NMR IN CHEMISTRY

Winners of the Nobel Prize in Physics 1952.

The late Felix Bloch (above) and Edward M. Purcell (left, taken in 1953). On Purcell's right is the home-made magnet with which he observed nuclear magnetic resonance. In Bloch's first account of his simultaneous work, he said 'We have thought of various investigations in which this effect can be used fruitfully'.

Photographs courtesy Stanford University (Bloch) and Harvard University (Purcell).

NMR in Chemistry

A Multinuclear Introduction

WILLIAM KEMP

M
MACMILLAN

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To Louie, Again

CONTENTS

<i>Preface</i>	<i>xi</i>		
<i>Acknowledgements</i>	<i>xiii</i>		
1 Introduction to Nuclear Magnetic Resonance – NMR	1		
1.1 The Principles of NMR Spectroscopy	2	2.13 Nuclei with Spin Quantum Number Greater than 1	22
1.2 The NMR Spectrometer	3	2.14 Quadrupole Moments	23
1.3 Chemical Shifts	4	2.15 Nuclear Quadrupole Resonance Spectroscopy – NQR	23
1.4 Field Strength and Frequency	6	2.16 Boltzmann Distributions in NMR – Effects of Field Strength and Temperature	24
1.5 The Units of Chemical Shift	7	2.17 Relaxation Phenomena	25
1.6 Frequency Standards	7	2.17.1 Spin-Lattice Relaxation and T_1	25
1.7 Chemical Shift Assignments	8	2.17.2 Spin-Spin Relaxation and T_2	26
1.8 Two Models of Nuclear Magnetic Resonance	8	2.18 The Heisenberg Uncertainty Principle and the Width of Absorption Lines	27
1.8.1 Quantum Mechanics	8	2.18.1 Effect of T_1 and T_2 on NMR Line Widths	27
1.8.2 The Precessing Nucleus	9	2.18.2 Line Shape and Peak Areas	27
1.9 Coupling and Decoupling of Magnetic Nuclei	11		
2 The Fundamental Basis of Magnetic Resonance	14	3 The NMR Spectrometer	29
2.1 The Spin of Electrons and Nuclei	15	3.1 NMR Magnets	30
2.2 Angular Momentum and Magnetic Moments of the Electron and the Proton	15	3.1.1 Permanent Magnets	30
2.3 Angular Momentum and Magnetic Moments of Other Nuclei	16	3.1.2 Electromagnets	30
2.4 The Spin Quantum Number	16	3.1.3 Superconducting Magnets	30
2.4.1 The Dimension of Spin Angular Momentum	17	3.1.4 The Search for Bigger Magnets – Resolution and Sensitivity	31
2.4.2 The Direction of Spin Angular Momentum	17	3.1.5 The Direction of B_0 – The z-axis Convention	32
2.5 Nuclei with Spin Quantum Number = $\frac{1}{2}$	17	3.2 Magnetic Field Homogeneity and Spectrometer Resolution	32
2.6 The Nuclear Magnetic Moment Vector, μ	17	3.2.1 Shim Coils	32
2.7 The Strengths of Nuclear Magnets – The Nuclear Magneton Unit, μ_N	19	3.2.2 Sample Spinning and Spinning Sidebands	32
2.8 The Magnetogyric Ratio – γ	19	3.3 Magnet Stability and Field-Frequency Lock	33
2.9 Precessional Frequency and γ – The Larmor Equation	19	3.4 Field Sweep and Frequency Sweep – Continuous Wave NMR Spectroscopy	33
2.10 Summary of NMR Theory	20	3.5 Pulsed Radiofrequency – Fourier Transform NMR Spectroscopy	34
2.11 Electron Spin Resonance Spectroscopy	20	3.5.1 Fourier Transforms	34
2.12 Nuclei with Spin Quantum Number = 1	20	3.5.2 Advantages of the Pulsed FT NMR Method	35
		3.6 Sensitivity in Multinuclear NMR	36
		3.6.1 Relative Abundance	36

