Abstract

This thesis describes double-resonance solid-state NMR connectivity experiments involving quadrupolar and spin-1/2 nuclei. Cross-polarization, transferred-echo double-resonance (TEDOR), rotational-echo double-resonance (REDOR), and dipolar-dephasing difference experiments were used to determine connectivities via the heteronuclear dipolar-couplings between quadrupolar and spin-1/2 nuclei. Two-dimensional extensions of the cross-polarization and TEDOR experiments reveal connectivities between specific resonances in two-dimensional correlation spectra.

Cross-polarization experiments were performed between $^{27}$Al and $^{31}$P nuclei in the aluminophosphate molecular sieves VPI-5 and AIPO4-8, and an experimental investigation of the parameters controlling the efficiency of the transfer is presented. REDOR, TEDOR, and dipolar-dephasing difference experiments are also demonstrated.

Increased efficiency in cross-polarization experiments involving quadrupolar nuclei is obtained between $^{27}$Al and $^{31}$P spins in VPI-5 by carrying out the cross-polarization step with the spinning axis parallel to the applied magnetic field. After the cross-polarization step, the spinning axis is rapidly switched to the "magic angle" for detection of the high-resolution signal.

The experiments developed for $^{27}$Al and $^{31}$P nuclei were extended to $^{27}$Al and $^{29}$Si nuclei for a series of representative zeolite frameworks, in which there is a relative enhancement of a given $^{29}$Si resonance which is approximately linear with the number of aluminum atoms in the neighbouring tetrahedral sites. Further extensions of the techniques to include $^{11}$B, $^{23}$Na, and $^{29}$Si nuclei are demonstrated for borosilicate glasses.

The $^{27}$Al/$^{31}$P and $^{27}$Al/$^{29}$Si connectivity experiments were used to determine the method of silicon substitution and reveal the presence of three types of aluminum environments in the silicoaluminophosphate molecular sieve SAPO-37. The experiments
were also applied to the aluminophosphate AlPO₄-5, confirming that the octahedral aluminum formed upon hydration remains bonded in the framework.

For the first time, INEPT and DEPT experiments were performed in the solid-state. These experiments utilize coherence-transfer based on heteronuclear J-couplings to detect through-bond connectivities. Examples presented show that the experiments are applicable to both quadrupolar and spin-1/2 nuclei, and that only the ±1/2 energy levels of the quadrupolar nuclei are involved in the coherence transfer.
Table of Contents

Abstract.................................................................................................................. ii
Table of Contents.................................................................................................. iv
List of Tables....................................................................................................... xi
List of Figures...................................................................................................... xii
Symbols and Abbreviations................................................................................ xvii
Acknowledgements............................................................................................. xx
Dedication.............................................................................................................. xxi

Chapter 1. Introduction......................................................................................... 1

1.1. Pulse Fourier Transform (FT) NMR.......................................................... 1

1.2. NMR Relaxation Processes......................................................................... 5
(a) Spin-Lattice Relaxation Time ($T_1$)............................................................... 5
(b) Spin-Spin Relaxation Time ($T_2$)................................................................. 7
(c) Spin-Lattice Relaxation Time in the Rotating Frame ($T_{1P}$)....................... 9
(d) Spin Temperature.......................................................................................... 11
(e) Dependence of Relaxation Times on Molecular Motions......................... 12

1.3. Two-Dimensional NMR Spectroscopy...................................................... 14
(a) Introduction.................................................................................................. 14
(b) Representation of Two-Dimensional NMR Data......................................... 16
(c) Classification of 2D NMR Experiments..................................................... 18
   (i) Chemical Shift Correlation Spectroscopy............................................... 18
   (ii) J-Spectroscopy......................................................................................... 18
(d) Discrimination of Frequency Sign in $F_1$ Dimension................................. 19
(e) Processing of Two-Dimensional NMR Experiments.................................. 20
1.4. Nuclear Spin Interactions in the Solid State ....................................................... 24
(a) Zeeman Interaction ......................................................................................... 25
(b) Chemical Shift Interaction ............................................................................. 26
(c) Dipolar Interaction ......................................................................................... 26
(d) Scalar Interaction ............................................................................................ 29
(e) Quadrupolar Interaction .................................................................................. 29

1.5. Techniques used to obtain high resolution NMR spectra of solids .............. 33
(a) High-Power Decoupling ............................................................................... 33
(b) Magic Angle Spinning (MAS) .......................................................................... 34
(c) MAS of Quadrupolar Nuclei .......................................................................... 37
(d) Double Rotation (DOR) and Dynamic Angle Spinning (DAS) Experiments .......................................................................................... 38

1.6. Solid-State Double-Resonance NMR Experiments ........................................ 41
(a) Cross-Polarization .......................................................................................... 41
(b) Cross-Polarization Between $X_1/X_2$ Nuclei ................................................. 44
(c) Cross-Polarization Involving Quadrupolar Nuclei ......................................... 45
(d) REDOR and TEDOR Experiments .................................................................. 51
(e) Dipolar-Dephasing Difference Experiments .................................................. 52

1.7. Solid-State NMR Experiments on Zeolites and Related Molecular Sieves ...... 53
(a) Introduction ..................................................................................................... 53
(b) Solid-State NMR Studies of Molecular Sieve Systems ................................... 60
(c) Three-Dimensional $^{29}$Si-O-$^{29}$Si Connectivities in Zeolite Frameworks from Two-Dimensional $^{29}$Si Homonuclear Correlation NMR Experiments .................................................................................. 67

1.8. Goal of Thesis.................................................................................................. 73
Chapter 1 References ............................................................................................ 74
Chapter 2. Development of Coherence-Transfer and Dipolar-Dephasing Experiments to Establish $^{27}$Al-O-$^{31}$P Connectivities in AlPO$_4$ Molecular Sieve Frameworks

2.1. Background to the Experiments

2.2. Experimental Section

(a) Equipment and Experimental Set-Up

(b) Cross-Polarization Experiment

(c) Dipolar-Dephasing Difference Experiments

(d) REDOR Experiments

(e) TEDOR Experiments

(f) $^{27}$Al and $^{31}$P MAS NMR Studies of VPI-5 and AlPO$_4$-8

2.3. Results and Discussion

(a) $^{27}$Al and $^{31}$P MAS NMR Experiments

(b) One-Dimensional $^{27}$Al/$^{31}$P Cross-Polarization NMR Experiments

(c) $^{27}$Al -> $^{31}$P Cross-Polarization with Variation of $^{31}$P $B_1$ Field

(d) $^{27}$Al -> $^{31}$P Cross-Polarization with Variation of Contact Time

(e) Cross-Polarization Difference Experiments

(f) Two-Dimensional Cross-Polarization Experiments

(g) $^{27}$Al/$^{31}$P Dipolar-Dephasing Difference Experiments

(h) $^{27}$Al/$^{31}$P REDOR Experiments on VPI-5 and AlPO$_4$-8

(i) $^{27}$Al -> $^{31}$P TEDOR Experiments on VPI-5 and AlPO$_4$-8

(j) Two-Dimensional TEDOR Experiments

(k) Spin Diffusion NMR Measurements

2.4. Conclusions

Chapter 2 References
Chapter 3. Increased Efficiency of Coherence-Transfer in Cross-Polarization from Quadrupolar Nuclei: Dynamic-Angle Cross-Polarization (DACP) ............................................................... 141

3.1. Introduction ........................................................................... 141
3.2. Experimental Section ............................................................. 142
3.3. Results and Discussion ........................................................... 146
3.4. Conclusions .......................................................................... 152
Chapter 3 References .................................................................. 154

Chapter 4. $^{27}$Al/$^{29}$Si Connectivity Experiments in Zeolite Molecular Sieves .............................................................. 155

4.1. Introduction ........................................................................... 155
4.2. Experimental Section ............................................................. 156
   (a) Materials ........................................................................... 156
   (b) NMR Experiments .............................................................. 156
4.3. Results and Discussion ........................................................... 157
   (a) Zeolite A ........................................................................ 157
   (b) Zeolite X ........................................................................ 171
   (c) Zeolite Y ........................................................................ 175
   (d) Zeolite Omega ................................................................. 180
4.4. Conclusions .......................................................................... 184
Chapter 4 References .................................................................. 185

Chapter 5. Structural Investigations of SAPO-37 by $^{27}$Al/$^{29}$Si and $^{27}$Al/$^{31}$P Coherence-Transfer and Dipolar-Dephasing Solid-State NMR Experiments ..................................................... 186

5.1. Introduction ........................................................................... 186
5.2. Experimental Section ............................................................. 187
5.3. Results and Discussion ................................................................. 189
5.4. Conclusions ................................................................................. 204
Chapter 5 References ........................................................................ 205

Chapter 6. $^{27}\text{Al}/^{31}\text{P}$ Solid-State NMR Structural Investigations of AlPO$_4$-5 Molecular Sieve ................. 207
6.1. Introduction ................................................................................ 207
6.2. Experimental Section ................................................................. 208
6.3. Results and Discussion ............................................................... 209
6.4. Conclusions ................................................................................. 221
Chapter 6 References ........................................................................ 222

Chapter 7. Coherence-Transfer and Dipolar-Dephasing Connectivity Experiments Involving $^{11}\text{B}$, $^{23}\text{Na}$ and $^{29}\text{Si}$ Nuclei in Borosilicate Glasses .................................................. 223
7.1. Introduction ................................................................................ 223
7.2. Experimental Section ................................................................. 223
    (a) Materials .................................................................................. 223
    (b) NMR Experiments ................................................................. 223
7.3. Results and Discussion ............................................................... 224
    (a) One-Dimensional $^{29}\text{Si}$, $^{11}\text{B}$ and $^{23}\text{Na}$ MAS Spectra ........ 224
    (b) $^{11}\text{B}/^{29}\text{Si}$ Connectivity Experiments ................................ 227
    (c) $^{23}\text{Na}/^{29}\text{Si}$ Connectivity Experiments .............................. 235
    (d) $^{23}\text{Na}/^{11}\text{B}$ Connectivity Experiments .............................. 236
7.4. Conclusions ................................................................................. 240
Chapter 7 References ........................................................................ 241
Appendix 10.  (a) Pulse program for the REDOR experiment................................. 272
   (b) Program to calculate the delays in the REDOR experiment........... 273
Appendix 11.  (a) Pulse program for the TEDOR experiment................................. 274
   (b) Program to calculate the delays in the TEDOR experiment........... 275
Appendix 12.  Pulse program for the two-dimensional TEDOR experiment........... 276
Appendix 13.  Pulse program for the dynamic-angle cross-polarization (DACP)
   experiment...................................................................................... 278
Appendix 14.  Pulse program for the INEPT experiment....................................... 279
Appendix 15.  Pulse program for the refocused INEPT experiment.......................... 280
Appendix 16.  Pulse program for the DEPT experiment........................................ 281
Appendix 17.  Pulse program for the two-dimensional INEPT experiment............. 282
List of Tables

Table 1. Classification of some common 2D NMR experiments.......................... 19
Table 2. Phase cycling of the pulses and the receiver used to distinguish positive
and negative modulation frequencies in the COSY experiment...................... 20
Table 3. $^{13}$C nuclear spin interactions in a 4.7 T magnetic field.......................... 24
Table 4. NMR-active nuclei present in zeolites and related molecular sieves......... 61
Table 5. Experimentally determined parameters for the cross-polarization
between $^{27}$Al and $^{31}$P nuclei in VPI-5.................................................. 112
Table 6. Experimentally determined T$_{1p}$ parameters for $^{31}$P and $^{27}$Al nuclei in
VPI-5........................................................................................................ 149
Table 7. Results for $^{27}$Al/$^{29}$Si connectivity experiments on zeolite A.............. 161
Table 8. Deconvolution of peaks in $^{27}$Al/$^{29}$Si connectivity experiments on
zeolite X........................................................................................................ 173
Table 9. Peak assignment for the $^{29}$Si MAS spectrum of zeolite omega from
Figure 63........................................................................................................ 183
Table 10. Probabilities of the five possible phosphorus environments in AlPO$_4$-5.. 218
Table 11. Relaxation parameters for the nuclei in the borosilicate glasses studied..... 225
List of Figures

Figure 1. Schematic representation of the pulse-FT NMR sequence in the rotating frame of reference .......................................................... 3
Figure 2. Schematic representation of the $180^\circ$-$\tau$-$90^\circ$ inversion recovery sequence used to measure $T_1$ relaxation times .................................................. 6
Figure 3. Schematic representation of the $90^\circ$-$\tau$-$180^\circ$-$\tau$ spin echo sequence used to measure $T_2$ relaxation times .................................................. 8
Figure 4. Schematic representation of the magnetization changes in the pulse sequence used for $T_{1p}$ measurements .......................................................... 10
Figure 5. The general behaviour of the $T_1$, $T_2$ and $T_{1p}$ relaxation times as a function of the correlation time $\tau_c$ for the molecular motion ........................................ 13
Figure 6. Timing sequence of a two-dimensional NMR experiment .......................................................... 15
Figure 7. Representation of a two-dimensional NMR data set .......................................................... 17
Figure 8. Common examples of time-domain apodization functions used in 2D NMR processing .......................................................... 22
Figure 9. Effect of sine-bell apodization on a 2D COSY spectrum .......................................................... 23
Figure 10. The geometric relationship of the internuclear vector $r$ and the angle $\theta$ for an isolated I-S spin pair in an applied magnetic field $B_0$ .......................................................... 28
Figure 11. The energy levels for a spin-$5/2$ nucleus under the influence of the Zeeman interaction and the first and second orders of the quadrupolar interaction .......................................................... 32
Figure 12. Schematic representation of the geometric arrangement for mechanical sample spinning .......................................................... 35
Figure 13. Schematic representation of (a) double rotation (DOR) and (b) dynamic-angle spinning (DAS) techniques .......................................................... 39
Figure 14. (a) Pulse sequence for cross-polarization experiment from I spins to S spins. (b) Vector diagrams for the $^1H \rightarrow ^{13}C$ cross-polarization experiment .......................................................... 42
Figure 15. (a) $^{17}O$ MAS and (b) $^1H \rightarrow ^{17}O$ CP/MAS spectra of an $^{17}O$-enriched sample of boehmite (AlO(OH)) .......................................................... 49
Figure 16. (a) $^{23}Na$ spin-locking efficiency and (b) $^1H \rightarrow ^{23}Na$ CP efficiency in NaOH under static and MAS conditions .......................................................... 50
Figure 17. Lattice structures of typical zeolites formed from the sodalite cage building block .......................................................... 55
Figure 18. Schematic representation of the aluminophosphate VPI-5 lattice framework................................................................. 58

Figure 19. Different types of size and shape selectivity in reactions within zeolite cavities......................................................................................... 59

Figure 20. (a) $^{29}\text{Si}$ MAS NMR spectrum of the zeolite analcite. (b) Characteristic chemical shift ranges of the five different local silicon environments.................. 62

Figure 21. $^{29}\text{Si}$ MAS NMR spectra of faujasite zeolites................................................................. 64

Figure 22. $^{31}\text{P}$ MAS NMR spectra of (a) VPI-5 and (b) AIPO$_4$-8. (c) $^{27}\text{Al}$ MAS NMR spectrum of VPI-5................................................................. 66

Figure 23. Contour plot of a COSY experiment on ZSM-12................................................................. 69

Figure 24. Contour plot of an INADEQUATE experiment on ZSM-12.................................................. 71

Figure 25. Contour plot of an INADEQUATE experiment on ZSM-5 loaded with 2 molecules of p-xylene per unit cell................................................................. 72

Figure 26. Pulse sequence for cross-polarization experiments: (a) Spin-locking pulse sequence used for polarization-transfer from I spins to S spins. (b) Two-dimensional cross-polarization experiment................................................................. 82

Figure 27. Pulse sequence for dipolar-dephasing difference experiments under MAS conditions................................................................. 86

Figure 28. Pulse sequences for REDOR and TEDOR experiments................................. 89-90

Figure 29. Diagram showing the relationship between the spinning axis, the external magnetic field $B_0$, and the I-S heteronuclear dipolar vector................................................................. 93

Figure 30. Projections ([001]) of layers in the framework structures for the two aluminophosphates AIPO$_4$-8 and VPI-5................................................................. 99

Figure 31. One-dimensional MAS spectra of AIPO$_4$-8 and VPI-5................................................................. 100-101

Figure 32. One-dimensional cross-polarization spectra of AIPO$_4$-8 and VPI-5...... 104-105

Figure 33. Variation of the $^{27}\text{Al} \rightarrow ^{31}\text{P}$ cross-polarization signal in VPI-5 as a function of the $^{31}\text{P}$ spin-locking $B_1$ field................................................................. 107

Figure 34. Variation of the $^{27}\text{Al} \rightarrow ^{31}\text{P}$ cross-polarization signal in VPI-5 as a function of contact time................................................................. 111

Figure 35. Pulse sequence for $^{31}\text{P} \rightarrow ^{27}\text{Al}$ cross-polarization difference experiments, which measure the draining of the $^{31}\text{P}$ signal by contact with $^{27}\text{Al}$ spins.... 114

Figure 36. Variation of the $^{31}\text{P} \rightarrow ^{27}\text{Al}$ cross-polarization difference signal as a function of contact time in VPI-5................................................................. 116

Figure 37. Two-dimensional $^{27}\text{Al} \rightarrow ^{31}\text{P}$ cross-polarization experiment on VPI-5...... 118

