## Contents

Preface v

Chapter 1 The NMR Spectrometer 1

1.1 Components of an NMR Spectrometer 1
  1.1.1 The Magnet 1
  1.1.2 The Spectrometer Cabinet 2
  1.1.3 The Computer 3
  1.1.4 Maintenance 3
  1.2 Tuning a Probe-Head 3
  1.3 The Lock Channel 4
  1.4 The Art of Shimming 6
    1.4.1 The Shim Gradients 6
    1.4.2 The Shimming Procedure 8
    1.4.3 Gradient Shimming 11

Chapter 2 Determination of Pulse-Duration 14

Exp. 2.1: Determination of the 90° ¹H Transmitter Pulse-Duration 15
Exp. 2.2: Determination of the 90° ¹³C Transmitter Pulse-Duration 18
Exp. 2.3: Determination of the 90° ¹H Decoupler Pulse-Duration 21
Exp. 2.4: The 90° ¹H Pulse with Inverse Spectrometer Configuration 24
Exp. 2.5: The 90° ¹³C Decoupler Pulse with Inverse Configuration 27
Exp. 2.6: Composite Pulses 30
Exp. 2.7: Radiation Damping 33
Exp. 2.8: Pulse and Receiver Phases 36
Exp. 2.9: Determination of Radiofrequency Power 39

Chapter 3 Routine NMR Spectroscopy and Standard Tests 43

Exp. 3.1: The Standard ¹H NMR Experiment 44
Exp. 3.2: The Standard ¹³C NMR Experiment 49
Exp. 3.3: The Application of Window Functions 54
Exp. 3.4: Computer-Aided Spectral Analysis 58
Exp. 3.5: Line Shape Test for ¹H NMR Spectroscopy 61
Exp. 3.6: Resolution Test for ¹H NMR Spectroscopy 64
Exp. 3.7: Sensitivity Test for ¹H NMR Spectroscopy 67
Exp. 3.8: Line Shape Test for ¹³C NMR Spectroscopy 70
Exp. 3.9: ASTM Sensitivity Test for ¹³C NMR Spectroscopy 73
Exp. 3.10: Sensitivity Test for ¹³C NMR Spectroscopy 76
Exp. 3.11: Quadrature Image Test 79
Exp. 3.12: Dynamic Range Test for Signal Amplitudes 82
Exp. 3.13: 13º Phase Stability Test 85
Exp. 3.14: Radiofrequency Field Homogeneity 88
Chapter 4 Decoupling Techniques

Exp. 4.1: Decoupler Calibration for Homonuclear Decoupling 92
Exp. 4.2: Decoupler Calibration for Heteronuclear Decoupling 95
Exp. 4.3: Low-Power Calibration for Heteronuclear Decoupling 98
Exp. 4.4: Homonuclear Decoupling 101
Exp. 4.5: Homonuclear Decoupling at Two Frequencies 104
Exp. 4.6: The Homonuclear SPT Experiment 107
Exp. 4.7: The Heteronuclear SPT Experiment 110
Exp. 4.8: The Basic Homonuclear NOE Difference Experiment 113
Exp. 4.9: 1D Nuclear Overhauser Difference Spectroscopy 116
Exp. 4.10: 1D NOE Spectroscopy with Multiple Selective Irradiation 119
Exp. 4.11: $^1$H Off-Resonance Decoupled $^{13}$C NMR Spectra 122
Exp. 4.12: The Gated $^1$H-Decoupling Technique 125
Exp. 4.13: The Inverse Gated $^1$H-Decoupling Technique 128
Exp. 4.14: $^1$H Single-Frequency Decoupling of $^{13}$C NMR Spectra 131
Exp. 4.15: $^1$H Low-Power Decoupling of $^{13}$C NMR Spectra 134
Exp. 4.16: Measurement of the Heteronuclear Overhauser Effect 137

