Handbook of High Resolution Multinuclear NMR

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HANDBOOK OF HIGH RESOLUTION MULTINUCLEAR NMR

**We do not remember days,
only moments**

PREFACE

The widespread availability of dedicated multinuclear high-resolution NMR spectrometers has opened up a new and exciting field in chemical research for the organic and inorganic chemist. A great many problems can now be tackled in the NMR study of "exotic" nuclei such as tungsten, oxygen, silicon, lead, silver, and cadmium. Actually, the entire periodic table has become accessible since the development of high or very high field, wide-bore multinuclear FT spectrometers.

It has been our goal in writing this book to implement initial NMR experiments on nuclei other than proton, fluorine, phosphorus or carbon 13. To begin with the experimenter will require any number of hints, among which might be the exact resonance frequency of a readily available compound or a clearcut chemical shift scale for the isotope already under study.

Of course, relaxation times, NOE effects, acquisition parameters (and folded lines!) are important in such experiments because most of these low sensitivity nuclei can be observed only in the Fourier mode: we describe steps fully in the first part of the book; the second part is a nucleus—one page on which to build.

It is our hope that this monograph will obviate too much time from being spent in cumbersome spectrometer tuning and will prepare the chemist to start at once with the NMR study of choice.

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C.B.
P.G.

USUAL CONSTANTS (MKSA)

From Handbook of Chemistry and Physics,
60th Edition, 1979-1980.

Avogadro's constant,	$N = 6.022045\ 10^{23}$ mole^{-1}
Planck's constant,	$h = 6.626176\ 10^{-34}$ J.s.
$\hbar$	$h/2\pi = 1.054589\ 10^{-34}$ J.s.
Boltzman's constant,	$k = 1.380662\ 10^{-23}$ J.K.$^{-1}$
Magnetic permeability of vacuum,	$\mu_o/4\pi = 10^{-7}$ m.kg.C^{-2}
Elementary charge,	$e = 1.6021892\ 10^{-19}$ C
Electron rest mass,	$m_e = 9.109534\ 10^{-31}$ kg
Proton rest mass,	$m_H = 1.6726485\ 10^{-27}$ kg
Bohr magneton,	$\mu_B = 9.274078\ 10^{-24}$ J.T.$^{-1}$
Nuclear magneton,	$\mu_N = 5.050824\ 10^{-27}$ J.T-^{1}
Proton moment,	$\mu_H = 1.4106171\ 10^{-26}$ J.T.$^{-1}$
Gyromagnetic ratio of proton,	$\gamma_H = 2.6751987\ 10^{8}$ rad $s^{-1}T^{-1}$
$\gamma_H/2\pi$,	$= 4.258222\ 10^{7}\ s^{-1}T^{-1}$
Electric permittivity of vacuum :	$\varepsilon_o = (1/36\pi)\ 10^{-9} m^{-3} kg^{-1} s^{2} C^{2}$

SYMBOLS AND ABBREVIATIONS

A	Hyperfine coupling constant
a%	Natural abundance
ADC	Analog to digital converter
AQT	Acquisition time
$\vec{B}_0$	Main induction
$\vec{B}_1$	Observing radiofrequency field
$\vec{B}_2$	Decoupling radiofrequency field
$C_{//}, C_{\perp}$,	Components ot the spin rotation tensor
D_{ij}	Direct coupling constant
e	Electron charge
FID	Free induction decay
FT	Fourier transformed
$\Delta G^{\neq}$	Free energy of activation
$\hbar$	$h/2\pi$ = reduced Planck constant
I	Eigenvalue of the angular spin momentum

I_x, I_y, I_z	Eigenvalues of the component of I
$I_{//}$, $I_{\perp}$	Components of inertial moment
$^nJ_{A-X}$	Indirect spin-spin coupling constant
$^nK_{A-X}$	Reduced indirect coupling constant
M, Mo, M_∞	Total magnetic moment
M_x, M_y, M_z	Components of M.
M_{eff}	Total magnetization along $\vec{B_o} + \vec{B_1}$
N, n	Number of scans
NOE	Nuclear Overhauser Enhancement
Q	Quadrupole moment
q	Electric field gradient
R_A	Receptivity of nucleus A
RF	Radiofrequency field
RFS	Repetitive frequency shift
r_{ij}	Distance between spin i and j
S	Eigenvalue of the spin momentum of the electron
$\Delta S^{\neq}$	Entropy of activation
SW	Sweep width
S/N	Signal to noise ratio
T	Temperature in°K
T_1	Spin lattice relaxation time
$T_{1\rho}$	Relaxation time in the rotating frame
T_2	Spin-Spin relaxation time
T_2^*	Apparent spin-spin relaxation time

t	Time interval
α or β	Pulse angle
γ_A	Gyromagnetic ratio of nucleus A
δ	Chemical shift in ppm
η	NOE enhancement factor
η_a	Asymmetry parameter of an electric field tensor
θ	Pulse angle
μ	Electronic magnetic moment
$\mu_o/4\pi$	Magnetic permeability of vacuum
ν	Resonance frequency
ν_{ref}	Resonance frequency of a reference line
ν_o	Frequency of the applied RF field
$\Delta\nu_{1/2}$	Half-line width
σ	Screening constant
$\sigma_{//}$, $\sigma_{\perp}$	Components of the screening tensor
τ	Time interval
τ_c	Correlation time
χ or χ_v	Volumic susceptibility
ω	Angular velocity