Figure 38. Two-dimensional $^{27}\text{Al} \rightarrow ^{31}\text{P}$ cross-polarization experiment on AIPO$_4$-8.. 119

Figure 39. Dipolar-dephasing difference experiments on VPI-5................................................................. 121
Figure 40. $^{27}\text{Al}^{31}\text{P}$ REDOR experiments in both directions for AIPO$_4$-8 and VPI-5

Figure 41. Evolution of $^{27}\text{Al}(^{31}\text{P})$ REDOR ($\Delta S/S_0$) signals for the $^{27}\text{Al}$ peaks in VPI-5

Figure 42. Evolution of $^{31}\text{P}(^{27}\text{Al})$ REDOR signals for the $^{31}\text{P}$ peaks in VPI-5

Figure 43. TEDOR signals from $^{27}\text{Al} \rightarrow ^{31}\text{P}$ coherence transfer in AIPO$_4$-8 and VPI-5

Figure 44. Evolution of the $^{27}\text{Al} \rightarrow ^{31}\text{P}$ TEDOR signal for the three $^{31}\text{P}$ sites in VPI-5

Figure 45. Two-dimensional $^{27}\text{Al} \rightarrow ^{31}\text{P}$ TEDOR experiment on VPI-5

Figure 46. (a) Conventional cross-polarization sequence used for CPMAS experiments. (b) Pulse sequence and rotor positioning for the dynamic-angle cross-polarization (DACP) experiment used for spinning samples. (c) Modified experiment for comparison of the CP efficiencies of the CPMAS and DACP experiments

Figure 47. (a) CPMAS spectrum and (b) DACP spectrum of $^{31}\text{P}$ in VPI-5

Figure 48. Total integrated cross-polarization signal from the $^{31}\text{P}$ nuclei in VPI-5 as a function of contact time in (a) the CPMAS experiment and (b) the DACP experiment

Figure 49. Simulations of cross-polarization dynamics with different relaxation parameters

Figure 50. $^{27}\text{Al} \rightarrow ^{29}\text{Si}$ TEDOR experiment for zeolite A

Figure 51. Variation of the $^{29}\text{Si}$ spin-locking field in the $^{27}\text{Al} \rightarrow ^{29}\text{Si}$ cross-polarization experiment on zeolite A

Figure 52. Variation of the peak intensity as a function of contact time in the $^{27}\text{Al} \rightarrow ^{29}\text{Si}$ cross-polarization experiment on zeolite A

Figure 53. Evolution of the $^{29}\text{Si}(^{27}\text{Al})$ REDOR signal in zeolite A

Figure 54. Evolution of the $^{27}\text{Al} \rightarrow ^{29}\text{Si}$ TEDOR signals in zeolite A for a variation of $180^\circ$ pulse placement during each rotor cycle after the coherence-transfer

Figure 55. Two-dimensional $^{27}\text{Al} \rightarrow ^{29}\text{Si}$ TEDOR experiment on a zeolite A/alumina mixture

Figure 56. (a) $^{27}\text{Al}$ 2D TEDOR projection and (b) $^{27}\text{Al}$ one-dimensional MAS spectrum of zeolite A/alumina mixture
Figure 57. Zeolite X: (a) $^{29}$Si MAS spectrum, (b) deconvolution of $^{29}$Si MAS spectrum, (c) predicted deconvolution of $^{29}$Si spectrum for $^{27}$Al/$^{29}$Si connectivity experiments, and (d) predicted spectrum for $^{27}$Al/$^{29}$Si connectivity experiments. 172

Figure 58. $^{27}$Al/$^{29}$Si connectivity experiments on zeolite X. (a) $^{29}$Si($^{27}$Al) REDOR experiment, (b) $^{27}$Al → $^{29}$Si TEDOR experiment, (c) $^{29}$Si($^{27}$Al) dipolar-dephasing difference experiment, and (d) $^{27}$Al → $^{29}$Si cross-polarization experiment. 174

Figure 59. Two-dimensional $^{27}$Al → $^{29}$Si TEDOR experiment on zeolite X. 176

Figure 60. Two-dimensional $^{27}$Al → $^{29}$Si cross-polarization experiment on zeolite X. 177

Figure 61. $^{29}$Si spectra of zeolite Y. (a) $^{29}$Si MAS spectrum, (b) $^{27}$Al → $^{29}$Si cross-polarization experiment, (c) $^{29}$Si($^{27}$Al) dipolar-dephasing difference experiment, and (d) $^{27}$Al → $^{29}$Si TEDOR experiment. 178

Figure 62. Two-dimensional $^{27}$Al → $^{29}$Si TEDOR experiment on zeolite Y. 179

Figure 63. $^{29}$Si experiments on zeolite omega. (a) $^{29}$Si MAS spectrum, (b) $^{27}$Al → $^{29}$Si cross-polarization experiment, (c) $^{29}$Si($^{27}$Al) dipolar-dephasing difference experiment, and (d) $^{27}$Al → $^{29}$Si TEDOR experiment. 181-182

Figure 64. Powder x-ray diffraction spectrum of SAPO-37. 190

Figure 65. (a) $^{29}$Si MAS spectrum and (b) $^{31}$P MAS spectrum of SAPO-37. 191

Figure 66. $^{27}$Al → $^{29}$Si TEDOR spectrum of SAPO-37. 192

Figure 67. $^{27}$Al → $^{31}$P TEDOR spectrum of SAPO-37. 194

Figure 68. $^{27}$Al MAS spectra of SAPO-37 acquired at the different spinning rates indicated. 195

Figure 69. Two-dimensional $^{27}$Al → $^{31}$P TEDOR experiment on SAPO-37. 197

Figure 70. (a) $^{27}$Al 2D TEDOR projection and (b) $^{27}$Al one-dimensional MAS spectrum of SAPO-37. 198

Figure 71. (a) $^{27}$Al spin echo spectrum (no $^{31}$P dephasing) and (b) $^{27}$Al($^{31}$P) dipolar-dephasing difference spectrum of SAPO-37. 200

Figure 72. (a) $^{27}$Al spin echo spectrum (no $^{29}$Si dephasing) and (b) $^{27}$Al($^{29}$Si) dipolar-dephasing difference spectrum of SAPO-37. 202

Figure 73. $^{27}$Al MAS spectrum of AlPO$_4$-5. 210

Figure 74. $^{31}$P MAS spectrum of AlPO$_4$-5. 211

Figure 75. (a) $^{27}$Al spin echo spectrum (no $^{31}$P dephasing), (b) $^{27}$Al($^{31}$P) dipolar-dephasing difference spectrum, and (c) $^{27}$Al($^{31}$P) dipolar-dephasing difference null spectrum of AlPO$_4$-5. 212
Figure 76. (a) $^{27}\text{Al} \rightarrow ^{31}\text{P}$ CP spectrum and (b) $^{27}\text{Al} \rightarrow ^{31}\text{P}$ TEDOR spectrum of AlPO$_4$-5 ........................................... 214

Figure 77. Two-dimensional $^{27}\text{Al} \rightarrow ^{31}\text{P}$ TEDOR experiment on AlPO$_4$-5 ........... 216

Figure 78. Two-dimensional $^{27}\text{Al} \rightarrow ^{31}\text{P}$ CP experiment on AlPO$_4$-5 .................. 217

Figure 79. $^{31}\text{P}$ rows through octahedral Al and tetrahedral Al from the two-
dimensional $^{27}\text{Al} \rightarrow ^{31}\text{P}$ CP experiment on AlPO$_4$-5 ........................................... 220

Figure 80. $^{29}\text{Si}, ^{11}\text{B}$ and $^{23}\text{Na}$ MAS spectra of soda glass and Corning 7740 .......... 226

Figure 81. $^{11}\text{B} \rightarrow ^{29}\text{Si}$ TEDOR spectra of soda glass and Corning 7740 ..................... 228

Figure 82. Evolution of $^{11}\text{B} \rightarrow ^{29}\text{Si}$ TEDOR and $^{11}\text{B}(^{29}\text{Si})$ REDOR signals in
Corning 7740 .................................................................................................................. 230

Figure 83. Two-dimensional $^{11}\text{B} \rightarrow ^{29}\text{Si}$ TEDOR spectrum of Corning 7740 .......... 231

Figure 84. $^{11}\text{B}(^{29}\text{Si})$ REDOR spectra of soda glass and Corning 7740 ..................... 234

Figure 85. $^{23}\text{Na} \rightarrow ^{11}\text{B}$ TEDOR spectra of soda glass and Corning 7740 ..................... 237

Figure 86. $^{11}\text{B}(^{23}\text{Na})$ REDOR spectra of soda glass and Corning 7740 ..................... 238

Figure 87. $^{23}\text{Na}(^{11}\text{B})$ dipolar-dephasing difference spectrum of Corning 7740 ........ 239

Figure 88. Pulse sequences used for INEPT and DEPT experiments ............................. 244-245

Figure 89. (a) $^{27}\text{Al} \rightarrow ^{29}\text{Si}$ INEPT spectrum of microcline and (b) $^{23}\text{Na} \rightarrow$
$^{29}\text{Si}$ refocused INEPT spectrum of albite ................................................................ 248

Figure 90. $^{27}\text{Al} \rightarrow ^{31}\text{P}$ refocused INEPT spectrum of VPI-5 .................................. 249

Figure 91. Two-dimensional $^{27}\text{Al} \rightarrow ^{31}\text{P}$ INEPT spectrum of AlPO$_4$-14 .......... 250

Figure 92. (a) Simple $^{31}\text{P}$ MAS spectrum, (b) $^{27}\text{Al} \rightarrow ^{31}\text{P}$ INEPT spectrum,
(c) $^{27}\text{Al} \rightarrow ^{31}\text{P}$ refocused INEPT spectrum, and (d) $^{27}\text{Al} \rightarrow ^{31}\text{P}$ DEPT
spectrum of compound (I) ......................................................................................... 252

Figure 93. Peak intensities in (a) the $^{27}\text{Al} \rightarrow ^{31}\text{P}$ INEPT spectrum of compound (I) as a function of the $\tau$ delay time, and (b) the $^{27}\text{Al} \rightarrow ^{31}\text{P}$ DEPT spectrum of compound (I) as a function of the magnitude of the $^{27}\text{Al}$
transfer pulse $\theta$ ............................................................................................... 253-254
Symbols and Abbreviations

Å    Angstrom unit; 1 Å = 10\(^{-10}\) m

B\(_0\)  strength of the static magnetic field

B\(_1\)  strength of the radiofrequency field during a pulse

COSY  chemical shift correlation spectroscopy

CP    cross-polarization

D    dipolar-coupling constant

DACP  dynamic-angle cross-polarization

DAS  dynamic-angle spinning

DD    dipolar-dephasing

DEPT  distortionless enhancement by polarization transfer

DOR  double rotation

F\(_1\), F\(_2\)  frequency dimensions corresponding to t\(_1\) and t\(_2\)

FID  free induction decay

FT    Fourier transformation

h    (i) hour
     (ii) Planck constant

H    Hamiltonian operator; subscripts indicate the nature of the operator

I, S  (i) general representation for nuclear spins, where I and S refer to two different types of nuclei
     (ii) spin quantum number for I and S nuclei, respectively

INADEQUATE  incredible natural abundance double quantum transfer experiment

INEPT  insensitive nuclei enhanced by polarization transfer

J    scalar J-coupling constant

MAS  magic angle spinning

m    number of rotor cycles of dipolar-dephasing after coherence-transfer in a TEDOR experiment
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>ms</td>
<td>millisecond</td>
</tr>
<tr>
<td>$M_0$</td>
<td>equilibrium macroscopic magnetization of a spin system in the presence of $B_0$</td>
</tr>
<tr>
<td>$M_X$, $M_Y$, $M_Z$</td>
<td>components of macroscopic magnetization</td>
</tr>
<tr>
<td>$n$</td>
<td>(i) number of rotor cycles of dipolar-dephasing in a REDOR experiment&lt;br&gt;(ii) number of rotor cycles of dipolar-dephasing before coherence-transfer in a TEDOR experiment</td>
</tr>
<tr>
<td>NMR</td>
<td>nuclear magnetic resonance</td>
</tr>
<tr>
<td>ppm</td>
<td>parts per million (frequency scale)</td>
</tr>
<tr>
<td>REDOR</td>
<td>rotational-echo double-resonance</td>
</tr>
<tr>
<td>$r$</td>
<td>internuclear distance between two nuclei</td>
</tr>
<tr>
<td>r.f.</td>
<td>radiofrequency</td>
</tr>
<tr>
<td>s</td>
<td>second</td>
</tr>
<tr>
<td>$S_f$, $S_0$</td>
<td>signal intensities in the REDOR experiment with and without dephasing, respectively</td>
</tr>
<tr>
<td>$\Delta S$</td>
<td>REDOR difference signal; $\Delta S = S_0 - S_f$</td>
</tr>
<tr>
<td>$\Delta S/S_0$</td>
<td>normalized REDOR difference signal</td>
</tr>
<tr>
<td>SEDOR</td>
<td>spin-echo double-resonance</td>
</tr>
<tr>
<td>S/N</td>
<td>signal-to-noise ratio</td>
</tr>
<tr>
<td>TEDOR</td>
<td>transferred-echo double-resonance</td>
</tr>
<tr>
<td>$t_1$</td>
<td>variable evolution time period in a two-dimensional NMR experiment</td>
</tr>
<tr>
<td>$t_2$</td>
<td>detection period in a two-dimensional NMR experiment</td>
</tr>
<tr>
<td>$T_1$</td>
<td>spin-lattice relaxation time</td>
</tr>
<tr>
<td>$T_{1\rho}$</td>
<td>spin-lattice relaxation time in the rotating frame</td>
</tr>
<tr>
<td>$T_2$</td>
<td>spin-spin relaxation time</td>
</tr>
<tr>
<td>$T_2^*$</td>
<td>spin-spin relaxation time including the effects of magnetic field inhomogeneity</td>
</tr>
<tr>
<td>Symbol</td>
<td>Definition</td>
</tr>
<tr>
<td>--------</td>
<td>------------</td>
</tr>
<tr>
<td>$T_{CP}$</td>
<td>cross-polarization time constant</td>
</tr>
<tr>
<td>TMS</td>
<td>tetramethylsilane</td>
</tr>
<tr>
<td>T-site</td>
<td>tetrahedral site in the zeolite framework</td>
</tr>
<tr>
<td>1D, 2D</td>
<td>one- and two-dimensional</td>
</tr>
<tr>
<td>I $\to$ S</td>
<td>coherence-transfer from I to S nuclei; e.g. $^{27}$Al $\to$ $^{31}$P</td>
</tr>
<tr>
<td>I(S)</td>
<td>observing I nuclei and dephasing S nuclei; e.g. $^{27}$Al($^{31}$P)</td>
</tr>
<tr>
<td>$\delta$</td>
<td>chemical shift (usually in ppm)</td>
</tr>
<tr>
<td>$\gamma_X$</td>
<td>magnetogyric ratio of nucleus X</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>dimensionless parameter in REDOR and TEDOR experiments; $\lambda = nD\tau_r$</td>
</tr>
<tr>
<td>$\mu s$</td>
<td>microsecond</td>
</tr>
<tr>
<td>$\Delta v_{1/2}$</td>
<td>full width of a resonance line at half-height</td>
</tr>
<tr>
<td>$v_r$</td>
<td>frequency of sample rotation (in Hz)</td>
</tr>
<tr>
<td>$\tau$</td>
<td>delay time in a pulse sequence</td>
</tr>
<tr>
<td>$\tau_c$</td>
<td>correlation time for the molecular motion</td>
</tr>
<tr>
<td>$\tau_r$</td>
<td>rotational period (time for one complete rotor cycle); $\tau_r = 1/v_r$</td>
</tr>
<tr>
<td>$\omega_r$</td>
<td>angular frequency of sample rotation (in radians)</td>
</tr>
<tr>
<td>$\omega_0$</td>
<td>Larmor precession frequency (in radians)</td>
</tr>
</tbody>
</table>
Acknowledgements

I would like to take this opportunity to thank the many people who have helped and supported me throughout my Ph.D. studies, and who have made my years at UBC truly enjoyable.

First and foremost, I would like to thank my supervisor Dr. Colin Fyfe for his ideas, support, enthusiasm, and patience towards not only this research, but also life in general. Colin always has time to listen to your concerns, and his many discussions and stories over coffee are memorable.

I would like to thank Dr. Karl T. Mueller for his help and support during the early, fundamental stages of this research, his tremendous patience and understanding in teaching a new graduate student the mechanics of experimental NMR, and his continued interest and support. I am also extremely grateful to Dr. Hiltrud Grondey and Dr. Yining Huang for their help and support, both research-wise and personally. In addition, I would like to thank the many other present and past members of the Fyfe group for making the lab such a pleasant environment in which to work.

I am severely indebted to Mr. Tom Markus of the Electronic Engineering Services for his expertise in tuning probes and modifying the spectrometer. In addition, I would like to thank Mr. Oskar Grenier of the Mechanical Engineering Services for his work in building and modifying probes.

I gratefully acknowledge the financial assistance of the Natural Sciences and Engineering Research Council and the University of British Columbia.

