



# **Nuclear Magnetic Resonance Spectroscopy of Nuclei Other Than Protons**

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## PREFACE

The contents of this volume are taken in large part from the Advanced Study Institute on "Nuclear Magnetic Resonance Spectroscopy of Nuclei Other Than Protons" held in Tirrenia (Pisa), Italy during September 1972.

Although the potential of NMR studies of nuclei other than protons was recognized very early, experimental difficulties rather than any fundamental limitations were responsible for the initial slow developments in the field. The recent advent of commercial pulse Fourier transform NMR spectrometers has revolutionized the field, and non-proton NMR is now one of the most rapidly expanding branches of chemistry. In a few short years NMR studies of other nuclei have become an essential part of molecular spectroscopy and an indispensable aid in the elucidation of molecular structures.

In contrast to conventional proton spectroscopy, NMR of such important nuclei as  $^2\text{H}$ ,  $^{11}\text{B}$ ,  $^{13}\text{C}$ ,  $^{14}\text{N}$ ,  $^{15}\text{N}$ ,  $^{17}\text{O}$ ,  $^{19}\text{F}$ ,  $^{29}\text{Si}$ , and  $^{31}\text{P}$  share certain characteristics that render the NMR experiment difficult; these include unfavorable natural abundance and/or low inherent sensitivity arising from their small magnetogyric ratios. The dramatic increase in sensitivity afforded by the pulse Fourier transform technique through multichannel excitation has made the study of these nuclei almost routine and has simultaneously accelerated progress in theory, applications, and instrumental development. One of the objectives of the institute, and of this book, is to bring together an authoritative and up-to-date treatment of the recent advances, problems, and new techniques involved in the study of the NMR parameters of the more important nuclei.



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## CHAPTER 1

# NUCLEI OTHER THAN HYDROGEN: A REVIEW OF SOME NUCLEAR PROPERTIES AND A DISCUSSION OF THEIR RELAXATION MECHANISMS

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If we adopt the familiar  $^1\text{H}$  resonance as a standard for comparison, then all other magnetic nuclei (except  $^2\text{H}$  and  $^3\text{H}$ ) are set apart by their enormously greater range of chemical shifts—usually hundreds of ppm, rather than the 10 ppm or so for hydrogen. In sensitivity, too, most nuclei are at least an order of magnitude (and often several orders of magnitude) lower than  $^1\text{H}$ . Thus both the problems of studying “other nuclei” and the information available are often quite different from those pertaining to proton NMR. The first portion of this chapter reviews briefly the pertinent nuclear properties and includes a discussion of such topics as chemical shift scales and references, isotope effects, and the consequences of negative magnetogyric ratios. The major portion of the chapter is devoted to an examination of how and why nuclei relax, since relaxation behavior governs many facets of the experimental methods we can apply. Moreover, among “other” nuclei, studies of relaxation can often provide valuable information on chemical bonding and molecular dynamics.

Table 1-1 lists the nuclear spin and relative sensitivity

TABLE 1-1. Some nuclear properties

Nucleus	Spin	Relative Sensitivity (S)	% Natural Abundance (A)	S × A
$^1\text{H}$	$\frac{1}{2}$	1.00	100.	100.
$^2\text{H}$	1	$9.65 \times 10^{-3}$	0.015	$1.4 \times 10^{-4}$
$^3\text{H}$	$\frac{1}{2}$	1.21	—	—
$^{10}\text{B}$	3	$1.99 \times 10^{-2}$	20.	0.40
$^{11}\text{B}$	$\frac{3}{2}$	0.17	80.	13.6
$^{13}\text{C}$	$\frac{1}{2}$	$1.59 \times 10^{-2}$	1.1	0.017
$^{14}\text{N}$	1	$1.01 \times 10^{-3}$	99.6	0.10
$^{15}\text{N}$	$\frac{1}{2}$	$1.04 \times 10^{-3}$	0.37	$3.8 \times 10^{-4}$
$^{17}\text{O}$	$\frac{5}{2}$	$2.91 \times 10^{-2}$	0.04	$1.2 \times 10^{-3}$
$^{19}\text{F}$	$\frac{1}{2}$	0.83	100.	83.
$^{23}\text{Na}$	$\frac{3}{2}$	$9.25 \times 10^{-2}$	100.	9.3
$^{29}\text{Si}$	$\frac{1}{2}$	$7.84 \times 10^{-3}$	4.7	0.037
$^{31}\text{P}$	$\frac{1}{2}$	$6.63 \times 10^{-2}$	100.	6.6
$^{199}\text{Hg}$	$\frac{1}{2}$	$5.67 \times 10^{-3}$	16.8	0.095
$^{207}\text{Pb}$	$\frac{1}{2}$	$9.16 \times 10^{-3}$	22.6	0.21

for many of the nuclei that are discussed in this volume. Except for  $^{19}\text{F}$  and the very infrequently studied  $^3\text{H}$ , the inherent sensitivities of all the nuclei are far below that of  $^1\text{H}$ . In addition, many magnetic nuclei exist at only low natural abundance, so that the sensitivity problem is compounded. Only within the last few years has it been possible to make studies of many of these nuclei in a wide variety of compounds, usually by pulse Fourier transform methods (see Chapter 2) for direct observation or by double resonance methods (see Chapters 3 and 23) for indirect study. Nuclei with spin  $> \frac{1}{2}$  usually relax rapidly by quadrupole interactions, as we shall see, with concomitant line broadening and reduction of the peak intensity even further