3.6.2	Sensitivity and Nuclear Magnetic Moments	36	4.4.2	Protons in Alkane Groups — Tables 15.1, 15.2 and 15.3	55
3.7	Radiofrequency Circuits	36	4.4.3	Protons of Alkene, Alkyne and Aromatic Systems — Tables 15.4 and 15.5	56
3.7.1	Radiofrequency Sources in Multi-nuclear NMR	37	4.5	Protons in OH, NH and SH Groups — Table 15.6	57
3.7.2	Single Coil and Crossed Coil Detection	37	4.5.1	Hydrogen Bonding and Proton Chemical Shifts	57
3.7.3	Forced Induction and Free Induction	38	4.5.2	Quadrupolar Broadening in NH Signals	59
3.7.4	The Components of RF Signals	39	4.6	Spin-Spin Coupling — Spin-Spin Splitting	59
3.7.5	Phase Sensitive Detectors and Quadrature Detection	40	4.6.1	Predicting Multiplicity from the ($n + 1$) Rule	59
3.7.6	RF Pulses and their Fourier Transforms	40	4.6.2	The Coupling Constant, J — Table 15.7	62
3.8	Data Handling in FT NMR	41	4.6.3	Theory of Spin-Spin Coupling — I	64
3.8.1	Sampling Rate and Fold-back	41	4.6.4	AX_2 , AX_3 , and A_2X_3 Coupling Systems	65
3.8.2	The Fast Fourier Transform — Real and Imaginary Solutions	42	4.6.5	Coupling of Protons to Other Nuclei with Spin = $\frac{1}{2}$	66
3.8.3	Phases and Filters	42	4.7	General Features of Simple Coupling Systems	67
3.8.4	Dynamic Range and Computer Word Length	43	4.7.1	Magnetic Equivalence in Proton NMR	67
3.9	Variable Temperature Probes	43	4.7.2	Successive Branching and Pascal's Triangle	68
4	Proton NMR Spectra	45	4.7.3	Long Range Coupling	70
4.1	Shielding, Deshielding and Proton Chemical Shifts	46	4.7.4	Coupling in Proton Exchange Processes	70
4.1.1	Electronegativity and Proton Chemical Shifts	46	4.7.5	AMX Coupling Systems	72
4.1.2	Van der Waals Radii and Proton Chemical Shifts	47	4.8	Coupling to Nuclei with Spin $I > \frac{1}{2}$	73
4.2	Anisotropic Effects and Proton Chemical Shifts	47	4.8.1	Predicted Multiplicity for Spin = 1 Nuclei	73
4.2.1	Aromatic Ring Currents	47	4.8.2	Effects of Quadrupole Moments on Observed Splitting	74
4.2.2	Double Bonds in Alkenes	49	4.9	Non-first Order Spectra	75
4.2.3	Carbonyl C=O Double Bonds	49	4.10	Simplification of Complex Spectra	77
4.2.4	Alkyne Triple Bonds	50	4.10.1	Increased Field Strength	77
4.2.5	Alkanes	51	4.10.2	Chemical Shift Reagents	77
4.3	Chemical and Magnetic Equivalence in Proton NMR	51	4.10.3	Spin Decoupling — Double and Triple Irradiation	80
4.3.1	Free Rotation and Molecular Conformations	51	4.11	Additional Problems	81
4.3.2	Restricted Rotation in Alkenes and Amides	52	5	Carbon-13 NMR Spectra	84
4.3.3	Proton Exchange in Alcohols, Amines, Carboxylic Acids and Keto-Enol Systems	52	5.1	Recording Carbon-13 NMR Spectra	85
4.3.4	Deuterium Exchange	53	5.1.1	Natural Abundance and Isotopomers	85
4.4	Protons Attached to Carbon Atoms — Chemical Shift Assignments	54	5.1.2	Magnetic Moment and Magnetogyric Ratio	85
4.4.1	Use of Correlation Tables 15.1–15.5	54	5.1.3	Coherent and Broad Band Decoupling — $^{13}\text{C}\{-^1\text{H}\}$ NMR Spectra	87