I would like to thank my family for all of their support and encouragement. To my wife, Pauline, I thank you for your love, support, patience, and understanding during these past four years.
To Pauline,
my inspiration
Chapter 1. Introduction

1.1. Pulse Fourier Transform (FT) NMR

Historically, NMR spectrometers acquired data in the "continuous wave" mode, in which the frequency range of interest was swept in a "continuous wave" fashion, and the spectrum recorded directly in the frequency domain. In modern-day NMR spectrometers, the pulse Fourier transform (FT) method, with the capability of increased sensitivity in a fixed period of time, is used [1,2]. In this mode, one or more radiofrequency (r.f.) pulses are applied at the frequency of interest, and the response of the spin system is measured as a function of time. This time response, which contains the frequencies of all the resonances in the spectrum, is called the free induction decay (FID).

To simplify further discussion, it is convenient to define a "rotating frame" of reference, coincident with the z axis and the external magnetic field $B_0$, which rotates around z with an angular velocity $\Omega$. In the rotating frame of reference, the magnetic field $B'$ appears to be reduced,

$$B' = B_0 - \frac{\Omega}{\gamma}$$  \hspace{1cm} (1)

where the prime (') designates the use of the rotating frame and $\gamma$ is the magnetogyric ratio of the nucleus. For example, if $\Omega$ is chosen to be equal to the Larmor precession frequency $\omega_0 = \gamma B_0$, then the nucleus appears to be static in this frame of reference.

When a radiofrequency (r.f.) field $B_1$ is applied (e.g. along the $x'$ axis in the rotating frame), the nucleus will experience an effective field $B_{\text{eff}}$

$$B_{\text{eff}} = k (B_0 - \Omega/\gamma) + i (B_1)$$  \hspace{1cm} (2)

where $k$ and $i$ are unit vectors along the z and $x'$ axes, respectively. If the $B_1$ field is applied exactly on resonance (i.e. at $\omega_0$), and $\Omega$ is chosen to be equal to $\omega_0$, then $B_{\text{eff}} = i (B_1)$, and the nuclei will experience only the applied field $B_1$. 
Therefore, in the rotating frame, when an r.f. pulse ($B_1$) is applied exactly on resonance, the effective field is $B_1$. Application of the $B_1$ pulse along $x'$ for a time $t_p$ causes the net magnetization $M_0$ to rotate around $x'$ by an angle $\theta$ such that

$$\theta = \gamma B_1 t_p = \omega_1 t_p \text{ (radians)}$$

(3)

This results in a magnetization component along $y'$ which can be detected as an induced current in the r.f. coil.

$$M_{y'} = M_0 \sin \theta$$

(4)

By choosing $t_p$ such that $\theta = 90^\circ$ (i.e. a "90° pulse"), the net magnetization is rotated down to the $y'$ axis (i.e. $M_{y'} = M_0$), and transverse relaxation ($T_2$) processes then cause dephasing of the spins in the $x'y'$ plane, as illustrated in Figure 1a. The free induction decay (FID) signal is recorded as an exponential decay of the time-domain magnetization, as shown in Figures 1b,c. (A detailed discussion of relaxation processes is presented in the next section.)

The frequency-domain NMR spectrum, $f(\omega)$, where $\omega = \omega_{\text{resonance}} - \omega_0$ with $\omega_{\text{resonance}}$ the resonance frequency of the signal, is obtained from the time-domain FID, $f(t)$, by Fourier transformation:

$$f(\omega) = \int_{-\infty}^{+\infty} f(t) \exp(i\omega t) \, dt$$

(5)

For example, the Fourier transform of a simple exponential decay in the time-domain obtained when the pulse is exactly on resonance ($\omega_0 = \omega_{\text{resonance}}$) is a Lorentzian signal at zero frequency (see Figure 1b). If, instead, the pulse is not exactly on resonance, the FID is an exponentially decaying sine or cosine oscillation, and the Lorentzian signal is offset from zero frequency by an amount equal to the frequency of the oscillation (see Figure 1c).
Figure 1. Schematic representation of the pulse-FT NMR sequence in the rotating frame of reference showing: (a) the behaviour of the magnetization as a function of time after being rotated 90° by an on-resonance r.f. pulse applied along the x' axis, and the subsequent dephasing of the spins in the x'y' plane, and (b) and (c) the magnetization decay and its Fourier transform, with detection exactly on resonance and slightly off resonance, respectively. (From ref [3])
Prior to Fourier transformation, however, the FID is often modified to improve the appearance of the final spectrum. To improve the resolution of the spectrum, "zero filling" is carried out in which data points, each containing only a zero, are added to the end of the FID such that the total number of data points is $2^n$ (which is usually 2 to 8 times the number of actual data points). One level of zero-filling (i.e. adding the same number of zero points as the number of actual data points) improves the resolution of the spectrum and increases the sensitivity (S/N ratio) by a factor of $\sqrt{2}$ [4]. Zero-filling beyond this level, however, improves the digitization of the spectrum and gives the spectrum a smoother appearance, but does not change the intrinsic resolution of the spectrum or result in any further increase in sensitivity.

The sensitivity of the spectrum can also be improved by apodization. The exponential decay of the FID implies that the S/N at the beginning of the time-domain is substantially greater than the S/N at the end. Apodization of the FID, which involves multiplying the time-domain by a decaying exponential function such that the beginning of the time-domain is enhanced, improves the S/N in the spectrum. However, this increase in S/N is accompanied by some line broadening due to "truncation" of the end of the FID.
1.2 NMR Relaxation Processes

The presence of molecular motions provides a well-defined relaxation mechanism for the nuclei via a modulation of the spin interactions. The most important of them in most situations is the dipolar interaction, both homo- and heteronuclear. The measurement of relaxation times, therefore, is a powerful technique for the detection and quantification of molecular motions. The relaxation times which are commonly measured are $T_1$, $T_2$ and $T_{1p}$. (The spectrometer pulse programs used to measure these relaxation times are given in Appendices 1-4.)

(a) Spin-Lattice Relaxation Time ($T_1$)

Spin-lattice relaxation is the process by which the population difference between two spin states exponentially reaches equilibrium (as defined by the Boltzmann distribution) after a perturbation. The term spin-lattice relaxation is derived from the fact that the relaxation process involves a transfer of Zeeman energy from an "excited" spin to the "lattice". The spin-lattice relaxation time $T_1$ is defined as:

$$\frac{dM_z}{dt} = -\frac{(M_z - M_0)}{T_1}$$

where $M_z$ and $M_0$ are the z components and equilibrium values, respectively, of the magnetization. Note that this is an exponential process. Since spin-lattice relaxation involves the restoration of magnetization along the z axis, it is sometimes termed "longitudinal relaxation".

The most commonly used technique used to measure $T_1$ is the inversion-recovery experiment, as illustrated in Figure 2. The pulse sequence is 180°-τ-90°-(acquire), where the variation in signal intensity vs. τ determines $T_1$. The disadvantage of this experiment is that the repeat time between successive scans must be long enough to ensure that the $M_z$ magnetization has fully returned to its equilibrium value (e.g. a repeat time of 5$T_1$)}
Figure 2. Schematic representation of the 180°-τ-90° inversion recovery sequence used to measure $T_1$ relaxation times (from ref [3]).
results in a 99.3% recovery of the magnetization). This necessitates some prior knowledge of the approximate $T_1$ value, and the repeat time can be quite long.

The saturation-recovery experiment is another technique used to measure $T_1$, and has the advantage that the repeat time between successive scans is independent of the $T_1$ value, and can be made very short (e.g. less than one second). The pulse sequence is (saturation)-$\tau$-90°-(acquire), where the saturation component involves a series of 90° or 180° pulses to ensure that saturation of the resonances is achieved (i.e. no net magnetization along the z axis).

(b) Spin-Spin Relaxation Time ($T_2$)

Spin-spin relaxation describes the decay of the $M_X$ and $M_Y$ components of the magnetization, and is thus often termed "transverse relaxation". The spin-spin relaxation time $T_2$ is defined as:

$$\frac{dM_X}{dt} = -\frac{M_X}{T_2}$$

with a similar expression for $M_Y$. The single exponential decay results in a Lorentzian lineshape, which is a good approximation in the solution-state and in many solid-state magic-angle spinning (MAS) experiments. While changes in $M_Z$ ($T_1$ processes) involve the exchange of Zeeman energy with the lattice, changes in $M_X$ and $M_Y$ ($T_2$ processes) do not change the total Zeeman energy of the spins, but instead involve a mutual exchange of spin energy (i.e. a mutual spin flip). Thus, the term "spin-spin relaxation" is used. The net effect of $T_2$ relaxation is to cause a loss of phase coherence in the x-y plane, and the decay of the bulk magnetization vector in this plane as previously noted.

A spin echo experiment is commonly used to measure $T_2$. The pulse sequence is 90°-\tau-180°-\tau-(acquire), with the variation in signal intensity vs. $\tau$ used to determine $T_2$, as illustrated in Figure 3. In solid-state MAS experiments, it is often desirable to ensure that each $\tau$ value used is an integral multiple of the rotational period $\tau_r = 1/v_r$ where $v_r$ is the
Figure 3. Schematic representation of the $90^\circ$-τ-$180^\circ$-τ spin echo sequence used to measure $T_2$ relaxation times (from ref [3]).
rotational frequency. This ensures that the rotational averaging of the dipolar interaction and chemical shift anisotropy is complete for each experiment.

The spin echo experiment refocuses the effects of magnetic field inhomogeneity (variation of $B_0$ through the sample volume), and thus a true value of $T_2$ is obtained. In the absence of a spin echo, however, the magnetic field inhomogeneity causes each nucleus to experience a slightly different value of $B_0$, with the result being a "fanning out" of individual magnetization vectors. This leads to a loss in phase coherence in addition to that caused by true $T_2$ processes, resulting in a rate of decay greater than $1/T_2$. The relaxation time $T_2^*$ is used when the decay includes the effects of magnetic field inhomogeneity, where the value of $T_2^*$ is less than $T_2$. 

$$\frac{1}{T_2^*} = \frac{1}{T_2} + \text{(rate of decay from magnetic field inhomogeneity)}$$  \hspace{1cm} (8)

(c) Spin-Lattice Relaxation Time in the Rotating Frame ($T_{1p}$)

The spin-lattice relaxation time in the rotating frame, $T_{1p}$, is an especially important parameter in the analysis of cross-polarization experiments in solid state NMR, as will be seen in Chapters 2, 3, and 4. $T_{1p}$ is determined using a spin-locking pulse sequence, as illustrated in Figure 4. An on-resonance 90° pulse is first applied along the $x'$ axis in the rotating frame, generating transverse magnetization along $y'$. With no delay, a second pulse is then applied along $y'$, that is, in the same direction as the net magnetization vector. This is often referred to as "phase shifting" of the initial pulse. The magnetization is now effectively locked along this axis by the $B_1$ r.f. field. Thus, the second pulse is called a "spin-locking" pulse, and while it is being applied, the spins are said to be "spin-locked". Spin-locking is an essential component of the cross-polarization experiment used in solid state NMR (see Section 1.6).

In the absence of the spin-locking pulse, the $y'$ magnetization would decay due to $T_2^*$ relaxation processes. The application of the spin-locking $B_1$ field, however, acts as a
Figure 4. Schematic representation of the magnetization changes in the pulse sequence used for $T_{1p}$ measurements (from ref [3]).
static field in the rotating frame of reference, and is thus analogous to $B_0$. The relaxation of $y'$ is thus analogous to conventional spin-lattice relaxation, and is called "spin-lattice relaxation in the rotating frame", which is described by the characteristic time decay constant $T_{1P}$. To measure the value of $T_{1P}$, the spin-locking pulse is applied for a variable time $\tau$, during which there will be some decay of the $y'$ magnetization which can be detected by recording the FID signal immediately after the spin-locking pulse, as shown in Figure 4. From the variation of signal intensity $I$ with $\tau$, the value of $T_{1P}$ can be determined from

$$I = I_0 \exp\left(-\tau/T_{1P}\right)$$  \hspace{1cm} (9)

where $I_0$ is the full signal intensity extrapolated to time $\tau = 0$.

(d) Spin Temperature

In the discussion of spin-locking fields, it is convenient to introduce the concept of "spin temperature". A spin system can be considered to behave in an analogous manner to a thermodynamic system. In thermodynamic systems, the concept of temperature has been proven experimentally. In spin systems, the establishment of "spin temperature" refers to all nuclei of a given type (e.g. all $^1\text{H}$ spins) having a single common set of relaxation times [1,2]. The distribution of the spins between two energy states is given by a Boltzmann distribution $\exp\{-E/kT_S\}$, where $E$ is the energy difference between the states, $k$ is the Boltzmann constant, and $T_S$ is spin temperature. In most cases, the energy difference is small, i.e. $E \ll kT_S$.

The concept of spin temperature is useful in describing the application of spin-locking fields. After generating transverse magnetization along the $+y'$ axis in the rotating frame (e.g. by application of a 90° pulse along $x'$), application of a spin-locking $B_1$ field along $+y'$ causes the individual spins to rotate around the $y'$ axis, with the net magnetization along $+y'$. The magnetization rotating around $+y'$ (parallel to $B_1$) is thus in
the lower energy level, while the magnetization rotating around -y' (anti-parallel) is in the higher energy level. (This is analogous to the situation of a spin-1/2 nucleus in the static magnetic field \( B_0 \), in which the spins precessing around the z axis can be aligned either parallel ("spin-up") or anti-parallel ("spin-down") to \( B_0 \).) For the spin-locking field applied along the +y' axis, the Boltzmann distribution of magnetization is:

\[
P_{-y}/P_{+y} = \exp{-E/kT_S}
\]

(10a)

where \( P_{\pm y} \) are the numbers of spins rotating around the \( \pm y' \) axes. When the direction of the spin-locking field is reversed 180° from +y' to -y', the distribution becomes

\[
P_{-y}/P_{+y} = \exp{E/kT_S} = \exp{-E/k(-T_S)}
\]

(10b)

Comparing Eqs. (10a) and (10b), we see that reversing the direction of the spin-locking field changes the spin temperature from \( T_S \) to \(-T_S\) (i.e. negative spin temperature). Therefore, there is an "inversion" or "reversal" of spin temperature. Spin temperature inversion [5] is used in the cross-polarization experiment in order to suppress experimental artifacts between successive scans (see Section 2.2b).

(e) Dependence of Relaxation Times on Molecular Motions

The \( T_1 \), \( T_2 \) and \( T_{1p} \) relaxation times are strongly dependent on the presence of molecular motions, which are characterized by a correlation time \( \tau_c \) for the motion. The dependence of the relaxation times on motion is shown in Figure 5, assuming a dipolar mechanism for relaxation. The \( T_1 \) curves depend on the Larmor precession frequency as indicated, with \( \nu_1 > \nu_2 \). (The Larmor frequency is proportional to the applied magnetic field \( B_0 \).) In addition, the activation energy \( E_a \) for the motion can be determined from the limiting slopes of the \( T_1 \) curves and from the fitting of the complete curve.

In solution, rapid isotropic motions (short \( \tau_c \) values) result in the \( T_1 \), \( T_2 \) and \( T_{1p} \) relaxation times being equal (the left side of the curves). In solids, however, many different situations can occur depending on the \( E_a \) and \( \tau_c \) values for the particular motion.
Figure 5. The general behaviour of the $T_1$, $T_2$ and $T_{1\rho}$ relaxation times as a function of the correlation time $\tau_c$ for the molecular motion. The $T_1$ curves depend on the Larmor frequency, with $\nu_1 > \nu_2$. (From ref [3].)
1.3. Two-Dimensional NMR Spectroscopy

(a) Introduction

The concept of extending NMR spectroscopy into two frequency dimensions was first proposed in 1971 by Jeener [6], who suggested that two-dimensional (2D) correlation spectroscopy (COSY) experiments would be possible. Since then, there has been a rapid growth in 2D NMR techniques, especially since Ernst and co-workers demonstrated various kinds of 2D NMR experiments in the solution-state [7].

The pulse sequences for 2D NMR experiments all follow the same basic format, consisting of: the preparation period, variable evolution time period (t₁), mixing period (if necessary), and detection period (t₂), as shown in Figure 6. In the preparation period, one or more r.f. pulses are applied to the spin system to initiate or "prepare" the magnetization for the experiment. During the evolution period (t₁), the prepared magnetization evolves under the influence of all the interactions involving the nuclei (these will depend on the nature of the preparation). If the magnetization present at the end of the evolution period is not in a detectable form (i.e. with Iₓ or Iᵧ components), a "mixing" r.f. pulse(s) is used to convert the magnetization into a detectable form. Finally, in the detection period, a free induction decay signal is recorded during the acquisition time t₂.

In the most common one-dimensional NMR experiment, the evolution time t₁ is zero, and the detection immediately follows the single pulse excitation (preparation). In 2D experiments, the t₁ evolution time is incremented by a constant amount throughout a series of experiments in which all other parameters are kept constant. The acquired signal, therefore, becomes a function of both time periods t₁ and t₂, and the data can be arranged in a two dimensional matrix S(t₁, t₂). Two-dimensional Fourier transformation (FT) of the data matrix converts the two time dimensions into frequency dimensions F₁ and F₂, and the data matrix is now in the form S(F₁, F₂).
Figure 6. Timing sequence for a two-dimensional NMR experiment.
2D NMR spectroscopy provides information when a systematic variation in the evolution period results in a periodic change of phase and/or amplitude in the magnetization at the end of the evolution period. If the spectra formed after the first FT contain one or more component modulation frequencies, the second FT determines the frequencies of the modulations. The spreading of the NMR spectrum in a second orthogonal dimension provides information about the spin interactions occurring during the evolution period. Often this will involve J-couplings, chemical shifts, etc. (A detailed discussion of nuclear spin interactions is given in the Section 1.4.)