PART ONE

CONTENTS

PART ONE

CHAPTER 1

NMR PARAMETERS

When Fourier transform NMR experiments are performed on nuclei other than proton, fluorine, or carbon 13 every experimentalist is faced with a "recording strategy" that requires a knowledge and clear definition of NMR parameters such as sensitivity, natural abundance, NOE effects and T_1 or T_2 relaxation mechanisms. These parameters are defined[1] and exemplified as broadly as possible in this chapter.

1.1 SENSITIVITY, NATURAL ABUNDANCE, AND RECEPTIVITY

1.1.1 Sensitivity

At constant induction B_o, the resonance strength of a given isotope X, is proportional to

$$K\ \underbrace{\gamma_X^3\ I_{(x)}\ (I_{(x)}}_{\text{sensitivity}} +1)$$

Where $I_{(x)}$ = isotope spin quantum number,

γ_X = isotope nuclear magnetogyric ratio.

1.1.2 Natural Abundance

Natural abundance is defined as

$$a_X\% = \frac{\text{number of nuclei (given isotope) in the sample}}{\text{total number of nuclei (natural element) in the sample}}$$

1.1.3 Receptivity

$$R_X = a_X \cdot \gamma_X^3 . I_{(X)} . (I_{(X)} +1)$$

This is the parameter to be considered in any observation of X isotopes. If enriched samples are used, a_X is replaced by the isotope enrichment value.

1.1.4 Relative Receptivity

$$R_X^Y = \frac{a_X \gamma_X^3 \; I_{(X)} (I_{(X)} +1)}{a_Y \gamma_Y^3 \; I_{(Y)} \; (I_{(Y)} +1)}$$

This formula compares X isotope receptivity with a standard Y nucleus. As an example,

$$R_{^{195}Pt}^{^{13}C} = 19.5$$

means that a ^{195}Pt signal should be 19.5 stronger than a ^{13}C signal for the same molarity. Of course, this relative receptivity does not take into account the dynamic effects or different relaxation mechanisms that can drastically modify signal-over-noise ratios under identical recording conditions for X and Y species.

1.2 CHEMICAL SHIFTS

1.2.1 Definition

$$\delta_{ppm} = \frac{\nu - \nu_{ref}}{\nu_{ref}} \cdot 10^6 = \frac{\Delta\nu \text{ (Hz)}}{\nu_{ref} \text{ (MHz)}}$$

Where ν = resonance frequency of the observed line,
ν_{ref} = resonance frequency of a reference line,
$\Delta\nu$ = $(\nu - \nu_{ref})$,

More information on chemical shift will be found in Refs. B10, Vol.2, and B31, Vol.2.

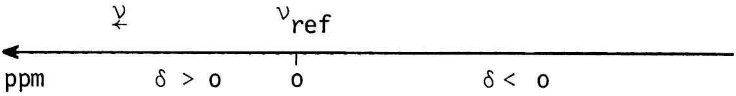
1.2.2 Chemical Shift Sign

The IUPAC convention clearly defines chemical shifts scales

(1,2). The following recommendations are made :

$\delta > o$ for any line detected at a higher frequency than the chosen reference (deshielding, low field);
$\delta < o$ for any line detected at a lower frequency than the chosen reference (shielding, higher field).

Because all Fourier spectrometers are similarly constructed, experimental results are always presented as



Remark. For heteronuclei the referencing resonance is generally concentration - and temperature-dependent. These two parameters must be clearly defined.

1.3 COUPLING CONSTANTS

1.3.1 Direct Coupling Constant (B8, Vol.1, p.1; Vol.9, p.1; B10, Vol.2)

$$D_{ij} = \frac{-1}{4\pi} \hbar \gamma_i \gamma_j < \frac{3\cos^2\theta_{ij} - 1}{r_{ij}^3} > \text{(in Hz)}$$

Where θ_{ij} is the angle between the induction $\vec{B}_o$ and the interconnecting vector (modulo r_{ij}) that links nuclei i and j; < > indicates a value averaged over all nonrandomly oriented magnetic (i,j) dipoles. Therefore, D_{ij}

(a) is nulled in solution ($<3\cos^2\theta_{ij}-1> = 0$);
(b) is measurable only in anisotropic systems such as solids, nematics, and smectics;
(c) is the subject of molecular geometry studies (B8, Vol.1, p.1) and relates to structural informations gathered on mesomorphic phases (B8, Vol.9, p.1)

1.3.2 Indirect or Scalar Coupling Constants (B21, Vol.7, p.246; B31, Vol.1, p.149)

Consider two nuclei A and B,

$$^{n}J_{AB} = k\gamma_A\gamma_B \quad \text{(in Hz)}$$