5.1.4	Off Resonance Decoupling	88	6.2	Energy Levels for an AX Coupling System	111
5.2	Relaxation Effects in Carbon-13 NMR Spectra	90	6.2.1	The Sign of the Coupling Constant, J	112
5.3	Chemical Shifts in Carbon-13 NMR Spectra	90	6.2.2	Factors Influencing the Coupling Constant, J	113
5.3.1	Theory of Carbon-13 Chemical Shifts	91	6.2.3	Non-first Order AB Spectra	114
5.4	Chemical Shift Assignments in Carbon-13 NMR Spectra	92	6.3	Energy Levels for an AMX Coupling System	114
5.4.1	Summarised Procedure — Use of Correlation Tables 15.8–15.16	93	6.4	Determination of the Relative Signs of J	114
5.4.2	Identifying the Parent Model	93	6.4.1	Spin Tickling	115
5.4.3	Alkane Chemical Shifts — Table 15.8	94	6.4.2	INDOR — Internuclear Double Resonance	115
5.4.4	Alkene Chemical Shifts — Table 15.9	95	6.5	Net Magnetisation and its Vector Representation	117
5.4.5	Alkyne Chemical Shifts — Table 15.10	96	6.6	Frames of Reference in NMR	118
5.4.6	Aromatic and Heterocyclic Chemical Shifts — Table 15.11	96	6.6.1	The Laboratory Frame	118
5.4.7	Influence of Functional Substituents on Alkane Chemical Shifts — Table 15.12	97	6.6.2	Rotating Frames of Reference	118
5.4.8	Influence of Functional Substituents on Alkene and Aromatic Chemical Shifts — Table 15.13	99	6.6.3	Axes of Rotating Frames, x' , y' and z	119
5.4.9	Carbonyl Group Chemical Shifts — Table 15.14	101	6.7	Pulsed Radiofrequency in the Rotating Frame	119
5.4.10	Miscellaneous Multiple-bonded Carbon Chemical Shifts — Table 15.15	101	6.7.1	Magnetisation on the y' -axis	119
5.4.11	Methyl Group Chemical Shifts — Table 15.16	101	6.7.2	Pulse Width and Flip Angle — 90° and 180° Pulses	119
5.5	Coupling Constants in Carbon-13 NMR Spectra — Table 15.17 — Satellites	101	6.8	Relaxation in the Rotating Frame	122
5.5.1	Coupling of Carbon-13 to Hydrogen and Deuterium	102	6.8.1	Longitudinal Relaxation — Spin-Lattice Relaxation — T_1	122
5.5.2	Homonuclear Carbon Coupling	102	6.8.2	Transverse Relaxation — Spin-Spin Relaxation — T_2	123
5.5.3	Coupling of Carbon-13 to Other Nuclei	102	6.8.3	T_2 and Field Homogeneity	123
5.6	Additional Problems	103	6.8.4	Line Width, Ringing, T_1 and T_2	123
6	More Advanced Theories of NMR	108	6.9	The Nuclear Overhauser Effect — NOE	124
6.1	Theory of Spin-Spin Coupling — II	109	6.9.1	The NOE in Stereochemistry	124
6.1.1	Electron-coupled Spin-Spin Interactions between Directly-bonded Nuclei	109	6.9.2	Theory of the NOE	126
6.1.2	Electron-coupled Spin-Spin Interactions between Protons in CH_2 Groups	110	6.9.3	The Size of the NOE	126
			6.9.4	The Sign of the NOE — Nuclei with Negative γ	127
			6.9.5	Time Dependence of Spin Decoupling and the NOE	127
			7	Multipulse and Computational Methods in NMR	128
			7.1	Gated Decoupling and NOE	129
			7.1.1	Coupling, NOE and Time	129
			7.1.2	Gated Decoupling — NOE with Spin Splitting	129
			7.1.3	Inverse Gated Decoupling — Spin Decoupling without NOE	131
			7.1.4	Quantitative Analysis in Decoupled Carbon-13 NMR Spectra	131