(b) Representation of Two-Dimensional NMR Data

The 2D data are usually represented in the form of a contour plot in which the two frequencies form the horizontal and vertical axes, and contour levels are drawn through points of equal intensity, similar to altitude lines on a geographical map (see Figure 7a). The contour lines define the shape of the resonances, while intensity information is indicated by the number of contour levels. The 2D contour plot \( S(F_1, F_2) \) is composed of \( n \) rows and \( k \) columns in the \( F_1 \) and \( F_2 \) dimensions, respectively, where \( n \) is the number of separate one-dimensional experiments performed, and \( k \) is the number of data points acquired during the acquisition time \( t_2 \). The number of experiments \( n \) is usually kept to the minimum number required to obtain the desired resolution in \( F_1 \), since the total experimental time is proportional to \( n \). (\( k \) is generally not limited in size since the acquisition period occurs during the usually much longer recycle delay of the experiment.)

Contour plots are the most common method of displaying data from 2D NMR experiments. In addition to contour plots, cross sections and projections are also used to examine, display, and interpret the 2D data. Cross sections in the 2D spectrum consist of rows and columns in the \( F_1 \) and \( F_2 \) dimensions, respectively. In practice, the peaks which contain information of interest lie on a limited number of cross sections, and it is often informative to plot these cross sections as separate one-dimensional spectra (see Figure...
Figure 7. Representation of a two-dimensional NMR data set (from ref [8]): (a) A contour plot with projections in both dimensions. (b) Three cross sections from the positions indicated in the contour plot.
7b). Projections of each dimension, generated by "projecting" the intensities of the cross sections onto each axis, are often displayed together with a contour plot (see Figure 7a).

(c) Classification of 2D NMR Experiments

2D NMR experiments can be classified into two main groups based on their objectives. Some examples are presented in Table 1.

(i) Chemical Shift Correlation Spectroscopy

This group of experiments uses spin interactions between groups of nuclei to establish correlations between them. The interactions that can be used are J-coupling and dipolar coupling. (A detailed discussion of nuclear spin interactions in solution and in the solid state is given in the Section 1.4.)

In the Fourier transformed 2D spectrum, both frequency axes represent the chemical shift, and the experiments can be either homonuclear (e.g. $^1\text{H}/^1\text{H}$) or heteronuclear (e.g. $^1\text{H}/^{13}\text{C}$) in nature. For example, the COSY experiment, shown in Figure 7a, is a homonuclear correlation experiment. In this thesis, all of the 2D experiments performed are heteronuclear correlation (HETCOR) experiments [9]. HETCOR experiments are extremely informative, since they give the chemical shifts of the $X_1$ nuclei (e.g. $^1\text{H}$) that are either scalar- or dipolar-coupled (depending on the experiment) to the various $X_2$ nuclei (e.g. $^{13}\text{C}$) in the sample.

(ii) J-Spectroscopy

In conventional-1D solution spectra, the multiplets often overlap, rendering assignment of the spectrum difficult. In 2D J-spectroscopy, the chemical shift ($\delta$) and scalar coupling ($J$) are separated in the two dimensions, allowing both parameters to be determined.
Table 1. Classification of some common 2D NMR experiments (from ref [10]).

<table>
<thead>
<tr>
<th>2D NMR Experiment</th>
<th>Interaction</th>
<th>Name</th>
<th>Dimension</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>F_1</td>
</tr>
<tr>
<td>Shift</td>
<td>Homonuclear</td>
<td>J-Coupling</td>
<td>δ(X_j)*</td>
</tr>
<tr>
<td>Correlation</td>
<td>Homonuclear</td>
<td>J-Coupling</td>
<td>δ(X_i)</td>
</tr>
<tr>
<td></td>
<td>Dipolar Coupling</td>
<td>NOESY</td>
<td>δ(X_i)</td>
</tr>
<tr>
<td>J-Resolved</td>
<td>Homonuclear</td>
<td>J-Coupling</td>
<td>δ(X_i)</td>
</tr>
<tr>
<td></td>
<td>Heteronuclear</td>
<td>J-Coupling</td>
<td>δ(X_i)</td>
</tr>
</tbody>
</table>

* Nuclei X_1 and X_2 can be $^1$H or any other nucleus.
** DQF stands for double quantum frequency

(d) Discrimination of Frequency Sign in F_1 Dimension

The original 2D COSY experiments proposed by Jeener [6] did not discriminate the sign of the frequencies (i.e. positive or negative) in the first time dimension ($t_1$). 2D Fourier transformation of the time-domain matrix thus results in a spectrum folded about the transmitter frequency in the F_1 frequency dimension. To overcome this, the transmitter frequency can be placed completely on one side of the spectrum. This method, however, has two distinct disadvantages. First, the transmitter power, which is symmetric about the transmitter frequency, is distributed unevenly across the spectrum. Second, only one-half of the collected data contains information of interest, while the other half is empty. Since each $t_1$ data point requires a separate one-dimensional experiment, the number of experiments (and thus the total experimental time) is unnecessarily doubled.

A more efficient and elegant mechanism to distinguish the sign of the modulation in F_1 is to use phase cycling. For example, the pulse sequence of the COSY experiment is $(90^\circ)_1$-$t_1$-$(-90^\circ)_2$-$t_2$(acquire), where the receiver phase is $\psi$. By phase cycling the
pulses \( (\phi_1, \phi_2) \) and the receiver \( (\psi) \) as shown in Table 2, positive and negative modulation frequencies can be distinguished in the F\(_1\) dimension. This allows the transmitter frequency to be placed in the middle of the F\(_1\) frequency range, without resulting in both positive and negative frequencies appearing for the same resonance. In addition, this allows the size of the F\(_1\) frequency range, and thus the total number of experiments needed, to be cut by half.

Table 2. Phase cycling of the pulses \( (\phi_1, \phi_2) \) and the receiver \( (\psi) \) used to distinguish positive and negative modulation frequencies in the COSY experiment.

<table>
<thead>
<tr>
<th>Experiment number</th>
<th>( \phi_1 )</th>
<th>( \phi_2 )</th>
<th>( \psi )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>2</td>
<td>x</td>
<td>y</td>
<td>-x</td>
</tr>
<tr>
<td>3</td>
<td>x</td>
<td>-x</td>
<td>x</td>
</tr>
<tr>
<td>4</td>
<td>x</td>
<td>-y</td>
<td>-x</td>
</tr>
</tbody>
</table>

(e) Processing of Two-Dimensional NMR Experiments

After completion of the acquisition, a two-dimensional NMR data set consists of \( n \) one-dimensional FID's, each of which is composed of \( k \) data points. To transform the data into the desired two-dimensional spectrum, the data set is processed as follows: zero filling, apodization (window multiplication), Fourier transformation, and phase correction.

As explained above, the digital resolution in the F\(_1\) domain is usually kept to a minimum in order to reduce the total time of the experiment. To improve the digital resolution in both the F\(_1\) and F\(_2\) domains, "zero filling" is carried out in each domain (as previously explained in the section "Pulse Fourier Transform NMR").

Apodization is the step which gives the operator the most control over the final presentation of the data. To enhance the S/N ratio, the time-domain FID in each dimension is multiplied by an appropriate apodization function. Fourier transformation
and phase correction are then performed in each dimension. Some examples of apodization functions commonly used are shown in Figure 8. For example, the sine-bell apodization shifted by $\pi/2$ (the left-most curve in Figure 8C) is a cosine function which starts at one and ends at zero. The sine-bell apodization is commonly used in 2D processing, and is optimally shifted and/or squared (see Figures 8C,D) in order to produce the desired S/N ratio and resolution. Figure 9 shows an example of the effect of sine-bell apodization on a 2D COSY spectrum.
Figure 8. Common examples of time-domain apodization functions used in 2D NMR processing (shown for a time-domain of 256 ms): (A) Exponential multiplication with LB = 1, 3 and 5 Hz, (B) Gaussian function with LB = -5 Hz and GB = 0.1, 0.3 and 0.5 times the time-domain, (C) sine-bell shifted by 0, π/2, π/4 and π/8 (labelled 0, 2, 4 and 8), and (D) sine-bell squared shifted by 0, π/2, π/4 and π/8. (From ref [11]).
Figure 9. Effect of sine-bell apodization of a 2D COSY spectrum (from ref [8]): (A) without any apodization, (B) with sine-bell apodization in the $F_2$ dimension, (C) with sine-bell apodization in the $F_1$ dimension, and (D) with sine-bell apodization in both dimensions.
1.4. Nuclear Spin Interactions in the Solid State

The interactions for a nuclear spin in an applied magnetic field can be divided into five main categories [3].

(a) Zeeman interaction of the nucleus with the applied magnetic field
(b) chemical shift interaction caused by magnetic shielding from the surrounding electrons
(c) dipolar interactions with other nuclei
(d) scalar coupling, or J-coupling, interactions with other nuclei
(e) quadrupolar interactions for spins greater than 1/2

In general, the Hamiltonian \( H \) which describes the total nuclear spin interaction may be written as the sum of the individual interactions

\[
H = H_Z + H_{CS} + H_D + H_{SC} + H_Q
\]

(11)

Table 3 compares the nuclear spin interactions in solids and in solution for \(^{13}\)C nuclei.

Table 3. \(^{13}\)C Nuclear Spin Interactions in a 4.7 T Magnetic Field (from ref [12]).

<table>
<thead>
<tr>
<th>Spin Interaction</th>
<th>Magnitude in Solution</th>
<th>Magnitude in Solids</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zeeman</td>
<td>50 MHz</td>
<td>50 MHz</td>
</tr>
<tr>
<td>Chemical Shift</td>
<td>isotropic value</td>
<td>up to 10 kHz</td>
</tr>
<tr>
<td>Dipolar</td>
<td>0</td>
<td>(\approx 15) kHz</td>
</tr>
<tr>
<td>Scalar</td>
<td>(\approx 200) Hz</td>
<td>(\approx 200) Hz</td>
</tr>
<tr>
<td>Dipolar coupling to quadrupolar nuclei</td>
<td>0</td>
<td>up to 1 MHz</td>
</tr>
</tbody>
</table>

In solution NMR, rapid molecular tumbling averages the dipolar and quadrupolar interactions to zero, and the chemical shift interaction to an isotropic value. In the solid-state, however, the interactions are anisotropic (orientation dependent) due to the
relatively fixed orientations of the molecules; therefore, the interactions have a much stronger effect. In general, the interactions in the solid-state are proportional to the product of the appropriate vectors (designated in bold font, e.g. \( \mathbf{I}, \mathbf{S}, \mathbf{B}_0 \)) and a second-rank tensor which describes the three-dimensional nature of the interaction (e.g. chemical shift tensor, \( \mathbf{\delta} \)).

Mathematically, a tensor is a set of quantities that transforms in prescribed ways. Scalar quantities are tensors of rank zero, and vectors are of rank one. Second-rank tensors are composed of \( n^2 \) quantities and can be represented as \( n \times n \) matrices. The chemical shift, dipolar, scalar, and quadrupolar interactions are each described by a \( 3 \times 3 \) matrix (or tensor) which characterizes the three-dimensional nature (i.e. the magnitudes and directions) of the interaction.

(a) Zeeman Interaction

The Zeeman interaction occurs for all nuclei with odd atomic mass or odd atomic number. The interaction between the magnetic moment of the nucleus and the applied magnetic field \( \mathbf{B}_0 \) causes the normally degenerate magnetic spin-energy levels to become non-degenerate, yielding \( 2I + 1 \) energy levels (where \( I \) is the nuclear spin quantum number) of separation \( \hbar \omega_0 / 2\pi = \gamma \hbar \mathbf{B}_0 / 2\pi \). Induced transitions between these energy levels produce the NMR resonance. The Zeeman interaction \( \mathbf{H}_Z \) may be written as

\[
\mathbf{H}_Z = -\frac{\hbar \omega_0}{2\pi} \mathbf{I}_Z = -\frac{\gamma \hbar \mathbf{B}_0}{2\pi} \mathbf{I}_Z = -g_N \beta_N \mathbf{B}_0 \mathbf{I}_Z
\]

where \( \gamma \) is the magnetogyric ratio, \( \omega_0 = \gamma B_0 \) the corresponding Larmor precession frequency, \( g_N \) the nuclear g factor, \( \beta_N \) the Bohr magneton for the particular nucleus, and \( \mathbf{I}_Z \) the spin operator. The energy difference between the quantized energy levels is proportional to \( \mathbf{B}_0 \). Since a larger energy difference leads to a greater population difference between the levels, which corresponds to an increase in the sensitivity of the NMR spectrum, it might seem that working at the highest possible magnetic field would
be most desirable. This is generally true, although the chemical shift interaction (see below) becomes larger at high fields, and is more difficult to average in solid state NMR experiments.

(b) Chemical Shift Interaction

In solution-state NMR, a chemically distinct environment generally gives a single NMR line at a unique resonance frequency, the isotropic chemical shift ($\delta_{\text{iso}}$). The isotropic chemical shift is related to the electronic screening or shielding around the nucleus, and therefore contains information about the chemical environment. Because rapid molecular tumbling occurs in solution, the three dimensional nature of the shielding is averaged to an isotropic value. The observed chemical shift represents this isotropic average.

In a solid, however, there are usually few or no rapid molecular motions. For a rigid solid, the chemical shift depends on the orientation of each crystal with respect to $B_0$. Therefore, in a polycrystalline or powder sample where all crystallite orientations are present, a broad resonance pattern or chemical shift powder pattern is observed.

The chemical shift interaction $H_{CS}$ for a spin $I$ can be expressed as

$$H_{CS} = \frac{\gamma I}{2\pi} \hat{\sigma} \cdot B_0$$

(13)

where $\hat{\sigma}$ is the chemical shift tensor which describes the magnitude and direction of the three-dimensional shielding. The chemical shift interaction varies linearly with the applied field $B_0$, and will therefore be more important at higher magnetic field strengths.

(c) Dipolar Interaction

In solution-state NMR, rapid molecular tumbling causes the dipolar interaction to be averaged to zero. In the solid-state, however, where molecules are much more rigid, the dipolar interaction does not undergo such averaging.
The dipolar interaction arises from the direct through-space dipole-dipole interaction between two nuclei. The dipolar interaction can be either heteronuclear (e.g. $^1$H-$^{13}$C) or homonuclear (e.g. $^1$H-$^1$H) in nature. The heteronuclear dipolar interaction $H_D$ between spins I and S can be written as

$$H_D = \mathbf{I} \cdot \hat{D} \cdot \mathbf{S} = \frac{Dh}{2\pi} (1-3\cos^2\theta) I_Z S_Z$$

(14)

where $D = \frac{\gamma_I \gamma_S h}{2\pi r^3}$

(15)

In Eqs. (14) and (15), $\hat{D}$ is the dipolar coupling tensor, $D$ is the dipolar coupling constant (which is equal to the splitting in a static dipolar powder pattern), $I_Z$ and $S_Z$ are the spin operators, $\gamma_I$ and $\gamma_S$ are the magnetogyric ratios, $r$ is the internuclear distance between the two nuclei, and $\theta$ is the angle between the internuclear vector and the applied magnetic field, as shown in Figure 10. The homonuclear dipolar interaction for a homonuclear I-S spin pair can be written as

$$H_D = \mathbf{I} \cdot \hat{D} \cdot \mathbf{S} = \frac{Dh}{4\pi} (1-3\cos^2\theta) (3I_Z S_Z - \mathbf{I} \cdot \mathbf{S})$$

(16)

There are several important features of the dipolar interaction. There is a strong inverse distance-dependence ($1/r^3$), which means that only neighbouring nuclei will experience a strong interaction. This distance-dependence can be utilized to accurately determine distances between pairs of nuclei. While the scalar coupling interaction (see below) is a through-bond interaction, the dipolar interaction is an entirely through-space interaction. This means that atoms need not be bonded to each other to experience a dipolar interaction. Unlike the chemical shift interaction, the dipolar interaction is independent of the applied magnetic field. Finally, the dipolar interaction is directly proportional to the magnetogyric ratios of the two nuclei; therefore, dipolar interactions will be more important for nuclei with large magnetic moments (e.g. $^1$H).
Figure 10. The geometric relationship of the internuclear vector $\mathbf{r}$ and the angle $\theta$ for an isolated I-S spin pair in an applied magnetic field $B_0$. 
(d) Scalar Interaction

Scalar coupling, or J-coupling, arises from indirect spin-spin coupling between two spins via their electronic surroundings. The coupling occurs when the spin of a nucleus correlates with the spin of a bonding electron, which in turn influences other neighbouring nuclear spins. The scalar interaction appears in an NMR spectrum as J-couplings, which are used extensively in solution spectra for structural and conformational analysis. Like the dipolar interaction, the scalar interaction can be either heteronuclear or homonuclear in nature. The heteronuclear scalar interaction $H_{SC}$ between spins I and S can be written as

$$H_{SC} = I \cdot \mathbf{J} \cdot S$$

(17)

where $\mathbf{J}$ is the scalar coupling tensor. The homonuclear scalar interaction for a homonuclear I-S spin pair can be written in an analogous manner.

