

CONTENTS

Preface	xi
Acknowledgments	xiii
Frequently Used Symbols and Abbreviations	xv
Chapter 1 SPECTROSCOPY: SOME PRELIMINARY CONSIDERATIONS	1
1.1 What is NMR Spectroscopy?	1
1.2 Properties of Electromagnetic Radiation	1
1.3 Interaction of Radiation with Matter: The Classical Picture	3
1.4 Uncertainty and the Question of Time Scale	4
Chapter Summary	5
Review Problems	5
Chapter 2 MAGNETIC PROPERTIES OF NUCLEI	6
2.1 The Structure of an Atom	6
2.2 The Nucleus in a Magnetic Field	9
2.3 Nuclear Energy Levels and Relaxation Times	12
2.4 The Rotating Frame of Reference	15
2.5 Relaxation Mechanisms and Correlation Times	18
Chapter Summary	20
Additional Resources	20
Review Problems	20
Chapter 3 OBTAINING AN NMR SPECTRUM	22
3.1 Electricity and Magnetism	22
3.2 The NMR Magnet	24
3.3 Signal Generation the Old Way: The Continuous-Wave (CW) Experiment	28
3.4 The Modern Pulsed Mode for Signal Acquisition	32
3.5 Line Widths, Lineshape, and Sampling Considerations	39
3.6 Measurement of Relaxation Times	41
Chapter Summary	46

Additional Resources	46
Review Problems	46
Chapter 4 A LITTLE BIT OF SYMMETRY	48
4.1 Symmetry Operations and Distinguishability	48
4.2 Conformations and Their Symmetry	51
4.3 Homotopic, Enantiotopic, and Diastereotopic Nuclei	53
4.4 Accidental Equivalence	54
Chapter Summary	54
Additional Resources	54
Review Problems	54
Chapter 5 THE ¹H AND ¹³C NMR SPECTRA OF TOLUENE	56
5.1 The ¹ H NMR Spectrum of Toluene at 80 MHz	56
5.2 The Chemical Shift Scale	59
5.3 The 250- and 400-MHz ¹ H NMR Spectra of Toluene	60
5.4 The ¹³ C NMR Spectrum of Toluene at 20.1, 62.9, and 100.6 MHz	62
5.5 Data Acquisition Parameters	64
Chapter Summary	67
Review Problems	67
Chapter 6 CORRELATING PROTON CHEMICAL SHIFTS WITH MOLECULAR STRUCTURE	68
6.1 Shielding and Deshielding	68
6.2 Chemical Shifts of Hydrogens Attached to Tetrahedral Carbon	70
6.3 Vinyl and Formyl Hydrogen Chemical Shifts	74
6.4 Magnetic Anisotropy	77
6.5 Aromatic Hydrogen Chemical Shift Correlations	78
6.6 Hydrogen Attached to Elements Other than Carbon	81
Chapter Summary	85
References	86
Additional Resources	86
Review Problems	87
Chapter 7 CHEMICAL SHIFT CORRELATIONS FOR ¹³C AND OTHER ELEMENTS	88
7.1 ¹³ C Chemical Shifts Revisited	88
7.2 Tetrahedral (<i>sp</i> ³ Hybridized) Carbons	88
7.3 Heterocyclic Structures	91
7.4 Trigonal Carbons	92
7.5 Triply Bonded Carbons	96
7.6 Carbonyl Carbons	96
7.7 Miscellaneous Unsaturated Carbons	97
7.8 Summary of ¹³ C Chemical Shifts	99
7.9 Chemical Shifts of Other Elements	101
Chapter Summary	102
References	102
Review Problems	103
SELF-TEST I	106
Chapter 8 FIRST-ORDER (WEAK) SPIN-SPIN COUPLING	110