Chapter 5 Dynamic NMR Spectroscopy

Exp. 5.1: Low-Temperature Calibration Using Methanol 141
Exp. 5.2: High-Temperature Calibration Using 1,2-Ethanediol 145
Exp. 5.3: Dynamic $^1$H NMR Spectroscopy on Dimethylformamide 149
Exp. 5.4: The Saturation Transfer Experiment 152
Exp. 5.5: Measurement of the Rotating-Frame Relaxation Time $T_{1p}$ 155

Chapter 6 1D Multipulse Sequences

Exp. 6.1: Measurement of the Spin–Lattice Relaxation Time $T_1$ 160
Exp. 6.2: Measurement of the Spin–Spin Relaxation Time $T_2$ 164
Exp. 6.3: $^{13}$C NMR Spectra with SEFT 167
Exp. 6.4: $^{13}$C NMR Spectra with APT 170
Exp. 6.5: The Basic INEPT Technique 173
Exp. 6.6: INEPT+ 176
Exp. 6.7: Refocused INEPT 179
Exp. 6.8: Reverse INEPT 182
Exp. 6.9: DEPT-135 185
Exp. 6.10: Editing $^{13}$C NMR Spectra Using DEPT 188
Exp. 6.11: DEPTQ 191
Exp. 6.12: Multiplicity Determination Using PENDANT 194
Exp. 6.13: 1D-INADEQUATE 197
Exp. 6.14: The BIRD Filter 201
Exp. 6.15: TANGO 204
Exp. 6.16: The Heteronuclear Double-Quantum Filter 207
Exp. 6.17: Purging with a Spin-Lock Pulse 210
Exp. 6.18: Water Suppression by Presaturation 213
Exp. 6.19: Water Suppression by the Jump-and-Return Method 216
Chapter 7 NMR Spectroscopy with Selective Pulses

Exp. 7.1: Determination of a Shaped 90° ¹H Transmitter Pulse 220
Exp. 7.2: Determination of a Shaped 90° ¹H Decoupler Pulse 223
Exp. 7.3: Determination of a Shaped 90° ¹³C Decoupler Pulse 226
Exp. 7.4: Selective Excitation Using DANTE 229
Exp. 7.5: SELCOSY 232
Exp. 7.6: SELINCOR: Selective Inverse H, C Correlation via ¹J(C,H) 235
Exp. 7.7: SELINQUATE 238
Exp. 7.8: Selective TOCSY 242
Exp. 7.9: INAPT 246
Exp. 7.10: Determination of Long-Range C, H Coupling Constants 249
Exp. 7.11: SELRESOLV 252
Exp. 7.12: SERF 255

Chapter 8 Auxiliary Reagents, Quantitative Determinations, and Reaction Mechanisms

Exp. 8.1: Signal Separation Using a Lanthanide Shift Reagent 259
Exp. 8.2: Signal Separation of Enantiomers Using a Chiral Shift Reagent 262
Exp. 8.3: Signal Separation of Enantiomers Using a Chiral Solvating Agent 265
Exp. 8.4: Determination of Enantiomeric Purity with Pirkle’s Reagent 268
Exp. 8.5: Determination of Enantiomeric Purity by ¹³P NMR 271
Exp. 8.6: Determination of Absolute Configuration by the Advanced Mosher Method 274
Exp. 8.7: Aromatic Solvent-Induced Shift (ASIS) 277
Exp. 8.8: NMR Spectroscopy of OH Protons and H/D Exchange 280
Exp. 8.9: Water Suppression Using an Exchange Reagent 283
Exp. 8.10: Isotope Effects on Chemical Shielding 286
Exp. 8.11: pKₐ Determination by ¹³C NMR 290
Exp. 8.12: Determination of Association Constants Kₐ 293
Exp. 8.13: Saturation Transfer Difference NMR 298
Exp. 8.14: The Relaxation Reagent Cr(acac)₃ 302
Exp. 8.15: Determination of Paramagnetic Susceptibility by NMR 305
Exp. 8.16: ¹H and ¹³C NMR of Paramagnetic Compounds 308
Exp. 8.17: The CIDNP Effect 312
Exp. 8.18: Quantitative ¹H NMR Spectroscopy: Determination of the Alcohol Content of Polish Vodka 315
Exp. 8.19: Quantitative ¹³C NMR Spectroscopy with Inverse Gated ¹H-Decoupling 318
Exp. 8.20: NMR Using Liquid-Crystal Solvents 321