There are some important features of the scalar interaction. It depends on through-bond interactions, rather than through-space interactions like the dipolar interaction. It is independent of the applied magnetic field, and is usually smaller than the other interactions under consideration (e.g. dipolar, quadrupolar). Finally, isotropic J-couplings are of very similar magnitude in solution and in the solid state, only differing if the geometry changes upon going from solid to solution.

(e) Quadrupolar Interaction

For nuclei with spin $I > 1/2$, a quadrupole moment $eQ$ arises from the non-spherical distribution of electric charge in the nucleus. The quadrupolar interaction arises from the interaction of the quadrupole moment with the non-spherically symmetrical electric field gradient (EFG) around the nucleus. The interaction may be written as

$$H_Q = I \cdot \hat{Q} \cdot I$$

(18)

where

$$\hat{Q} = \frac{eQ}{2I(2I-1)\hbar} \hat{V}$$

(19)
In Eqs. (18) and (19), $\hat{Q}$ is the quadrupolar coupling tensor which describes the three-dimensional nature of the interaction, and $\hat{V}$ is the EFG tensor at the nuclear site. The components of $\hat{V}$ completely describe the orientation and magnitude of the EFG. In a suitable coordinate system (the principal axis system), $\hat{V}$ is converted to a diagonal form where the principal elements $q_{xx}$, $q_{yy}$ and $q_{zz}$ describe the size and shape of the EFG, with $q_{zz}$ being the principal component of $\hat{V}$. Often, $q_{zz}$ is simply referred to as the "electric field gradient". The value of an asymmetry parameter $\eta_Q$ is defined as

$$\eta_Q = \frac{q_{xx} - q_{yy}}{q_{zz}}$$  (20)

If the EFG is symmetric about the principal axis, $q_{zz}$ is unique, $q_{xx} = q_{yy}$, $\eta_Q = 0$, and the EFG is "axially symmetric".

Many of the nuclei present in inorganic systems, and most of the nuclei observable by NMR, are quadrupolar with non-integral spins, such as $^{27}$Al ($I = 5/2$), $^{23}$Na ($I = 3/2$), and $^{17}$O ($I = 5/2$). The effect of the quadrupolar interaction on the Zeeman splitting for a spin-5/2 nucleus is shown in Figure 11. The central $+1/2 \leftrightarrow -1/2$ transition is unaffected by the first-order quadrupolar interaction, $H_Q^{(1)}$, since both levels are shifted by the same amount in the same direction, and is usually the only transition observed in the spectrum. For the other transitions, the first-order quadrupolar frequencies are anisotropic (i.e. dependent on the orientation of the crystallite to the magnetic field). These are called the satellite transitions, and are usually too broad (due to the anisotropy) and shifted too far from resonance to be observed directly. The central transition is affected only by the anisotropic second-order quadrupolar interaction, $H_Q^{(2)}$, which broadens the resonance, distorts its lineshape, and shifts its observed frequency by

$$\omega_{CG} - \omega_0 = -\frac{1}{30} \frac{\omega_Q^2}{\omega_0} \left\{ I(I + 1) - \frac{3}{4} \right\} \left\{ 1 + \frac{1}{3} \eta_Q^2 \right\}$$  (21)
where \( \omega_Q = \frac{3e^2 q_{zz} Q}{2I(2I - 1)h} \)  

In Eqs. (21) and (22), \( \omega_{CG} \) is the centre of gravity of the observed peak, \( \omega_0 \) the Larmor frequency (in Hz), and \( \omega_Q \) the quadrupolar frequency. From Eq. (21), the second-order quadrupolar interaction is inversely proportional to \( \omega_0 \) (i.e. inversely proportional to \( B_0 \) since \( \omega_0 = \gamma B_0 \)). Therefore, lineshape distortions and peak shifts from the second-order quadrupolar interaction can be minimized by working at as high a magnetic field strength as possible.

In conclusion, there are fundamental differences between solution and solid-state NMR spectroscopy. In solution, rapid and random molecular motions produce an isotropic average of each of the interactions equal to \( \frac{1}{3} \) of the trace (sum of the diagonal elements) of the diagonalized matrix of the corresponding second-rank tensor. Since the dipolar coupling and quadrupolar coupling tensors are traceless, their isotropic values are zero, and these interactions are not observed in the solution NMR spectrum. The chemical shift tensor and scalar coupling tensors have non-zero traces, resulting in discrete isotropic values for these interactions which are observed as the isotropic chemical shift (\( \delta \)) and J-coupling, respectively. Since these both depend on the local chemical environments, they are widely and successfully used for structure determinations in solution. In the solid-state, however, the interactions are not averaged or are only partly averaged since the molecules are much less mobile. The NMR spectra of solids are therefore more complex, with linewidths up to several kHz (see Table 3), but potentially they contain more information than solution spectra as the individual principal components of the interactions may be found rather than just their average values. However, in order to obtain easily interpretable structural information, the solid-state spectra must be simplified to obtain higher resolution. Techniques developed for this purpose will be discussed in the following section.
Table 1. Comparison of energy levels for a spin-5/2 nucleus under the influence of the Zeeman interaction and the first and second orders of the quadrupolar interaction.

<table>
<thead>
<tr>
<th>m</th>
<th>No Quadrupolar Interaction</th>
<th>First-Order Quadrupolar Interaction</th>
<th>Second-Order Quadrupolar Interaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>-5/2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-3/2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-1/2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>+1/2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>+3/2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>+5/2</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 11. The energy levels for a spin-5/2 nucleus under the influence of the Zeeman interaction and the first and second orders of the quadrupolar interaction. The central +1/2 $\leftrightarrow$ -1/2 transition is indicated by the vertical arrow.
1.5. Techniques used to obtain high resolution NMR spectra of solids

As discussed in the previous section, nuclear spin interactions in the solid state yield NMR spectra with linewidths up to several kHz. There are some important experimental techniques, however, which can be employed to average or reduce the interactions in order to obtain high resolution spectra of solids. Two commonly used techniques are high-power decoupling and magic angle spinning (MAS). In the case of quadrupolar nuclei, however, MAS does not completely average the second-order quadrupolar interaction, and lineshape distortions and peak shifts may occur. To overcome this, the recently introduced techniques of double rotation (DOR) and dynamic angle spinning (DAS) can be used.

(a) High-Power Decoupling

For most dilute spin-1/2 systems (i.e. with a low concentration of magnetically active nuclei, e.g. $^{13}$C), the major source of linebroadening in solid state NMR spectra is the heteronuclear dipolar coupling between the dilute spins and abundant spins (usually $^1$H), which causes a modulation of the effective local field around the dilute nucleus. It is possible to eliminate this interaction by applying a strong radiofrequency field to the $^1$H spins at their Larmor frequency. This causes the interconversion frequency of the $z$-components of the $^1$H spins to be large compared to the dipolar interaction, causing their contribution to the effective local field to become zero on the NMR timescale. Therefore, the $^1$H spins are "decoupled" from the dilute spins, greatly improving the resolution of the dilute spin spectrum.

Decoupling is a concept familiar from solution-state NMR, in which $^1$H decoupling is employed to remove scalar couplings. Since the scalar couplings are very small ($\leq 200$ Hz), only low-power decoupling ($\sim 5$ W) is required. The dipolar interactions in the solid-state, however, are much larger than the scalar interactions.
Therefore, the decoupling power required in the solid-state must be high enough so that the interconversion frequency of the z-components of the $^1$H spins is large compared to the magnitudes of all of the spin-spin interactions (i.e. both $^1$H-$^1$H and $^1$H-$^1$C). Since the total $^1$H-$^1$H dipolar interactions can be very large (up to 40 kHz in rigid organic solids), a decoupling power of approximately 1000 W is usually required.

(b) Magic Angle Spinning (MAS)

Linebroadening in solid state NMR spectra is primarily due to the dipolar, chemical shift anisotropy, and quadrupolar interactions. All of these interactions have, to first order, an orientation dependence containing the factor $(3 \cos^2 \theta - 1)$ where $\theta$ is the angle between a specific molecule-fixed vector (e.g. the internuclear vector for the dipolar interaction) and the applied magnetic field $B_0$ (see Figure 10). In solution, rapid molecular tumbling averages the value of $(3 \cos^2 \theta - 1)$ to zero, yielding narrow lines.

In the solid state, even when the molecules are rigid, motion of the nuclei can be introduced if the sample is rotated with an angular velocity $\omega_t$ about an axis $R$ which is inclined at an angle $\alpha$ to $B_0$, as shown in Figure 12. The specific molecule-fixed vector $\mathbf{r}$ makes an angle $\beta$ with respect to the spinning axis $R$. The angle $\theta$ between $\mathbf{r}$ and $B_0$ will thus vary between $(\alpha - \beta)$ and $(\alpha + \beta)$. The value of each interaction depends on the average value of $(3 \cos^2 \theta - 1)$ about the conical path, which can be expanded as [13]:

$$
(3 \cos^2 \theta - 1) = \frac{1}{2} (3 \cos^2 \alpha - 1) (3 \cos^2 \beta - 1) + \frac{3}{2} \sin^2 \alpha \sin^2 \beta \cos(\omega_t t) + \frac{3}{2} \sin^2 \alpha \sin^2 \beta \cos(2\omega_t t)
$$

A sufficiently high value of $\omega_t$ (i.e. "fast spinning" compared to the frequency of the interaction) averages the time-dependent parts of Eq. (23) to zero (i.e. the average values of both $\cos(\omega_t t)$ and $\cos(2\omega_t t)$ become zero). The term $1/2 (3 \cos^2 \alpha - 1)$, therefore, acts as a scaling factor for $(3 \cos^2 \theta - 1)$ since the angle $\alpha$ is under experimental control. If $\alpha = 0^\circ$ (rotation about $B_0$), then $1/2 (3 \cos^2 \alpha - 1) = 1$, and there is no scaling of the
Figure 12. Schematic representation of the geometric arrangement for mechanical sample spinning: The solid sample is rotated with an angular velocity $\omega_R$ about an axis $R$, which is inclined to the magnetic field axis $B_0$ by an angle $\alpha$. The specific molecule-fixed vector $\mathbf{r}$ makes an angle $\beta$ with the rotation axis, and is inclined to the magnetic field by an angle $\theta$ which varies periodically as the sample rotates.
interactions. Therefore, measuring a spectrum while spinning at 0° is equivalent to measuring a spectrum of a stationary sample. At an angle of $\alpha = 54.7^\circ$, however, 

$$\frac{1}{2} (3 \cos^2 \alpha - 1) = 0.$$ 

Therefore, the average value of $(3 \cos^2 \theta - 1)$ is zero for all orientations, and the effects of all first-order interactions in the spectrum are entirely removed (provided the spinning speed is fast enough), resulting in sharp NMR resonances. The angle 54.7° is therefore called the "magic angle", and spinning about 54.7° is known as "magic angle spinning" (MAS). The discovery of MAS was made independently in 1958-59 by Andrew et al. [14] and Lowe [15].

Therefore, MAS simulates isotropic molecular tumbling, resulting in high resolution spectra of solids. There are, however, limitations to the MAS technique.

Homonuclear dipolar interactions can only be completely averaged by spinning faster than the static coupling strength [16], which can be up to several tens of kHz. This has led to the development of ultra-fast spinning devices [17] which are, at present, capable of reaching speeds as high as 25 kHz. The problem of homonuclear dipolar coupling does not occur, however, if the nucleus being studied is of low natural abundance (e.g. $^{13}$C, 1.1% abundance), since the NMR active nuclei are diluted in the sample (i.e. a "dilute" nucleus). In cases where the natural abundance is high, there may be physical dilution if few such nuclei are present (often the case for $^{31}$P), or the nucleus may be artificially diluted in a different isotope (e.g. $^1$H diluted in $^2$H in highly deuterated materials).

For a dilute nucleus where homonuclear interactions are absent, spinning at frequencies lower than the frequency width of the chemical shift anisotropy powder pattern does not completely average the time-dependent parts of Eq. (23). This produces a series of spinning sidebands spaced at multiples of the rotation frequency and centred about the isotropic chemical shift [18]. Since the width of the chemical shift anisotropy pattern is proportional to the applied magnetic field strength, there will be a larger sideband pattern at higher field strengths for the same spinning rate.
In the case of quadrupolar nuclei, the central \( +1/2 \leftrightarrow -1/2 \) transition is independent of the quadrupolar interaction to first-order, but is broadened and shifted from its isotropic chemical shift by the second-order interaction. (This is described in detail in the previous section on Nuclear Spin Interactions in the Solid State.) The second-order quadrupolar interaction, which becomes larger as the quadrupolar interaction becomes larger, is reduced but not completely eliminated by MAS. Therefore, undesired lineshape distortions and peak shifts caused by the second-order quadrupolar interaction may still be present under MAS conditions, although they are smaller at higher magnetic field strengths (i.e. proportional to \( 1/B_0 \)). Therefore, for quadrupolar nuclei, it is often desirable to use as high a magnetic field strength as possible.

For quadrupolar \( I \) spins in a solid sample, usually only the central \( (+1/2 \leftrightarrow -1/2) \) transition is excited and detected in the spectrum. For the \( I \) spins in solution, however, the energy levels are degenerate and all of the transitions are observed. In this situation, the 90° pulse length for the \( I \) nuclei in the solid sample is scaled by a factor of \( 1/(1+1/2) \) as compared to the 90° pulse length for the \( I \) nuclei in solution [19,20]. For \( ^{27}\text{Al} \) (\( I=5/2 \)) nuclei, for example, the 90° pulse length measured on a solid sample is \( 1/3 \) of the 90° pulse length for \( ^{27}\text{Al} \) spins in solution.

As an additional consideration, the different resonances in the spectrum may have different quadrupolar couplings. It has been shown [21] that in this situation, the signal from each resonance as a function of the pulse angle \( \theta \) is only quantitative when \( \theta \leq 90°/(2I + 1) \). Therefore, to obtain quantitative spectra, small pulse angles should be used (e.g. for \( ^{27}\text{Al} \) (\( I=5/2 \)), the pulse angle should not exceed 15°).

Although the resonances in the MAS spectra of quadrupolar nuclei are broadened due to the second-order quadrupolar interaction, in many cases there is still enough resolution to clearly distinguish signals from distinct environments. For example, in \( ^{27}\text{Al} \) MAS spectra, resonances from tetrahedral and octahedral aluminum can usually be
distinguished. In other cases, however, the second-order quadrupolar interaction can broaden the peaks to the extent that MAS can no longer resolve the resonances from different environments. To overcome this problem, two new experiments have recently been introduced which involve rotation around two angles to average the second-order quadrupolar interaction, resulting in sharp spectral lines. These two new techniques, which will be discussed next, are double rotation and dynamic angle spinning.

(d) Double Rotation (DOR) and Dynamic Angle Spinning (DAS) Experiments

For many quadrupolar nuclei such as $^{27}$Al and $^{17}$O, the quadrupolar interaction is the dominant line broadening mechanism in the spectrum. Although the quadrupolar interaction is averaged to first-order by MAS, there is no single angle at which the sample can be spun to average the second-order interaction. Therefore, even under MAS, the anisotropy of the second-order quadrupolar interaction can result in severe line broadening. In recent years, two new experiments have been introduced [22] which use rotation around two angles to average the second-order quadrupolar interaction to its isotropic value, resulting in sharp lines in the spectra of quadrupolar nuclei: double rotation (DOR) and dynamic angle spinning (DAS).

In DOR experiments [23,24], there are two spinners spinning simultaneously around two independent axes, as shown in Figure 13a: an outer spinner inclined to the magnetic field at the "magic angle" of 54.74°, and an inner spinner, which contains the sample, inclined at an angle of 30.56° with respect to the outer spinner. These two angles are chosen such that simultaneous spinning averages the second-order quadrupolar interaction to its isotropic value.

For DAS experiments [25,26], the sample, contained within a single spinner, is first spun at one angle ($\theta_1$) for a fixed period of time. The spinner is then "hopped" to spin at a second angle ($\theta_2$) for another fixed period of time (see Figure 13b). Sets of complementary angles ($\theta_1$, $\theta_2$) are available which will average the second-order
Figure 13. Schematic representation of (a) double rotation (DOR) and (b) dynamic-angle spinning (DAS) techniques (from ref [27]).
quadrupolar interaction to its isotropic value, but different times must be spent at each of the two individual angles depending on the pair of angles chosen. For the complementary angles $\theta_1 = 37.38^\circ$ and $\theta_2 = 79.19^\circ$, equal times are spent at both angles [26,28].