8.2	The ^1H Spectrum of Diethyl Ether	110
8.3	Homonuclear ^1H Coupling: The Simplified Picture	112
8.4	The Spin–Spin Coupling Checklist	113
8.5	The $n + 1$ Rule	114
8.6	Heteronuclear Spin–Spin Coupling	117
8.7	Review Examples	122
	Chapter Summary	125
	Review Problems	125
Chapter 9	FACTORS THAT INFLUENCE THE SIGN AND MAGNITUDE OF J: SECOND-ORDER (STRONG) COUPLING EFFECTS	132
9.1	Nuclear Spin Energy Diagrams and the Sign of J	132
9.2	Factors that Influence J : Preliminary Considerations	135
9.3	One-Bond Coupling Constants	136
9.4	Two-Bond (Geminal) Coupling Constants	138
9.5	Three-Bond (Vicinal) Coupling Constants	138
9.6	Long-Range Coupling Constants	142
9.7	Magnetic Equivalence	143
9.8	Pople Spin System Notation	144
9.9	Slanting Multiplets and Second-Order (Strong Coupling) Effects	145
9.10	Calculated Spectra	149
9.11	The $\text{AX} \rightarrow \text{AB} \rightarrow \text{A}_2$ Continuum	151
9.12	More About the ABX System: Deceptive Simplicity and Virtual Coupling	154
	Chapter Summary	155
	References	155
	Review Problems	156
Chapter 10	THE STUDY OF DYNAMIC PROCESSES BY NMR	158
10.1	Reversible and Irreversible Dynamic Processes	158
10.2	Reversible Intramolecular Processes Involving Rotation Around Bonds	159
10.3	Simple Two-Site Intramolecular Exchange	159
10.4	Reversible Intramolecular Chemical Processes	163
10.5	Reversible Intermolecular Chemical Processes	164
10.6	Reversible Intermolecular Complexation	165
10.7	Other Examples of Reversible Complexation: Chemical Shift Reagents	168
	Chapter Summary	171
	References	172
	Review Problems	172
Chapter 11	ELECTRON PARAMAGNETIC RESONANCE SPECTROSCOPY AND CHEMICALLY INDUCED DYNAMIC NUCLEAR POLARIZATION	176
11.1	Electron Paramagnetic Resonance	176
11.2	Free Radicals	176
11.3	The g Factor	177
11.4	Sensitivity Considerations	179
11.5	Hyperfine Coupling and the a Value	179
11.6	A Typical EPR Spectrum	181
11.7	CIDNP: Mysterious Behavior of NMR Spectrometers	182
11.8	The Net Effect	182
11.9	The Multiplet Effect	183
11.10	The Radical-Pair Theory of The Net Effect	185

11.12	A Few Final Words about CIDNP	188
	Chapter Summary	189
	References	189
	Review Problems	189
Chapter 12 DOUBLE-RESONANCE TECHNIQUES AND COMPLEX PULSE SEQUENCES		191
12.1	What is Double Resonance?	191
12.2	Heteronuclear Spin Decoupling	192
12.3	Polarization Transfer and the Nuclear Overhauser Effect	193
12.4	Gated and Inverse Gated Decoupling	196
12.5	Off-Resonance Decoupling	196
12.6	Homonuclear Spin Decoupling	198
12.7	Homonuclear Difference NOE: The Test for Proximity	198
12.8	Other Homonuclear Double-Resonance Techniques	200
12.9	Complex Pulse Sequences	201
12.10	The <i>J</i> -Modulated Spin Echo and the APT Experiment	203
12.11	More About Polarization Transfer	205
12.12	Distortionless Enhancement by Polarization Transfer	210
	Chapter Summary	210
	References	211
	Additional Resources	211
	Review Problems	211
Chapter 13 TWO-DIMENSIONAL NUCLEAR MAGNETIC RESONANCE		215
13.1	What is 2D NMR Spectroscopy?	215
13.2	2D Heteroscalar Shift-Correlated Spectra	218
13.3	2D Homonuclear Shift-Correlated Spectra	222
13.4	NOE Spectroscopy (NOESY)	228
13.5	Hetero- and Homonuclear 2D <i>J</i> -Resolved Spectra	229
13.6	1D and 2D INADEQUATE	230
13.7	2D NMR Spectra of Systems Undergoing Exchange	236
	Chapter Summary	236
	References	236
	Additional Resources	236
	Review Problems	236
SELF-TEST II		244
Chapter 14 NMR STUDIES OF BIOLOGICALLY IMPORTANT MOLECULES		252
14.1	Introduction	252
14.2	NMR Line Widths of Biopolymers	252
14.3	Exchangeable and Nonexchangeable Protons	253
14.4	Chemical Exchange	254
14.5	The Effects of pH on the NMR Spectra of Biomolecules	256
14.6	NMR Studies of Proteins	256
14.7	NMR Studies of Nucleic Acids	263
14.8	Lipids and Biological Membranes	270
14.9	Carbohydrates	275
	Chapter Summary	277
	References	277

Additional Resources	277
Review Problems	277
Chapter 15 SOLID-STATE NMR SPECTROSCOPY	283
15.1 Why Study Materials in the Solid State?	283
15.2 Why is NMR of Solids Different from NMR of Fluids?	284
15.3 Chemical Shifts in Solids	286
15.4 Spin–Spin Coupling	294
15.5 Quadrupole Coupling	297
15.6 Overcoming Long T_1 : Cross Polarization	299
Chapter Summary	304
Additional Resources	304
Review Problems	304
Chapter 16 NMR IN MEDICINE AND BIOLOGY: NMR IMAGING	306
16.1 A Window into Anatomy and Physiology	306
16.2 Biomedical NMR	306
16.3 Pictures with NMR: Magnetic Resonance Imaging	309
16.4 Image Contrast	317
16.5 Higher Dimensional Imaging	322
16.6 Chemical Shift Imaging	323
16.7 NMR Movies: Echo Planar Imaging	325
16.8 NMR Microscopy	325
16.9 In Vivo NMR Spectroscopy	326
16.10 Nonmedical Applications of MRI	329
Chapter Summary	333
Additional Resources	333
Appendix 1 ANSWERS TO REVIEW PROBLEMS	334
Appendix 2 PERIODIC TABLE	369
SUBJECT INDEX	370
CHEMICAL COMPOUNDS INDEX	379