7.2	Measurement of T_1 – the Spin-Lattice (or Longitudinal) Relaxation Time	131	8.1.3	Line Shape (Band Shape) and Exchange Rates	163
7.2.1	Inversion Recovery Measurement of T_1	131	8.1.4	Relaxation Times and Exchange Rates	163
7.2.2	Other Pulse Sequences for Measuring T_1	134	8.2	Energy of Activation	164
7.2.3	Significance of T_1 Values	134	8.2.1	The Arrhenius Equation and the Eyring Equation	164
7.2.4	Peak Suppression Methods	135	8.2.2	Typical Values of Activation Energies	165
7.3	Measurement of T_2 – the Spin-Spin (or Transverse) Relaxation Time	136	8.3	Theory of Coalescence	165
7.3.1	Spin Echoes – the Simple Homonuclear Case	136	8.4	The NMR Time Scale – What is it?	166
7.3.2	Carr-Purcell-Meiboom-Gill (CPMG) Measurement of T_2	137	8.5	Chemically Induced Dynamic Nuclear Polarisation – CIDNP	167
7.3.3	Significance of T_2 Values	138	8.5.1	Applications of CIDNP	167
7.3.4	Coupling Constants and Phase Modulation in Spin Echoes	138	8.5.2	The Nature of CIDNP	168
7.4	Polarisation Transfer and Cross Polarisation	141	9	Fluorine-19 NMR Spectra	169
7.4.1	Selective Population Inversion	142	9.1	Fluorine-19 Chemical Shifts	170
7.5	Summarised Principles of Spin Echoes and Polarisation Transfer	143	9.2	Fluorine-19 Coupling Constants	171
7.6	INEPT, DEPT, and Spectrum Editing by ADEPT	143	9.2.1	Coupling of Fluorine-19 with Fluorine-19	171
7.6.1	Spectrum Editing – Carbon Subspectra	143	9.2.2	Coupling of Fluorine-19 with Proton and Phosphorus-31	174
7.7	Two-dimensional NMR – 2D NMR	146	9.2.3	Coupling of Fluorine-19 with Carbon-13	174
7.7.1	J -resolved 2D NMR Spectra	148	9.2.4	Coupling of Fluorine-19 with Nitrogen-14	174
7.7.2	Shift-correlated 2D NMR Spectra	149	10	Phosphorus-31 NMR Spectra	176
7.7.3	Recording 2D FT NMR Spectra – τ and the Second Time Domain Axis	149	10.1	Phosphorus-31 Chemical Shifts	177
7.7.4	^{13}C Satellite Spectroscopy – Carbon-Carbon Connectivity Plots – CCCP	149	10.2	Phosphorus-31 Coupling Constants	177
7.8	Solid State NMR Spectra	151	10.2.1	Coupling of Phosphorus-31 with Phosphorus-31	178
7.8.1	Magic Angle Spinning – MAS	152	10.2.2	Coupling of Phosphorus-31 with Proton and Fluorine-19	178
7.8.2	Dipolar Decoupling and Cross Polarisation	152	10.2.3	Coupling of Phosphorus-31 with Carbon-13	178
7.8.3	Applications of Solid State NMR	154	11	Nitrogen-14 and Nitrogen-15 NMR Spectra	182
7.9	Biological NMR	154	11.1	Nitrogen Isotopes – ^{14}N and ^{15}N	183
7.9.1	NMR Imaging – Zeugmatography, Tomography	154	11.1.1	Isotope Abundance	183
7.9.2	Surface Detection and Topical Magnetic Resonance – TMR	156	11.1.2	Sensitivity Enhancement – INEPT and DEPT	183
8	Dynamic NMR	158	11.2	Nitrogen Chemical Shifts	184
8.1	Rate Processes and the Heisenberg Uncertainty Principle	160	11.2.1	Reference Standards for Nitrogen-15 NMR	184
8.1.1	Chemical Shift and Exchange Rates	160	11.2.2	Factors Influencing Nitrogen-15 Chemical Shifts	185
8.1.2	Spin Coupling and Exchange Rates	163			