DAS experiments have proved most useful in obtaining high-resolution $^{17}$O spectra of $^{17}$O-enriched highly-ordered mineral samples. (To date, however, no DAS results have been reported on molecular sieve materials.) Although the MAS spectra give substantial line narrowing compared to the static spectra, the second-order quadrupolar interaction is still dominant. The DAS spectra, however, show very sharp lines, reflecting the averaging of the second order quadrupolar interaction. In contrast to DAS experiments, DOR experiments have been reported for molecular sieve systems. In the aluminophosphate molecular sieve VPI-5, for example, there are two crystallographically inequivalent tetrahedral Al positions in the hydrated framework. The $^{27}$Al MAS spectrum, however, shows only one resonance in the tetrahedral region, in addition to the octahedral Al resonance. With DOR, however, the resonances are much narrower, and furthermore, the tetrahedral resonance is now split into two signals, reflecting the two tetrahedral Al positions [29].
1.6. Solid-State Double-Resonance NMR Experiments

(a) Cross-Polarization

The techniques of magic angle spinning (MAS) and high-power decoupling (if $^1$H nuclei are present) usually provide the resolution necessary to obtain chemical and structural information about individual dilute spins in solids [18]. However, for most dilute spin-1/2 nuclei (e.g. $^{13}$C), the pulse NMR experiment suffers from the disadvantages of low sensitivity and the requirement of long recycle delays due to the relatively long $T_1$ relaxation times. The technique of cross-polarization (CP), introduced by Pines, Gibby and Waugh [30,31], in which spin polarization and thus net magnetization is transferred from abundant spins (usually $^1$H) to dilute spins (e.g. $^{13}$C, $^{15}$N, $^{29}$Si) via the dipolar interaction, eliminates these disadvantages. The CP experiment provides a maximum signal enhancement of $\gamma_I/\gamma_S$ where I and S represent the abundant and dilute spins, respectively. (For the usual case of $^1$H $\rightarrow$ $^{13}$C CP, the maximum enhancement is $\gamma_H/\gamma_C = 4$.) CP also allows for much shorter recycle delays, since the repeat time of the experiment is determined by the $T_1$ value of the source $^1$H nuclei, which is usually much shorter than those of the dilute nuclei.

The cross-polarization experiment is a double-resonance experiment with polarization transfer from I spins to S spins, where the I and S spins are normally both spin-1/2 (e.g. $^1$H and $^{13}$C). Figure 14a shows the pulse sequence for the CP experiment, while Figure 14b shows the corresponding vector diagrams (in the rotating frame) for the usual case of $^1$H $\rightarrow$ $^{13}$C CP. Initially, both I and S spins are at their equilibrium magnetization distributions. The first step in the CP experiment is to apply a 90° radiofrequency (r.f.) pulse (along the x' axis in the rotating frame) to the I spins, which rotates the I spin magnetization down to the y' axis. The I spin magnetization is then spin-locked by applying a spin-locking r.f. field of strength $B_{1,I}$ along y'. Note that the phase of the spin-lock pulse is shifted by 90° from the phase of the initial pulse. This
Figure 14. (a) Pulse sequence for cross-polarization experiment from I spins to S spins. (b) Vector diagrams for the $^1\text{H} \rightarrow ^{13}\text{C}$ cross-polarization experiment, as described in the text (from ref [12]).
spin-locking field causes the individual magnetization vectors to rotate around the y' axis, resulting in a net magnetization along y'. During this $B_{1,I}$ spin lock pulse, a field $B_{1,S}$ is applied to the S spins. The time period during which both spin-locking fields are applied is known as the "contact time". The amplitudes of the two r.f. fields are adjusted so that the Hartmann-Hahn matching condition (see below) is satisfied during the contact time.

The Hartmann-Hahn matching condition [32] means that, in their respective rotating frames, the I and S nuclei both precess at equal frequencies around their spin locking fields. Therefore, the energy required for spin flips is identical for both spins, allowing an efficient transfer of magnetization via the dipolar interaction. For cross-polarization involving only spin-1/2 nuclei (e.g. $^1\text{H} \rightarrow ^{13}\text{C}$ CP), the matching condition is set such that the two r.f. field strengths, $\gamma_X B_{1,X}$, are equal:

$$\gamma_I B_{1,I} = \gamma_S B_{1,S} \quad (24)$$

with $\gamma_X$ the magnetogyric ratio, and $B_{1,X}$ the strength of the X nucleus r.f. field (in tesla). Since the r.f. field strength (in frequency units) is equal to the reciprocal of the 360° pulse time, $t_{360}^X$, viz.:

$$\gamma_X B_{1,X} = \frac{1}{t_{360}^X} = \frac{1}{4 t_{90}^X} \quad (25)$$

the matching condition corresponds experimentally to setting the 90° pulse times, $t_{90}^X$, to be equal on both channels.

After the contact time where both r.f. fields are on, the S spin free induction decay signal is recorded in the presence of the $B_{1,I}$ field for decoupling of the I ($^1\text{H}$) spins. The CP experiment is selective in that only the S nuclei which are dipolar-coupled (i.e. close in space or "connected") to the I nuclei will show signals in the spectrum, while any uncoupled S nuclei will be absent.
(b) Cross-Polarization Between $X_1/X_2$ Nuclei

Historically, cross-polarization has been used to transfer spin coherence from abundant spins to a dilute spin system [33]. Protons ($^1H$) have been used almost exclusively as the abundant spin system, although there have been some examples where other abundant nuclei such as $^{19}F$ have been used [34,35]. Another notable exception is found in the studies of Schaefer and co-workers involving magnetization transfer between $^{13}C$ and $^{15}N$ in isotopically enriched materials [36,37]. For a review of cross-polarization experiments involving less common pairs of nuclei, see reference [38].

For a pair of isolated spins $X_1$ and $X_2$ (neither of which is $^1H$) where both types of nuclei are spin-$1/2$, and where there are no other dipolar-coupled nuclei (particularly protons) present, the $X_1 \rightarrow X_2$ cross-polarization experiment is generally as described previously in section (a). There is usually not as large an enhancement of the signal-to-noise ratio as in the corresponding $^1H \rightarrow X$ CP experiment, however, for several reasons: $\gamma_{X_1}$ is considerably smaller than $\gamma_H$ (the maximum signal enhancement is $\gamma_{X_1}/\gamma_{X_2}$ instead of $\gamma_{H}/\gamma_X$), the $T_1$ values of the source $X_1$ nuclei (which determine the repeat time of the experiment) are usually longer, the dipolar interactions (through which polarization transfer occurs) are smaller due to both smaller magnetogyric ratios and larger internuclear distances, and the natural abundances of the $X_1$ and $X_2$ isotopes will often be less than 100% unless isotopically enriched. However, although the S/N ratio is not enhanced as much, the $X_1 \rightarrow X_2$ CP experiment is still important in that it offers selectivity. Only the $X_2$ nuclei which are dipolar-coupled (i.e. close in space or "connected") to the $X_1$ nuclei will show signals in the $X_1 \rightarrow X_2$ CP spectrum, while any uncoupled $X_2$ nuclei will be absent. Therefore, connectivities between $X_1$ and $X_2$ nuclei may be determined using the CP experiment.

In the more general case, protons will be present, and thus a triple-resonance experiment $^1H/X_1/X_2$ must be performed since the $^1H$ nuclei must be decoupled during acquisition. The technical complexity of the experiment is a disadvantage, particularly in
probe construction, but there is a substantial advantage in that $^1\text{H}$ can be used as the primary magnetization reservoir, and the signal-to-noise ratio of the whole experiment improved. This is the case for the double-cross-polarization experiment.

The elegant technique of double-cross-polarization (DCP), introduced by Schaefer, Stejskal, and McKay [36], enables one to selectively observe one type of NMR active nuclear spin (e.g. $^{15}\text{N}$) which is directly bonded to another (e.g. $^{13}\text{C}$) by successive cross-polarization transfers. For example, cross-polarization from $^1\text{H}$ to $^{13}\text{C}$ and then from $^{13}\text{C}$ to $^{15}\text{N}$ with final $^{15}\text{N}$ detection will yield a $^{15}\text{N}$ spectrum showing resonances from only those $^{15}\text{N}$ nuclei bonded to $^{13}\text{C}$, since the $^{13}\text{C}$ to $^{15}\text{N}$ polarization transfer is the only source of $^{15}\text{N}$ magnetization. Similarly, successive CP transfers from $^1\text{H}$ to $^{15}\text{N}$ to $^{13}\text{C}$ with $^{13}\text{C}$ detection will yield a $^{13}\text{C}$ spectrum with resonances from only those $^{13}\text{C}$ nuclei directly bonded to $^{15}\text{N}$. In both cases, the initial cross-polarization from $^1\text{H}$ to the first set of nuclei maximizes the difference between their magnetizations and that of the third set of nuclei, optimizing the second CP step.

The DCP technique has been used by Schaefer et al. to study $^{15}\text{N}$-$^{13}\text{C}$ labels in glycine [36], and in soybean leaves to non-destructively determine the rate of protein turnover [37]. In a more recent application of the DCP experiment, Hagaman et al. [39] have selectively observed carbon atoms that are directly attached to phosphorus atoms in a variety of organophosphorus compounds.

(c) Cross-Polarization Involving Quadrupolar Nuclei

Double-resonance NMR connectivity experiments involving quadrupolar nuclei are a major topic of this thesis. Therefore, previous examples of CP experiments involving quadrupolar nuclei are discussed in this section.

Very few examples exist of cross-polarization experiments involving quadrupolar nuclei, and they all involve magnetization transfer from protons to quadrupolar nuclei [39-50]. Prior to the work described in this thesis, there were no reports of cross-
polarization in which quadrupolar nuclei were used as the magnetization source (i.e. transfer from quadrupolar to spin-1/2 nuclei). This is due to the difficulty in spin-locking quadrupolar spins under MAS conditions. As previously described in the section "Nuclear Spin Interactions in the Solid State", in solid-state NMR investigations of quadrupolar nuclei with non-integral spins (S=3/2, 5/2, 7/2, etc.), it is usually only the central +1/2 ↔ -1/2 transition which is observed since this transition is unaffected by the quadrupolar interaction to first-order. However, it is affected to second-order and MAS does not completely average the effect, giving rise to distorted lineshapes and shifts in resonance frequencies. Where necessary, the second order quadrupolar interaction may be averaged to its isotropic value by double rotation (DOR) and dynamic-angle spinning (DAS) techniques (as described previously), but in many cases the spectra are sufficiently well resolved using MAS at high field, and it is mainly these cases which have been investigated in the present work.

For CP involving protons (I=1/2) and quadrupolar nuclei (S=3/2, 5/2, etc.), a more general expression [33] for the Hartmann-Hahn matching condition must be used, as compared to Eq. (24).

\[ \gamma_H B_{1,H} = (S+1/2) \gamma_S B_{1,S} \]  

(26)

Here, \( \gamma \) and \( B_1 \) are the magnetogyric ratios and r.f. field strengths, respectively, of the nuclei involved. The term \( (S+1/2) \) may be viewed as a scaling factor of the r.f. field in solids when only irradiating the central transition, compared to the non-selective pulse applied in solution. For \( S=3/2 \) (e.g. \( ^{23}\text{Na} \), \( ^{11}\text{B} \)), \( (S+1/2)=2 \), and for \( S=5/2 \) (e.g. \( ^{27}\text{Al} \), \( ^{17}\text{O} \)), \( (S+1/2)=3 \).

The maximum gain obtainable from an I → S CP experiment depends on the ratio of the magnetogyric ratios and the heat capacities of the two reservoirs.

\[ \frac{M_{\text{CP}}}{M_O} = \frac{\gamma_I}{\gamma_S} \left[ \frac{1}{1+\varepsilon} \right] \]  

(27)
Here, the factor $\epsilon$ is the ratio of the two heat capacities, as in Eq. (28), where $N_S$ and $N_I$ are the numbers of the respective spins which can be estimated, to a degree, if the detailed structure is known, and the transition is between the $m$ and $(m-1)$ levels (usually $m=1/2$).

$$
\epsilon = \frac{N_S}{N_I} \left[ \frac{S(S+1) - m(m-1)}{I(I+1)} \right]
$$

For the usual case of $^1\text{H} \rightarrow ^{13}\text{C}$ CP, there is a large excess of protons (i.e. $N_I >> N_S$), and the factor $\epsilon$ becomes negligible. Thus, the theoretical CP enhancement (Eq. (27)) is usually expressed as $\gamma_I/\gamma_S$. For CP experiments involving quadrupolar nuclei, however, neither nucleus may be in large excess (i.e. $N_I = N_S$), and the factor $\epsilon$ becomes important. For $I=1/2$ (protons) and $S=3/2$, this factor $\epsilon$ equals 16/3, and for $S=5/2$, $\epsilon$ equals 12. This greatly reduces the potential gains from the CP process for quadrupolar nuclei.

In an ideal situation, a solid reference material can be found where the quadrupolar nucleus is present in a perfectly cubic environment, the spin energy levels are degenerate, and therefore the nucleus behaves as a spin-1/2 system. In this way, the Hartmann-Hahn matching condition may be optimized experimentally, and the correct matching condition for the same nucleus in non-cubic environments set by reducing the 90° pulse length for the quadrupolar nucleus by the scaling factor $(S+1/2)$ according to Eq. (26).

Such a situation was identified by Harris and Nesbitt [47] for the case of $^{23}\text{Na}$ ($S=3/2$). In $\text{Na}^+\text{BH}_4^-$, the lattice is face-centered cubic, and there is also rotation of the tetrahedral $\text{BH}_4^-$ ion giving a perfectly cubic environment for the $\text{Na}^+$ ion. At 4.7 T, the $^{23}\text{Na}$ nucleus behaves like a spin-1/2 system and responds well to a conventional $^1\text{H} \rightarrow ^{23}\text{Na}$ cross-polarization experiment. In non-cubic environments such as borax ($\text{Na}_2\text{B}_2\text{O}_7\cdot10\text{H}_2\text{O}$) cross-polarization is again achieved, but with the $^{23}\text{Na}$ r.f. field reduced by a factor of $(S+1/2)=2$. 

One very important factor to be considered in the case of quadrupolar nuclei is that their spin-lattice relaxation times are usually very short, and spectra are often easily obtained without the need for cross-polarization. Thus, cross-polarization will be useful usually only in terms of the selectivity that it introduces into the experiment. For example, Oldfield and co-workers [45] have used $^1H \rightarrow ^{17}O$ cross-polarization to select the $^{17}O$ spectrum of the "surface" oxygen in Si-OH groups in various inorganic systems. Figure 15 shows the $^{17}O$ MAS and $^1H \rightarrow ^{17}O$ CP/MAS spectra of an $^{17}O$-enriched sample of boehmite (AlO(OH)) which has two equally abundant oxygen sites: Al-O-Al and Al-O-H. The $^1H \rightarrow ^{17}O$ CP spectrum clearly discriminates in favour of the O-H functionality as expected from the short $r_{O-H}$ distance. Similarly, in the case of zeolites, $^1H \rightarrow ^{27}Al$ cross-polarization has been used to select the aluminum atoms in the vicinity of hydroxyl functionalities in aluminas [41].

Recently, a theoretical description of the behaviour of quadrupolar spins under spin-locking conditions, an essential component of the CP experiment, was presented by Vega [49]. He showed that for quadrupolar nuclei, the spin-locking of the central $+1/2 \leftrightarrow -1/2$ transition under MAS conditions is a complex process due to the time-dependence of the first-order quadrupolar splitting, which results in the spin-locking efficiency being drastically reduced during the sample rotation as compared to a static experiment (shown in Figure 16a for the case of $^{23}Na$ spin-locking efficiency in NaOH).

Of particular importance, Vega demonstrated that this reduced spin-locking efficiency leads to a dramatic reduction in the efficiency of the cross-polarization process [50]. This is illustrated for the case of $^1H \rightarrow ^{23}Na$ cross-polarization in NaOH, presented in Figure 16b. The $^{23}Na$ magnetization generated by cross-polarization drops off very abruptly and does not reach as high a value in the MAS case as compared to the static sample. Even though the behaviour is a complex function of the spinning rate, spin-locking r.f. field strength, and quadrupolar coupling frequency, the following general rule should be kept in mind for cross-polarization involving quadrupolar nuclei under MAS.
Figure 15. (A) $^{17}\text{O}$ MAS and (B) $^1\text{H} \rightarrow ^{17}\text{O}$ CP/MAS spectra of an $^{17}\text{O}$-enriched sample of boehmite (AlO(OH)), with spinning sidebands indicated by * (from ref [45]).
Figure 16. (a) $^{23}$Na spin-locking efficiency and (b) $^1$H → $^{23}$Na CP efficiency in NaOH under static and MAS conditions (from ref [50]).
conditions: Cross-polarization efficiency is optimized under either very slow or very fast sample spinning, but at intermediate speeds, the loss of magnetization out of the central transition of the quadrupolar nuclei during spin-locking will cause loss of signal.

Inorganic materials such as zeolite and aluminophosphate molecular sieves, gels, and ceramics are of great technological importance, and contain many quadrupolar nuclei but few protons. The attainment of cross-polarization from quadrupolar nuclei to spin-1/2 nuclei, which will be described in Chapter 2, may be particularly important in materials chemistry since quadrupolar nuclei usually have very short $T_1$ relaxation times. Spin-1/2 nuclei in dense inorganic systems usually have much longer $T_1$ values, ranging from several seconds to hours, often precluding their direct observation. By using CP from the quickly relaxing quadrupolar spins, spectra of the spin-1/2 nuclei could perhaps be obtained using much shorter recycle delays. Additional information regarding the local structure and bonding in these systems might also be obtained from the distance dependence of the dipolar interaction through which which the CP experiment occurs.

(d) REDOR and TEDOR Experiments

Besides cross-polarization, there are other double-resonance (i.e. involving two nuclear spins, $X_1/X_2$) NMR experiments which could be used to determine heteronuclear connectivities in solids. The REDOR (rotational-echo double-resonance) [51,52] and TEDOR (transferred-echo double-resonance) [53,54] experiments were introduced by Schaefer and co-workers to measure heteronuclear dipolar couplings in solids. Since the dipolar coupling is strongly distance-dependent (Eq. (15)), the internuclear distance can then be accurately determined. (The REDOR and TEDOR experiments are described in detail in Section 2.2e and f.)

