or even, I will have half-integral values 1/2, 3/2, 5/2, etc.
3. If A is even and Z is odd, I will have integral values 1, 2, 3, etc.

Thus, some very common isotopes, such as ^{12}C, ^{16}O, and ^{32}S, have no magnetic moment and cannot be observed by NMR. This is really a blessing, however, for if these nuclei did have magnetic moments, the spectra of organic molecules would be much more complex than they are.

1.3 THE NUCLEAR MAGNETIC RESONANCE PHENOMENON

Nuclei with spins of 1/2, such as protons, are often likened to tiny bar magnets. But because of their small size and because they spin, their behavior differs in some ways from the ordinary behavior of macroscopic bar magnets. When placed in a magnetic field, the spinning nuclei do not all obediently flip over and align their magnetic moments in the field direction. Instead, like gyroscopes in a gravitational field, their spin axes undergo *precession* about the field direction, as shown in Fig. 1.1. The frequency of this so-called Larmor precession is designated as ω_0 in radians per second or ν_0 in Hertz (Hz), cycles per second ($\omega_0 = 2\pi\nu_0$). If we try to force the nuclear moments to become aligned by increasing B_0, they only precess faster. They *can* be made to flip over, however, by applying a second magnetic field, designated as B_1, at right angles to B_0 and causing this second field to rotate at the precession frequency ν_0. This second field is represented by the horizontal vector in Fig. 1.1, although in practice (as we shall see in Chapter 2) it is actually very much smaller in relation to B_0 than this figure suggests. It can be seen that if B_1 rotates at a frequency close to but not exactly at the precession frequency, it will cause at most only some wobbling or *nutation* of the magnetic moment μ. If, however, B_1 is made to rotate exactly at the precession frequency, it will cause large

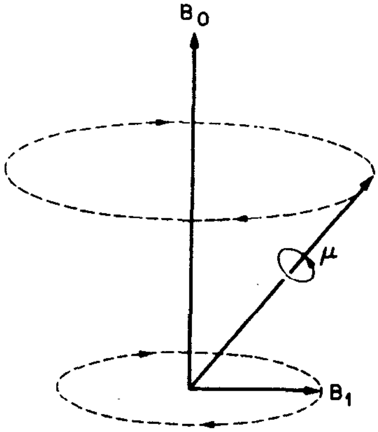

Fig. 1.1. Nuclear moment in a magnetic field.

oscillations in the angle between μ and B_0. If we vary the rate of rotation of B_1 through this value, we will observe a resonance phenomenon as we pass through ν_0.

One might suppose that the Larmor precession of the nuclear moments could itself be detected by some means without the need to invoke a resonance phenomenon. This, however, is not possible because each nucleus precesses with a completely random phase with respect to that of its neighbors and there is therefore no macroscopic property of the system that changes at the Larmor frequency.

By a well-known relationship, the Larmor precession frequency is given by

$$\omega_0 = \gamma B_0 \tag{1.5}$$

or, from Eq. (1.2)

$$h\nu_0 = \frac{\mu B_0}{I} \tag{1.6}$$

The result of this classical treatment can also be obtained by a quantum mechanical description, which is in some ways a more convenient way of regarding the resonance phenomenon. It is best, however, not to try to adopt either approach to the exclusion of the other, since each provides valuable insights. From the quantum mechanical viewpoint, the quantity $h\nu_0$ is the energy separation ΔE between the magnetic energy levels (often termed Zeeman levels, after the investigator who first observed the corresponding splitting in atomic spectra) in a magnetic field B_0, as shown in Fig. 1.2. For a nucleus of spin 1/2, ΔE will be $2\mu B_0$, and as we have seen, only two energy levels are possible. For a nucleus of spin 1, there are three energy levels, as illustrated in Fig. 1.2. The quantum mechanical treatment gives us an additional result for such systems with $I \geqslant 1$, which the classical treatment does not: it tells us that only transitions between adjacent energy levels are allowed, i.e., that the magnetic quantum number can only change by ±1. Thus, transitions between the $m = -1$ and $m = 0$ levels and between the $m = +1$ and $m = 0$ levels are possible, but transitions between the $m = -1$ and the $m = +1$ levels are not possible.

In Fig. 1.3 the separation of proton magnetic energy levels is shown as a function of magnetic field strength for a number of values of the latter employed in current spectrometers. The resonant proton rf field frequency is indicated (in megahertz, MHz, 10^6 Hz) and is a common way of

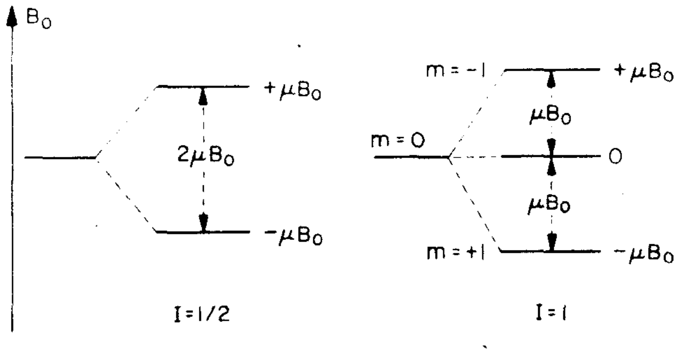

Fig. 1.2. Magnetic energy levels for nuclei of spin 1/2 and 1.

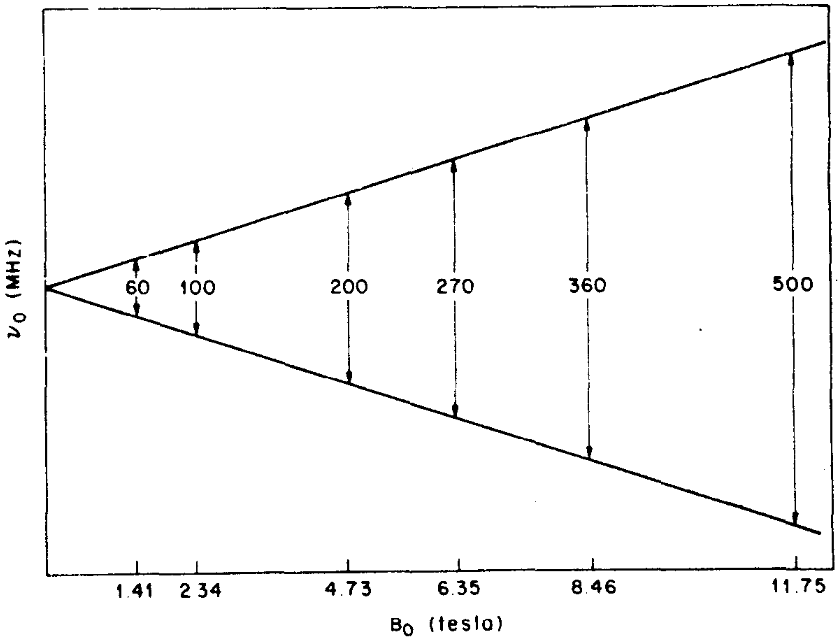

Fig. 1.3. The splitting of magnetic energy levels of protons, expressed as resonance frequency ν_0 as a function of magnetic field strength, expressed in tesla (T).