11.2.3	Influence of Protonation and Solvent on Nitrogen-15 Chemical Shifts	185	15.2	Influence of functional group X on the chemical shift position (δ) of CH_3 , CH_2 and CH protons β to X	212
11.3	Use of Paramagnetic Complexes in Nitrogen-15 NMR	187	15.3	Proton chemical shifts (δ) for CH_2 and CH groups bearing more than one functional substituent	212
11.4	Nitrogen-15 Coupling Constants	187	15.4	Proton chemical shifts (δ) for protons attached to unsaturated and aromatic groups	213
12	Oxygen-17 NMR Spectra	189	15.5	Influence of functional group X on the chemical shift of protons on benzene rings	214
12.1	Oxygen-17 Chemical Shifts	190	15.6	Proton chemical shifts (δ) for OH, NH and SH groups	214
12.2	Oxygen-17 Coupling Constants	191	15.7	Proton-proton coupling constants	215
13	NMR Spectra from Other Nuclei	193		Carbon-13 Data	
13.1	Deuterium NMR Spectra	194		^{13}C Chemical Shift Summary Chart	216
13.2	Tritium NMR Spectra	195	15.8	^{13}C Chemical shifts (δ) in alkane groups	217
13.3	Boron-11 NMR Spectra	195	15.9	^{13}C Chemical shifts (δ) in alkenes	218
13.4	Aluminium-27 NMR Spectra	195	15.10	^{13}C Chemical shifts (δ) in alkynes	219
13.5	Silicon-29 NMR Spectra	196	15.11	^{13}C Chemical shifts (δ) in aromatic and heterocyclic molecules	220
13.6	Selenium-77 NMR Spectra	196	15.12	Influence of functional group X on the chemical shift of nearby carbons in alkane chains	221
13.7	Chlorine, Bromine and Iodine NMR Spectra	196	15.13	Influence of functional group X on the chemical shift of nearby carbons in alkene groups and benzene rings	222
13.8	Other Elements and their NMR Spectra	197	15.14	^{13}C Chemical shifts (δ) in carbonyl groups	223
14	Background Physics and Biography of NMR	200	15.15	^{13}C Chemical shifts (δ) for carbons in various multiple-bonded environments	223
14.1	Vector Quantities – Torque and Angular Momentum	201	15.16	^{13}C Chemical shifts (δ) for methyl groups in common environments	224
14.2	Gyroscopic Behaviour	203	15.17	^{13}C - ^1H Coupling constants	225
14.3	Magnetic and Electrical Phenomena	204	15.18	^{13}C Relaxation times – T_1 (in seconds)	226
14.3.1	Bar Magnets and Magnetic Moments	204		Other Data	
14.3.2	Wire Loops and Spinning Charges	204	15.19	Solvents used in NMR work	227
14.3.3	Alternating Current	204	15.20	Greek Alphabet	227
14.3.4	Signal-to-noise Ratios	205		<i>Further Reading</i>	228
14.4	Quadrupole Moments	206		<i>Answers to Problem Examples</i>	230
14.5	Historical Retrospects in NMR	206		<i>Appendix of Magnetic Isotopes</i>	233
14.5.1	Biographical Notes	207		<i>Compendium of Acronyms in NMR</i>	235
14.6	Nocturnal Processes	209		<i>Index</i>	237
15	Tables of Reference Data	210			
	Proton Data				
15.1	Proton chemical shifts (δ) for CH_3 , CH_2 and CH groups attached to functional group X	211			

Preface

In the last few years the horizons of nuclear magnetic resonance spectroscopy have all but been pushed out of sight as new and ever more sophisticated instruments are built and reports of new applications flood the literature.

For chemists who are active developers of the science, in whatever aspect, it is difficult merely to read all of the new publications. For chemists who use the method, among other methods, to solve their chemical problems it is well-nigh impossible to keep up to date.

This book is an attempt to introduce NMR to a wide audience of users, in such a cohesive way that all of its potential can be tapped and exploited: it is not a book about the physics and mathematics of NMR, but concerns the interpretation of NMR spectra by those who do not consider themselves particularly mathematical by inclination: the minimum prerequisites are some knowledge of general spectroscopic principles and a familiarity with the chemical properties of common functional classes.