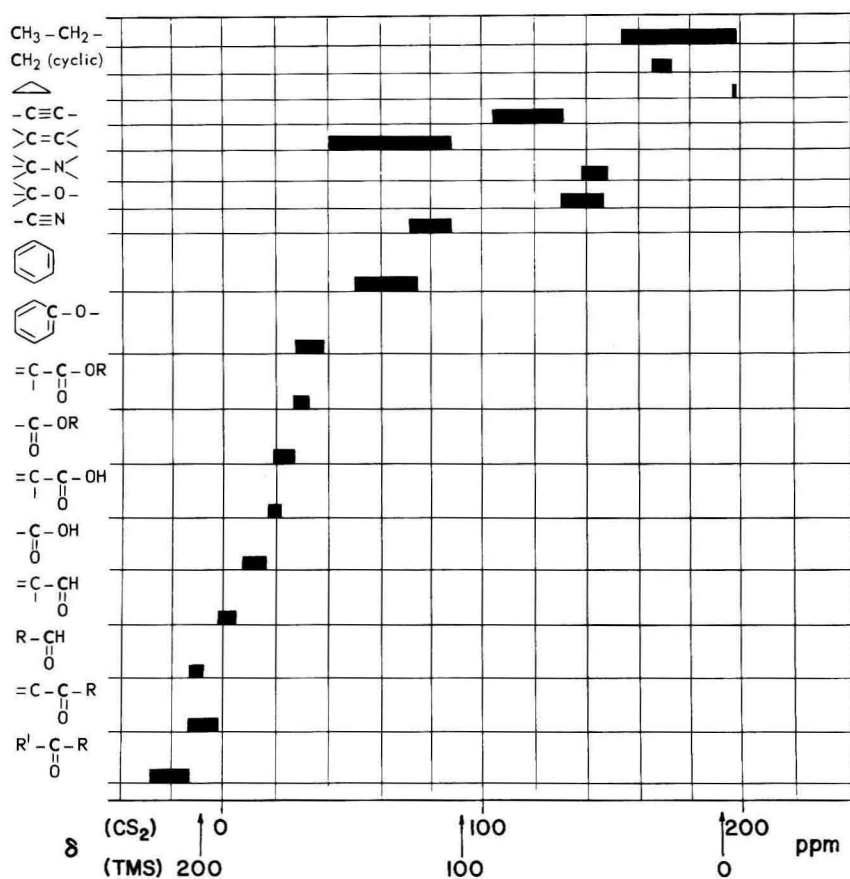


Figure 1-1. Correlation of  $^{13}\text{C}$  chemical shifts with functional groups.

than would be suggested by the figures in Table 1-1.

For nuclei other than hydrogen the dominant effect in determining chemical shifts is the temperature-independent paramagnetic term, in contrast to hydrogen, where this term is almost negligible.<sup>1</sup> One result is that the range of chemical shifts commonly found for "other" nuclei is at least an order of magnitude greater than that found for hydrogen, as exemplified in Fig. 1-1, an approximate correlation chart for  $^{13}\text{C}$ .

Figure 1-1 gives two scales for  $^{13}\text{C}$  chemical shifts, one relative to  $^{13}\text{CS}_2$ , which has been used widely in the past, and



one relative to  $^{13}\text{C}$  in tetramethylsilane (TMS). The latter reference has been employed in three books<sup>2</sup> on  $^{13}\text{C}$  NMR and seems likely to be accepted by most NMR spectroscopists. In general, as we begin extensive studies of a variety of nuclei, it is important to agree on reference compounds for each nucleus and to establish a sign convention for chemical shifts. The vast body of data for proton NMR is based on the internationally accepted  $\delta$  scale in which the reference, TMS, occurs at lower frequency (higher field) than most other resonances.<sup>3</sup> To provide mostly positive numbers for chemical shifts, then, the scale has been chosen to increase with increasing frequency. The TMS-based scale for  $^{13}\text{C}$  is in accord with this convention, and it seems highly desirable that data for other nuclei be expressed in a compatible manner. (At least one major NMR publication requires that data for all nuclei be expressed with values of  $\delta$  increasing with increasing frequency.<sup>4</sup>)

In several instances it is possible to observe NMR with more than one isotope of a given element; often different isotopes have specific advantages. One good example is nitrogen, where there is an advantage of narrow lines arising from  $^{15}\text{N}$ , compared with the generally broad lines from rapidly relaxing  $^{14}\text{N}$ . On the other hand, the almost 300-fold advantage in natural abundance of  $^{14}\text{N}$  relative to  $^{15}\text{N}$  makes it the isotope of choice in many cases. It is important to know to what accuracy data obtained for different isotopes can be compared. Some early NMR data suggested that chemical shifts for  $^{14}\text{N}$  and  $^{15}\text{N}$  in the same compound might differ substantially—a “zero-bond” isotope effect analogous to well-known effects on the chemical shift of a nucleus on isotopic substitution of nearby atoms.<sup>5</sup> We can write the Larmor equation, including the chemical shielding  $\sigma$ , for the two isotopes:

$$^{15}\nu = \frac{^{15}\gamma}{2\pi} B_0 (1 - ^{15}\sigma)$$

$$^{14}\nu = \frac{^{14}\gamma}{2\pi} B_0 (1 - ^{14}\sigma) .$$