Chapter 9 Heteronuclear NMR Spectroscopy

Exp. 9.1: ¹H-Decoupled ¹⁵N NMR Spectra Using DEPT 330
Exp. 9.2: ¹H-Coupled ¹⁵N NMR Spectra Using DEPT 333
Exp. 9.3: ¹⁹F NMR Spectroscopy 336
Exp. 9.4: ²⁹Si NMR Spectroscopy Using DEPT 339
Exp. 9.5: $^{29}\text{Si}$ NMR Spectroscopy Using Spin-Lock Polarization 342
Exp. 9.6: $^{119}\text{Sn}$ NMR Spectroscopy 346
Exp. 9.7: $^2\text{H}$ NMR Spectroscopy 349
Exp. 9.8: $^{11}\text{B}$ NMR Spectroscopy 352
Exp. 9.9: $^{17}\text{O}$ NMR Spectroscopy Using RIDE 355
Exp. 9.10: $^{47/49}\text{Ti}$ NMR Spectroscopy Using ARING 358

Chapter 10 The Second Dimension 362

Exp. 10.1: 2D J-Resolved $^1\text{H}$ NMR Spectroscopy 367
Exp. 10.2: 2D J-Resolved $^{13}\text{C}$ NMR Spectroscopy 370
Exp. 10.3: The Basic H,H-COSY Experiment 373
Exp. 10.4: Long-Range COSY 377
Exp. 10.5: Phase-Sensitive COSY 380
Exp. 10.6: Phase-Sensitive COSY-45 383
Exp. 10.7: E.COSY 386
Exp. 10.8: Double-Quantum-Filtered COSY with Presaturation 389
Exp. 10.9: Fully Coupled C,H Correlation (FUCOUP) 393
Exp. 10.10: C,H-Correlation by Polarization Transfer (HETCOR) 396
Exp. 10.11: Long-Range C,H-Correlation by Polarization Transfer 399
Exp. 10.12: C,H Correlation via Long-Range Couplings (COLOC) 402
Exp. 10.13: The Basic HMQC Experiment 405
Exp. 10.14: Phase-Sensitive HMQC with BIRD Filter and GARP Decoupling 409
Exp. 10.15: Poor Man's Gradient HMQC 412
Exp. 10.16: Phase-Sensitive HMBC with BIRD Filter 415
Exp. 10.17: The Basic HSQC Experiment 418
Exp. 10.18: The HOHAHA or TOCSY Experiment 422
Exp. 10.19: HETLOC 426
Exp. 10.20: The NOESY Experiment 430
Exp. 10.21: The CAMELSPIN or ROESY Experiment 434
Exp. 10.22: The HOESY Experiment 438
Exp. 10.23: 2D-INADEQUATE 441
Exp. 10.24: The EXSY Experiment 445
Exp. 10.25: X,Y-Correlation 448

Chapter 11 1D NMR Spectroscopy with Pulsed Field Gradients 453

Exp. 11.1: Calibration of Pulsed Field Gradients 455
Exp. 11.2: Gradient Pre-emphasis 458
Exp. 11.3: Gradient Amplifier Test 461
Exp. 11.4: Determination of Pulsed Field Gradient Ring-Down Delays 464
Exp. 11.5: The Pulsed Field Gradient Spin-Echo Experiment 467
Exp. 11.6: Excitation Pattern of Selective Pulses 470
Exp. 11.7: The Gradient Heteronuclear Double-Quantum Filter 474
Exp. 11.8: The Gradient zz-Filter 477
Exp. 11.9: The Gradient-Selected Dual Step Low-Pass Filter 480
Exp. 11.10: gs-SEL COSY 484
Exp. 11.11: gs-SEL TOCSY 488
Exp. 11.12: DPFGSE-NOE 492
Exp. 11.13: gs-SELINCOR 496
Exp. 11.14: α/β-SELINCOR-TOCSY 499
Exp. 11.15: GRECCO 503
Exp. 11.16: WATERGATE 506
Exp. 11.17: Water Suppression by Excitation Sculpting 509
Exp. 11.18: Solvent Suppression Using WET 512
Exp. 11.19: DOSY 515
Exp. 11.20: INEPT-DOSY 518
Exp. 11.21: DOSY-HMQC 521