Clear non-mathematical pictures of magnetic resonance must inevitably be distortions of more fundamental laws, but a worthwhile sacrifice is made in forming a bridge between physics and chemical application. The book is obviously not monographic in style or depth, but it will serve its intent if, having read it, the reader is thereby equipped and encouraged to tackle the necessarily more rigorous specialist works.

The emphasis is multinuclear, with a deliberate attempt being made to demystify the NMR studies of the less common NMR elements. Likewise, Fourier transforms and superconducting magnets are introduced very early, and are not given any special status as 'recent developments': continuous wave spectrometers are not referred to as 'conventional', and the use of the terms upfield and downfield is minimised for the same pedagogic reasons (being replaced by lower frequency and higher frequency respectively).

The problem of order of presentation, of finding a beginning, a middle and an end, is not unique to the study of NMR: the chapter sequence adopted should not therefore be taken as a recommended learning programme,

but merely as an approximate indicator of the way in which most teachers introduce the subject, building upon the familiar to construct a framework of advanced understanding.

Chapter 1 is set at the most elementary conceptual level, and is an obligatory launching point for the multi-nuclear approach.

Chapter 4 (on proton NMR) and chapter 5 (on carbon-13 NMR) form the mainstay of the subject; some teachers begin with proton while others begin with carbon-13. Surprisingly little theory is needed to interpret such spectra: for this reason, while chapter 2 is fairly full in explanation, most students will tend to attack this chapter in several short sorties, as the need to know becomes more expansive. The same is true of the instrument details given in chapter 3 which, while fairly detailed and self-contained, can profitably be absorbed in separate parts at different times.

The set of chapters 2, 3, 4 and 5 completes a study of NMR to intermediate level.

Chapters 6 and 7 interrelate with each other at the next most advanced conceptual level: here are introduced the theories and practice made accessible only by micro-processor controlled instrumentation. An argument can be made for introducing some of the chapter 6 theory at an earlier stage, and of course this is not precluded: but there is a strong case to be adduced for consolidating the basic applications in the early chapters before tackling the three-dimensional complexities of the rotating frames of reference, with all the perceptual traps involved.

The study of dynamic molecular processes by NMR is treated separately in chapter 8. Some of the simpler ideas of dynamic NMR are, however, interspersed in the earlier chapters, since to gather them all in a late chapter would be artificial and distorting.

Chapters 9-13 are all self-sufficient to a degree, and are the barest indications, by example, of the kind of information contained in the NMR spectra of a selection of other nuclei. Given the multinuclear treatment of the earlier chapters, there is no need here for extensive detail.

Chapter 14 very much embodies two personal views.

Many details of physics are easily forgotten (or may not have been learnt) and having them gathered together serves as a useful aide-memoire for non-physicists. We also often learn nothing about the people who helped to assemble the enormous construct of science, and the sparse biographical notes given here on a few of the famous names in NMR may whet an appetite or two.

Although informative data are supplied as necessary throughout the book, chapter 15 contains a large amount of reference data, which can be accessed for systematic or detailed needs. Extensive tables of chemical shifts, coupling constants and relaxation times are gathered here, with details of common NMR solvents.

There are many problem examples throughout the book. It has been established that one major reason for lack of success in problem solving is an inability to collect and identify only that information which is necessary

for solution. In an endeavour to side-step this difficulty, most of the problem examples are preceded by worked examples, so that confidence will rise through knowing which method to apply. Most problems are also seen within the context of the learning objectives under discussion (although other problem examples test more comprehensive understanding).

While it is demonstrably possible to interpret many NMR spectra without intimate study of theory or of spectrometer operation, hopefully the presentation of the subject matter in this book will stimulate an intellectual curiosity, such that a spectrum can be interpreted in the morning, and explained in the afternoon. If the book fulfils its purpose, the user will go back the following morning for more. There is always another experiment to be done.

Heriot-Watt University, Edinburgh

W. K.

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Johnson and Jankowsky, *Carbon-13 NMR Spectra*, New York, Wiley (1972) was the source (with permission) of figures 5.1(a), 5.5, 5.6, 5.7, 5.8, 5.9, 5.10 and 9.4.

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