Schaefer and co-workers have used the REDOR experiment to determine heteronuclear dipolar couplings between isotopically-enriched $^{13}\text{C}^{15}\text{N}$ spin pairs in amino acids and peptide fragments [51,55,56]. Since the magnitude of the dipolar
coupling is proportional to the inverse third power of the internuclear distance, this
allows the internuclear distance to be determined very accurately. For example, REDOR
was used to measure a precise $^{13}$C-$^{15}$N interatomic distance in a double-labelled fragment
of the helical peptide antibiotic, emerimicin [55].

The REDOR experiment marks a significant advance in the structural
determination techniques available for protein systems. Immobilized proteins with solid-
like properties (for example, proteins embedded in membranes, or rigidly attached to cell
walls) are not amenable to X-ray or solution NMR techniques. The problem lies in the
inability to prepare samples in a crystalline form suitable for X-ray analysis, or to
interpret the solution NMR spectra which display the broad lines of membrane-bound
species with solid-like properties. However, for these systems, and for crystalline and
noncrystalline solid proteins, peptides, and their complexes, the measurement of
individual internuclear distances is made possible by the REDOR experiment.

The TEDOR experiment has been used to measure $^{13}$C-$^{15}$N internuclear distances
in double-labelled amino acids and the linear peptide antibiotic, gramicidin [54]. In a
landmark experiment [57], a combination of REDOR and TEDOR experiments was used
to measure an 8 Å $^{19}$F-$^{13}$C internuclear distance in the double-labelled helical peptide
antibiotic, emerimicin.

(e) Dipolar-Dephasing Difference Experiments

The dipolar-dephasing difference MAS NMR experiment, introduced by Veeman
and co-workers [58], has been used to demonstrate $^{27}$Al-$^{31}$P and $^{27}$Al-$^{29}$Si connectivities
in the molecular sieves AlPO$_4$-5 and zeolite NaA, respectively. In both of these systems,
however, there is only one resonance present for each of the nuclei. The dipolar-
dephasing difference experiments can only be used to determine qualitative
connectivities, but not distance information as in the REDOR and TEDOR experiments.
(The dipolar-dephasing difference experiment is described in detail in Section 2.2c.)
1.7. Solid State NMR Experiments on Zeolites and Related Molecular Sieves

Zeolites and other related molecular sieves are well-defined crystalline materials, and were thus investigated in this thesis both as test samples and as useful applications of the techniques.

(a) Introduction

Zeolites are open framework aluminosilicates, widely used in industrial applications as catalysts, molecular sieves, cation exchangers and adsorbents [59-62]. The worldwide annual use is estimated at over 550,000 metric tons, with a value of over US$600 million [63]. The name "zeolite" is derived from the Swedish word zeolit, which was coined by Cronstedt in 1756 from the Greek words zein (to boil) and lithos (stone) to describe the behaviour of the then newly discovered mineral stilbite. Cronstedt observed that when heated with a flame, the stilbite frothed due to water being released, and therefore appeared to boil.

After the discovery of this first natural zeolite, however, there was little interest in these materials until 1932 when McBain [64] selectively adsorbed molecules in zeolites and coined the term "molecular sieves." Barrer, who also demonstrated the molecular sieving ability of zeolites [65,66], derived the hydrogen forms of zeolites which are strong acid catalysts [67]. Up until the 1950's, only naturally occurring zeolites were known. An explosive growth into the field of synthetic zeolites was started by Milton's synthesis of zeolite A [68], which does not occur in nature. Zeolite A is commonly known in research laboratories as "molecular sieve", and is used as a drying agent. Today, the major industrial use of zeolite A is as a replacement for phosphates in detergents (375,000 tons per year) [63]. In detergents, zeolite A exchanges "hard" Ca$^{2+}$ and Mg$^{2+}$ ions for "soft" Na$^+$ ions, thereby acting as a water softener.

As catalysts, zeolites are used in several stages of petroleum refining. Zeolite X was converted into a petroleum-cracking catalyst by workers at Mobil Corporation [69],
and this development has had a tremendous economic impact. In addition, the zeolite ZSM-5 [70] (also known as MFI), a high silica zeolite, is used in a number of catalytic processes, including the conversion of methanol to gasoline.

Zeolites are framework aluminosilicates described by the general oxide formula (29), where the part within brackets represents the lattice.

\[ \text{M}^{x+}_{n/\text{c}} [(\text{SiO}_2)_m (\text{AlO}_2)_n] \cdot y\text{H}_2\text{O} \quad (29) \]

The Si/Al ratio (= \( m/n \)) can range from unity to infinity, and the distribution of Si and Al over the framework is generally disordered. Because of the difference in atomic charge between Si and Al, one charge-balancing cation (\( \text{M}^{x+} \)) must be present for each AlO\(_2\) unit. These cations are not part of the framework and may be easily exchanged. Therefore, zeolites are widely used as ion-exchangers. In addition, water molecules of hydration are usually present, but are also not part of the framework. It is important to note that zeolites with unique and distinct crystal structures may have the same chemical composition (e.g. zeolites A and X). Thus, elemental analysis alone is not sufficient to differentiate different zeolites.

Zeolites show unique properties of being highly crystalline and also extremely size- and shape selective. Zeolites are formed from open arrangements of SiO\(_4\) and AlO\(_4\) tetrahedra. The Si and Al atoms, collectively referred to as the tetrahedral- or "T-sites", are linked by sharing oxygen atoms. The frameworks of several common zeolites can be assembled from a single building unit, as shown in Figure 17. The sodalite cage subunit (Figure 17a) has faces of 4- and 6-membered rings where the vertices are Si or Al T-atoms. (The linking oxygen atoms are omitted in the diagrams for clarity, and are not included when counting the number of ring members.) When two of these cages are joined through their 4-membered rings (with bridging oxygens), the structure shown in
Figure 17. Lattice structures of typical zeolites formed from the sodalite cage building block (see text).
Figure 17b is formed. In this structure, the two cages are said to be joined by a "double 4-ring", since one 4-membered ring on each cage is involved in the connection. Linking two of the units in Figure 17b together results in the structure in Figure 17c, which is the basic lattice structure of zeolite A. There is a large central cavity accessible from three orthogonal straight channels. It is this pore and channel structure which gives zeolites their unique "molecular sieving" characteristics, allowing the lattice to control the size and shape of the molecules sorbed and the reaction products. Because of this chemical selectivity, they are widely used as sorbents and catalysts, especially in the petroleum industry for catalytic cracking, alkylations, isomerizations, and hydrogen transfers.

The catalytic activity of zeolites is generated by converting them to an "acid form", as outlined in Eq. (30).

\[
\begin{align*}
\text{zeolite-} & \text{Na}^+ \xrightarrow{\text{exchange}} \text{zeolite-} \text{NH}_4^+ \xrightarrow{\text{calcine} \ 500 \ ^\circ\text{C}} \text{zeolite-} \text{H}^+ + \text{NH}_3 \ 
\end{align*}
\]

(30)

First, the zeolite is ion-exchanged with a solution of (for example) NH\(_4\)Cl to produce the "ammonium form", which is then heated (calcined) at high temperature. The calcination causes decomposition of the NH\(_4^+\) ions, leaving a zeolite where the charge-balancing cations are, at least formally, H\(^+\). The acid form of the zeolite can now act as a powerful acid catalyst, particularly important in the reactions of hydrocarbons which are central to the petroleum refining process.

During the 1980's, there was an explosive growth in research on a related class of molecular sieves: the aluminophosphates, denoted as AlPO\(_4\)-n [71]. In this case, the Al/P ratio is always unity according to

\[
[(\text{AlO}_2)_m (\text{PO}_2)_m] \cdot y\text{H}_2\text{O}
\]

(31)

Further, there is exact alternation of the AlO\(_4\) and PO\(_4\) tetrahedra, resulting in a perfectly ordered structure. The AlPO\(_4\) molecular sieves are neutral, with no charge-balancing
extra-framework cations present. As a result, they cannot act as acid catalysts or ion-exchangers, although they have similar molecular sieving properties as zeolites. One AIPO₄ of considerable research interest is VPI-5 [72]. (VPI refers to the Virginia Polytechnic Institute, where the material was synthesized.) VPI-5 is a very large pore molecular sieve with a unidimensional channel system (see Figure 18). It is made up of 18-membered rings with internal dimensions of 12.5 Å, and can accommodate organic molecules as large as porphyrins. Note that since the framework is neutral and there are no cations, these AIPO₄ molecular sieves cannot act as catalysts unless other elements are introduced into the framework. This has led to the development of the silicoaluminophosphate (SAPO) molecular sieves [73].

From the above discussion, it can be seen that zeolites are unique catalytic materials, combining size and shape selectivity towards organic reactant and product species with high reactivity. In fact, zeolites show many of the characteristics of enzymes. The size and shape selectivity is illustrated in Figure 19. In the top diagram, the selectivity is based on the reactants, where a straight chain molecule will be accepted into the cavity and will react to form products, while the branched hydrocarbon will be rejected. The production of p-xylene (centre diagram) shows selectivity in terms of the size and shape of the product molecules. The reaction will in fact yield all three possible isomers, but only the para isomer is able to exit the zeolite structure through the pore system. The bottom diagram shows that the selectivity can also take place via a selection of transition states. In the upper case, the transition state is too large to fit within the cavity, and the corresponding product is not observed. In the lower case, however, the transition state fits within the cavity, and the product is formed.

The determination of zeolite lattice structures is crucial because the characteristics of zeolites (e.g. catalytic properties) depend on their unique framework structures. Although zeolites are highly crystalline materials, the structural information which may
Figure 18. Schematic representation of the aluminophosphate VPI-5 lattice framework (from ref [74]).
Figure 19. Different types of size and shape selectivity in reactions within zeolite cavities (from ref [75]).
be obtained from x-ray diffraction measurements is severely limited because zeolites are microcrystalline, with crystal dimensions (on the order of micrometres) which are too small for conventional single-crystal x-ray diffraction studies. As a result, structure determinations must be attempted from powder x-ray diffraction data, which provides only limited information about the overall lattice structure. Even with the use of synchrotron radiation sources [76] and Rietveld refinement procedures [77], it is very difficult to determine their framework structures. There are additional complications to consider as well. First, since Si and Al differ by only one mass unit, their x-ray scattering factors are almost identical, so it is often impossible to clearly distinguish them. Second, the Si and Al atoms in zeolites are usually disordered over the T-sites, and thus only average structures will be obtained from diffraction measurements.

(b) Solid-State NMR Studies of Molecular Sieve Systems

Over the last 15 years, high-resolution solid-state NMR spectroscopy [3] has emerged as a powerful complementary technique to x-ray diffraction for structural investigations of molecular sieve systems [27,78,79]. The techniques are complementary in that x-ray diffraction is most sensitive to long-range ordering and periodicities, and less sensitive to the perfection and nature of the short-range ordering. NMR spectroscopy, on the other hand, is affected by the local magnetic environments around the nuclei, and is thus extremely sensitive to short-range ordering and local structure.

Since there are usually no protons covalently bonded to the zeolite framework, cross polarization cannot be carried out, and high-power $^1$H decoupling is not necessary. Therefore, the experiment reduces to the very simple one of magic angle spinning (MAS) using single pulses. The experiments can usually be easily performed at high magnetic field strengths using conventional high resolution NMR instrumentation. All of the atoms which are present in zeolites and most intercalated non-framework species have NMR-active isotopes, as indicated in Table 4.
Table 4. NMR-active nuclei present in zeolites and related molecular sieves.

<table>
<thead>
<tr>
<th>Nucleus</th>
<th>Natural Abundance (%)</th>
<th>Spin (I)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{29}\text{Si}$</td>
<td>4.7</td>
<td>1/2</td>
</tr>
<tr>
<td>$^{27}\text{Al}$</td>
<td>100</td>
<td>5/2</td>
</tr>
<tr>
<td>$^{31}\text{P}$</td>
<td>100</td>
<td>1/2</td>
</tr>
<tr>
<td>$^{1}\text{H}$</td>
<td>99.98</td>
<td>1/2</td>
</tr>
<tr>
<td>$^{17}\text{O}$</td>
<td>0.037</td>
<td>5/2</td>
</tr>
<tr>
<td>$^{23}\text{Na}$</td>
<td>100</td>
<td>3/2</td>
</tr>
<tr>
<td>$^{15}\text{N}$</td>
<td>0.37</td>
<td>1/2</td>
</tr>
<tr>
<td>$^{11}\text{B}$</td>
<td>80.42</td>
<td>3/2</td>
</tr>
</tbody>
</table>

$^{29}\text{Si}$ MAS NMR has yielded the most information about zeolite structures (see below). $^{27}\text{Al}$ and $^{17}\text{O}$ are both quadrupolar nuclei ($I = 5/2$), and their spectra are often much more complex. In addition, the extremely low natural abundance of $^{17}\text{O}$ means that isotopic enrichment will be required. $^{1}\text{H}$ can be present as water of hydration (which is not part of the lattice, and is usually mobile), or in OH groups at defect sites. In addition, $^{23}\text{Na}$ NMR can be used to determine the mobility of $\text{Na}^+$ ions which are often present as charge-balancing cations. In $\text{AlPO}_4$ systems, $^{31}\text{P}$ MAS NMR can be used to determine the number of inequivalent $^{31}\text{P}$ sites present.

In the case of low Si/Al ratio zeolites, the $^{29}\text{Si}$ MAS NMR spectra of the simplest systems show five resonances corresponding to the five local silicon environments \[80,81]: \text{Si[4Al]}, \text{Si[3Al, Si]}, \text{Si[2Al, 2Si]}, \text{Si[Al, 3Si]} \text{ and } \text{Si[4Si]}, \text{where } \text{Si[4Al]} \text{ refers to Si with four Al atoms as neighbouring tetrahedral sites (T-sites), as indicated in Figure 20a for the zeolite analcite. Furthermore, these chemical shifts fall within reproducible ranges over a wide variety of structures \[82], as shown in Figure 20b. Under Loewenstein's rule \[83], which postulates that Al-O-Al linkages are avoided if possible, the Si/Al ratio of the framework may be calculated from the five peak areas in the $^{29}\text{Si}$ spectrum according to Eq. (32)
Figure 20. (a) $^{29}$Si MAS NMR spectrum of the zeolite analcite (from ref [3]). (b) Characteristic chemical shift ranges of the five different local silicon environments (from ref [82]).
\[
\frac{\text{Si}}{\text{Al}} = \frac{\sum_{n=0}^{4} I(n\text{Al})}{\sum_{n=0}^{4} 0.25n I(n\text{Al})}
\]

where \(I\) is the peak intensity and \(n\) is the number of coordinated Al atoms for a given peak. This formula includes only those Al atoms attached to Si atoms in the framework, since the Al concentration is detected indirectly from its effect on the \(^{29}\text{Si}\) spectrum. A bulk chemical analysis, on the other hand, detects both Al which is present within the framework, and also extralattice Al (e.g. trapped within the zeolite cavities). Thus, the Si/Al ratio calculated from Eq. (32) represents the true Si/Al ratio of the zeolite framework. The \(^{29}\text{Si}\) MAS NMR spectra of a series of faujasite zeolites are shown in Figure 21 [84], together with the peak deconvolutions which are used in Eq. (32) to calculate the Si/Al ratios indicated.

Because of the lack of Si/Al ordering in the zeolite framework, the \(^{29}\text{Si}\) resonances are relatively broad, with linewidths on the order of 5 ppm. The aluminum atoms can be removed from the framework by treatment with water vapour at elevated temperatures (hydrothermal dealumination) [85,86] or by chemical treatments [87] such as silicon tetrachloride (SiCl\(_4\)), thus producing a completely siliceous zeolite framework which is perfectly ordered. The \(^{29}\text{Si}\) MAS NMR spectrum now shows very sharp resonances (linewidths less than 1 ppm) whose number correspond to the number of crystallographically inequivalent sites in the unit cell and whose relative intensities reflect the populations of these sites [88,89]. A direct link can thus be made between the NMR and diffraction methods [79]. In these ordered systems it is now possible to establish the three-dimensional \(^{29}\text{Si}-\text{O}-^{29}\text{Si}\) bonding connectivities in the framework by two-dimensional \(^{29}\text{Si}\) homonuclear correlation experiments such as COSY and INADEQUATE, and a number of studies have demonstrated their reliability [79].
Figure 21. $^{29}$Si MAS NMR spectra of faujasite zeolites, with the peak deconvolutions used to calculate the indicated Si/Al ratios (from ref [84]).
detailed discussion of these two-dimensional $^{29}$Si correlation experiments will be given in the next section.)

In zeolites, Loewenstein's rule states that Al-O-Al linkages are avoided if possible. Therefore, every Al in the framework has the environment Al[4Si], and the $^{27}$Al MAS NMR spectra of the tetrahedral Al in zeolites usually show only a single resonance. Only in zeolite omega at 154.5 MHz ($^1$H at 600 MHz) has MAS NMR clearly detected crystallographically inequivalent $^{27}$Al sites [90]. However, the NMR spectra are very sensitive to the Al coordination, with tetrahedral Al occurring in the range of 50-65 ppm and octahedral Al occurring near 0 ppm (for $B_0 = 9.4$ T or $^1$H at 400 MHz, since the second-order quadrupolar shift is field dependent). The octahedral Al observed is due to extralattice amorphous Al which is not part of the zeolite framework. As before, it is not necessary to decouple the dipolar interaction with $^1$H since the protons present are generally mobile (e.g. water) and do not contribute significantly to the $^{27}$Al linewidths.