Chapter 12 2D NMR Spectroscopy With Field Gradients 525

Exp. 12.1: gs-COSY 526
Exp. 12.2: Constant-Time COSY 530
Exp. 12.3: Phase-Sensitive gs-DQF-COSY 534
Exp. 12.4: gs-HMQC 538
Exp. 12.5: gs-HMBC 542
Exp. 12.6: ACCORD-HMBC 546
Exp. 12.7: HMSC 550
Exp. 12.8: Phase-Sensitive gs-HSQC with Sensitivity Enhancement 554
Exp. 12.9: Edited HSQC with Sensitivity Enhancement 558
Exp. 12.10: HSQC with Adiabatic Pulses for High-Field Instruments 563
Exp. 12.11: gs-TOCSY 567
Exp. 12.12: gs-HMQC-TOCSY 571
Exp. 12.13: gs-HETLOC 575
Exp. 12.14: gs-j-Resolved HMBC 581
Exp. 12.15: 2Q-HMBC 585
Exp. 12.16: 1H-Detected 2D INEPT-INADEQUATE 589
Exp. 12.17: 1,1-ADEQUATE 593
Exp. 12.18: 1,n-ADEQUATE 597
Exp. 12.19: gs-NOESY 601
Exp. 12.20: gs-HSQC-NOESY 604
Exp. 12.21: gs-HOESY 608
Exp. 12.22: 1H,15N Correlation with gs-HMQC 612

Chapter 13 The Third Dimension 616

Exp. 13.1: 3D HMQC-COSY 618
Exp. 13.2: 3D gs-HSQC-TOCSY 622
Exp. 13.3: 3D H,C,P-Correlation 626
Exp. 13.4: 3D HMBC 630

Chapter 14 Solid-State NMR Spectroscopy 634

Exp. 14.1: Shimming Solid-State Probe-Heads 635
Exp. 14.2: Adjusting the Magic Angle 639
Exp. 14.3: Hartmann–Hahn Matching 642
Exp. 14.4: The Basic CP/MAS Experiment
Exp. 14.5: TOSS
Exp. 14.6: SELTICS
Exp. 14.7: Connectivity Determination in the Solid State
Exp. 14.8: REDOR
Exp. 14.9: High-Resolution Magic-Angle Spinning

Chapter 15 Protein NMR

Exp. 15.1: Pulse Determination for Protein NMR
Exp. 15.2: HN-HSQC
Exp. 15.3: HC-HSQC
Exp. 15.4: MUSIC
Exp. 15.5: HN-Correlation using TROSY
Exp. 15.6: HN-TOCSY-HSQC
Exp. 15.7: HNCA
Exp. 15.8: HN(CO)CA
Exp. 15.9: HNCO
Exp. 15.10: HN(CA)CO
Exp. 15.11: HCACO
Exp. 15.12: HCCH-TOCSY
Exp. 15.13: CBCANH
Exp. 15.14: CBACA(CO)NH
Exp. 15.15: HBHACA(BACA)NH
Exp. 15.16: HN(CA)NNH
Exp. 15.17: HN-NOESY-HSQC
Exp. 15.18: HC-NOESY-HSQC
Exp. 15.19: 3D HCN-NOESY
Exp. 15.20: HNCA-J

Appendix 1
Pulse Programs

Appendix 2
Instrument Dialects

Appendix 3
Classification of Experiments

Appendix 4
Elementary Product Operator Formalism Rules

Appendix 5
Chemical Shift and Spin-Coupling Data for Ethyl Crotonate and Strychnine

Glossary and Index