In AlPO$_4$ molecular sieves, spin-1/2 $^{31}$P nuclei are present, occupying tetrahedral framework positions. Since there is an exact Al/P alternation, each P atom is in a P[4Al] environment. As a result, the $^{31}$P MAS spectra of many AlPO$_4$'s show only single resonances [40]. However, in some AlPO$_4$ systems with more complex unit cells, there can be several crystallographically inequivalent sites, and multiple $^{31}$P resonances result [91,92]. For example, Figure 22a and b show the $^{31}$P MAS spectra of VPI-5 and AlPO$_4$-8 where, in both cases, several signals are observed.

The $^{27}$Al MAS spectra of many AlPO$_4$'s also show single resonances, since in the simplest case, each Al is in a tetrahedral Al[4P] environment. In certain AlPO$_4$ molecular sieves (e.g. AlPO$_4$-11, AlPO$_4$-18), however, $^{27}$Al MAS NMR shows crystallographically inequivalent tetrahedral Al sites. In addition, when certain AlPO$_4$ molecular sieves (e.g. AlPO$_4$-5, AlPO$_4$-8, and VPI-5) become hydrated, some of the framework tetrahedral Al atoms change to octahedral by the coordination of two molecules of water. Such changes are clearly detectable in the $^{27}$Al MAS NMR spectra,
Figure 22. $^{31}\text{P}$ MAS NMR spectra of (a) VPI-5 and (b) AlPO$_4$-8. (c) $^{27}\text{Al}$ MAS NMR spectrum of VPI-5 (from ref [91]).
and are illustrated for the example of VPI-5 in Figure 22c, which shows resonances from tetrahedral and octahedral Al at 41 ppm and approximately -18 ppm, respectively.

Oxygen is a very important element in molecular sieve systems, but since the natural abundance of the NMR-active $^{17}\text{O}$ isotope is extremely low (0.037%), $^{17}\text{O}$ enrichment must be used. (However, $^{17}\text{O}$-enriched compounds such as $\text{H}_2^{17}\text{O}$ and $^{17}\text{O}_2$ gas are very expensive.) There are only two possible environments for an oxygen atom in the zeolite framework: oxygen between two silicon atoms, or oxygen in between an aluminum and a silicon. (The third possible environment, oxygen between two aluminum atoms, is ruled out by Loewenstein’s rule.) In the static $^{17}\text{O}$ NMR spectra (i.e. without MAS), the resonances are very broad, being strongly affected by both chemical shift anisotropy and the second order quadrupolar interaction. The quadrupolar interaction, however, can be used to separate the contributions from the two oxygen environments, most effectively for static samples [93].

(c) Three-Dimensional $^{29}\text{Si}-^{17}\text{O}-^{29}\text{Si}$ Connectivities in Zeolite Frameworks from Two-Dimensional $^{29}\text{Si}$ Homonuclear Correlation NMR Experiments

Two-dimensional NMR correlation experiments based on scalar J-couplings have been successfully used to establish connectivities in the solid state. For example, Benn and co-workers [94] have demonstrated $^{13}\text{C}/^{13}\text{C}$ connectivities in the plastic crystal camphor using the INADEQUATE experiment, and $^{29}\text{Si}/^{29}\text{Si}$ connectivities in the reference molecule $\text{Q}_8\text{M}_8$ using the COSY experiment. Although these experiments involved molecular crystals, in principle, the connectivities derived from them could be used to define the complete three-dimensional lattices of zeolites and other framework materials. This section describes the use of two-dimensional $^{29}\text{Si}$ homonuclear correlation experiments such as COSY and INADEQUATE by Fyfe and co-workers [79] to establish three-dimensional $^{29}\text{Si}-^{17}\text{O}-^{29}\text{Si}$ connectivities in zeolite frameworks.
The two-dimensional $^{29}\text{Si}$ homonuclear correlation experiments utilize the J-couplings in $^{29}\text{Si}-\text{O}-^{29}\text{Si}$ spin pairs, which have only a 0.22% probability of occurring (calculated by squaring the 4.7% natural abundance of $^{29}\text{Si}$). As a result, the experiments are inherently insensitive, and will require optimization of experimental parameters (e.g. shimming the magnetic field, setting the magic angle, measuring 90° pulse times) and involve relatively long experiment times.

The $^{29}\text{Si}$ MAS spectrum of zeolite ZSM-12 shows seven clearly separated resonances of equal intensity, reflecting the seven tetrahedral sites with equal occupancies. A two-dimensional COSY experiment [95], acquired using the $[(90^\circ)_{\phi_1}-t_1-(45^\circ)_{\phi_2}-t_2, \text{acquire}]$ sequence, was performed on ZSM-12 [96]. The contour plot, shown in Figure 23, shows clear connectivities in the unsymmetrized plot. Using the connectivities predicted from the x-ray data [97,98], the connectivities in the COSY spectrum can be assigned, yielding the labelling of the cross-peaks as shown and the assignment of the $^{29}\text{Si}$ resonances to the specific T-sites. When the number of points in $t_2$ is increased, the resulting 2D contour plot (not shown) shows the same connectivities, but more importantly shows doublet splittings for the cross-peaks in the $F_2$ dimension. The observed J-coupling values of between 9 and 16 Hz represent the first direct observation of scalar $^{29}\text{Si}-\text{O}-^{29}\text{Si}$ couplings in the solid state.

Determination of the scalar couplings is important in that it facilitates the application of the INADEQUATE experiment [99,100]. The conventional pulse sequence is $[(90^\circ_x)-\tau-(180^\circ)-\tau-(90^\circ)-t_1-(135^\circ)-t_2, \text{acquire}]$, where the maximum signal intensity is obtained when $\tau = 1/(4J)$, assuming $T_2 >> 1/J$. The INADEQUATE experiment has two advantages compared to the COSY experiment: in general, a better signal-to-noise ratio (S/N) is expected since there is a twofold decrease in the multiplicity of the cross-peaks, and the main (noncoupled) diagonal signals are subtracted, making it easier to observe connectivities between closely spaced resonances near the diagonal.
Figure 23. Contour plot of a COSY experiment on ZSM-12 (from ref [96]).
The main potential disadvantage is that a reasonable estimate of the J-coupling value must be made in order to calculate the optimal value of τ, and the J-couplings are often not directly observable.

All of the connectivities found and assigned in the previous COSY experiment on ZSM-12 are confirmed in the INADEQUATE experiment [96] (Figure 24), including the one between T₄ and T₆, which is clearly resolved in the INADEQUATE experiment, but is ambiguous in the COSY experiment due to the proximity of the cross-peaks to the large diagonal signals.

Zeolite ZSM-5 has the most complicated unit cell of any zeolite system, with either 12 or 24 T-sites depending on the phase, and is thus a very good and also very demanding candidate for these 2D connectivity experiments. COSY and INADEQUATE experiments have been performed for the orthorhombic form of low-loaded ZSM-5 (2 molecules of p-xylene per 96 T-atom unit cell). From single-crystal x-ray refinements [101-104], a total of 22 ²⁹Si-O-²⁹Si connectivities are expected for this phase. While the COSY spectrum (not shown) shows only 12 of these connectivities, the INADEQUATE experiment (Figure 25) is superior, with 21 of the 22 connectivities being clearly visible [105-107]. From the knowledge that only four silicons have self-connectivities, and using the expected connectivities from the x-ray derived structures, a complete self-consistent assignment of the NMR resonances was obtained.

Therefore, the COSY and INADEQUATE experiments give the complete three-dimensional connectivity pattern and the assignment of the ²⁹Si resonances to specific T-sites. In general, the INADEQUATE experiment, while more demanding, gives superior performance to the COSY, and will usually be the preferred experiment.
Figure 24. Contour plot of an INADEQUATE experiment on ZSM-12 (from ref [96]).
Figure 25. Contour plot of an INADEQUATE experiment on ZSM-5 loaded with 2 molecules of \textit{p}-xylene per unit cell (from ref [105-107]).
1.8. Goal of Thesis

The goal of the work described in this thesis is to develop double-resonance solid-state NMR experiments involving quadrupolar and spin-1/2 nuclei which can be used to determine heteronuclear connectivities in zeolites, related molecular sieves, and other inorganic materials. Chapter 2 describes the development of cross-polarization, REDOR, TEDOR, and dipolar-dephasing difference experiments to establish $^{27}\text{Al}-^{31}\text{P}$ connectivities in the aluminophosphate molecular sieves VPI-5 and AIPO$_4$-8 via $^{27}\text{Al}-^{31}\text{P}$ dipolar couplings. Chapter 3 demonstrates the increased efficiency of cross-polarization from quadrupolar nuclei which can be achieved in the dynamic-angle cross-polarization experiment. In Chapter 4, the experiments developed for $^{27}\text{Al}$ and $^{31}\text{P}$ nuclei are extended to $^{27}\text{Al}$ and $^{29}\text{Si}$ nuclei in a series of representative zeolite molecular sieve frameworks. In Chapters 5 and 6, these experiments are applied to SAPO-37 and AlPO$_4$-5 molecular sieves, respectively, to address specific questions about the framework structures. Extensions of the $^{27}\text{Al}^{31}\text{P}$ and $^{27}\text{Al}^{29}\text{Si}$ experiments to include $^{11}\text{B}$, $^{23}\text{Na}$, and $^{29}\text{Si}$ nuclei are demonstrated in Chapter 7 using borosilicate glasses. Finally, Chapter 8 describes the first application of INEPT and DEPT experiments in solid state NMR. These last experiments, which utilize coherence-transfer based on heteronuclear J-couplings to detect through-bond connectivities, are shown to be applicable to both quadrupolar and spin-1/2 nuclei.
Chapter 1 References


103. H. Gies and B. Marler, unpublished results.
Chapter 2. Development of Coherence-Transfer and Dipolar-Dephasing Experiments to Establish \(^{27}\text{Al-O-}^{31}\text{P}\) Connectivities in \(\text{AlPO}_4\) Molecular Sieve Frameworks

2.1. Background to the Experiments

An important recent advance in the NMR of solids is the ability to determine connectivities between nuclei which are coupled via scalar or dipolar interactions [1]. Information about the distance, \(r\), between two heteronuclei can be obtained by measurement of the heteronuclear dipolar coupling, \(D\), between them, using \(D = \gamma_1 \gamma_S h/(2\pi r^3)\). Since the magnitude of the dipolar coupling is proportional to the inverse third power of the internuclear distance, the dipolar coupling falls off very rapidly with increasing internuclear distance, and will only be significant for closely-neighbouring nuclei. In addition, the inverse third power dependence of the dipolar coupling with internuclear distance means that only a reasonable estimate of the dipolar coupling is needed to obtain an accurate value of the internuclear distance.

The value of the heteronuclear dipolar coupling can be obtained directly from the NMR spectrum of a static sample if the spin interactions are simple enough to show a well-resolved multiplet or Pake pattern, although this is rarely the case. When a broad line shape in a static sample is composed of contributions from some nuclei with no heteroatoms nearby and others with dipole-coupled spin partners, the technique of SEDOR (spin-echo double-resonance) may be used to discern between the "connected" and "unconnected" species [2,3]. In the SEDOR experiment, an S spin echo under static conditions is created by an S spin \(\pi\) pulse, and the I-S dipolar coupling is measured by the extent to which this echo is prevented from refocusing by an I spin \(\pi\) pulse. In cases where there are many resonances in the spectrum which are broad and overlapping, magic angle spinning (MAS) can be used to narrow and resolve the resonances. This improved resolution, however, is at the expense of averaging the dipolar couplings to zero over each rotor period, which may be undesirable since the dipolar couplings contain
information about connectivities and distances between nuclei. Munowitz and Griffin [4] introduced MAS experiments where the dipolar and chemical shift interactions were separated in a two-dimensional correlation plot, aimed specifically at large heteronuclear dipolar couplings such as those found between $^{13}\text{C}$ and $^1\text{H}$ in organic solids (e.g. D=21 kHz for r=1.1 Å). For weaker dipolar couplings (less than 1 kHz), however, this method becomes impractical due to the need for very slow MAS spinning which introduces the complication of a large number of sidebands in the spectrum.

To determine connectivities using weak dipolar couplings, several experiments have been utilized in this thesis: cross-polarization, REDOR, TEDOR, and dipolar-dephasing difference experiments. These techniques will be discussed after a description of the equipment and experimental set-up used for all of the NMR experiments.

2.2. Experimental Section

(a) Equipment and Experimental Set-Up

The NMR experiments were performed on a Bruker MSL 400 spectrometer where the resonance frequencies for $^{27}\text{Al}$ and $^{31}\text{P}$ were 104.264 MHz and 161.977 MHz, respectively. Initially, the $^{31}\text{P}$ channel was the normal X channel on the spectrometer and the $^{27}\text{Al}$ channel was obtained by external modification (mixing, amplification, and remixing before detection) of the frequency from the $^1\text{H}$ channel. (In later experiments (Chapters 4-8), a "proper" third r.f. channel was used for the second X nucleus.) The probehead contained a home-built MAS system with a double-tuned solenoid coil. Internal trapping of the $^{31}\text{P}$ frequency was employed, complemented by external filters on both channels to prevent pulse breakthrough back to the amplifiers and the receiver. The rotational frequency of the MAS spinner was kept constant during each of the experiments, monitored through the sidebands in the $^{31}\text{P}$ MAS spectrum of VPI-5. The spinning speeds in different experiments ranged from 2.9 to 3.3 kHz. The 90° pulse lengths for both channels were 11 μs. For the spin-1/2 $^{31}\text{P}$ nuclei, the pulse length was
set by a null 180° pulse (22 μs). For the 27Al nuclei, however, the quadrupolar interaction can lead to non-ideal response to longer pulses, and the 90° pulse length (11 μs) was set by a maximum signal intensity in the solid samples themselves. The 27Al 90° pulse was found to be approximately 1/3 of the 90° pulse length for 27Al spins in solution (saturated aqueous Al(NO₃)₃). For 27Al (I=5/2), this scaling factor of 1/(I+1/2) = 1/3 confirmed that only the central (+1/2 ↔ -1/2) transition was being irradiated and detected [5,6]. The power of the 31P pulses was varied for certain experiments using an attenuator inserted before the high-power r.f. amplifier.

The next four sections (Sections 2.2b-e) describe the pulse sequences used for the cross-polarization, dipolar-dephasing difference, REDOR, and TEDOR experiments. The spectrometer pulse programs (including the phase cyclings) used for these experiments are given in Appendices 5-12.

(b) Cross-Polarization Experiment

Cross-polarization experiments were performed using the conventional spin-lock sequence [7,8] as shown in Figure 26a. (For a general description of the cross-polarization experiment, see Section 1.6a.) For I and S spins which are not necessarily spin-1/2, the Hartmann-Hahn matching condition [9] is modified (from Eq. (24)) since only the central +1/2 ↔ -1/2 transitions are irradiated:

\[(I + 1/2) \gamma I B_{1,I} = (S + 1/2) \gamma S B_{1,S}\]  

(33)

where the r.f. field strength \(\gamma X B_{1,X}\) is determined experimentally (in frequency units) from the 90° pulse time \(t_{90,X}\) by:

\[\gamma X B_{1,X} = \frac{1}{4 t_{90,X}}\]  

(34)

In the case of 27Al (I = 5/2) and 31P (S = 1/2) nuclei, Eq. (33) becomes:

\[3 \gamma Al B_{1,Al} = \gamma P B_{1,P}\]  

(35)
Figure 26. Pulse sequence for cross-polarization experiments: (a) Spin-locking pulse sequence used for polarization-transfer from I spins to S spins. (b) Two-dimensional cross-polarization experiment. The $t_1$ time period (I spin evolution) is varied for a series of experiments with acquisition of the S spin free induction decay during the $t_2$ period.
As with cross-polarization involving only spin-1/2 nuclei, the matching condition in Eq. (35) still corresponds to setting the pulse power on both channels so that the 90° pulse times in the solid sample are equal. The measured 90° pulse time for $^{27}\text{Al}$ in the solid state, $t_{90}^{\text{Al}}(\text{solid})$, is 1/3 the 90° pulse time in solution, $t_{90}^{\text{Al}}$:

$$t_{90}^{\text{Al}}(\text{solid}) = \frac{1}{3} t_{90}^{\text{Al}}$$

For $^{27}\text{Al}$ ($I=5/2$), this scaling factor of $1/(I+1/2) = 1/3$ arises because only the central +1/2 $\leftrightarrow$ -1/2 transitions are being irradiated and detected [5,6]. Thus, for $^{27}\text{Al}$, Eq. (34) can be written as:

$$3\gamma_{\text{Al}} B_{1,\text{Al}} = \frac{1}{4 t_{90}^{\text{Al}}(\text{solid})}$$

Comparing Eq. (34) for $^{31}\text{P}$ and Eq. (37) for $^{27}\text{Al}$, the modified matching condition in Eq. (35) thus corresponds to setting both 90° pulse times in the solid sample to be equal (i.e. $t_{90}^{\text{P}} = t_{90}^{\text{Al}}(\text{solid})$).

The CP experiments were performed with reversal of spin temperature in order to suppress experimental artifacts [10]. (For an explanation of the concept of spin temperature, see Section 1.2d.) In this method, the phase (direction) of the spin-lock pulse of the source nucleus is reversed by 180° for every other acquisition, while the phase of the spin-lock pulse of the observed nucleus is kept constant, and the signals are alternately added and subtracted from memory (i.e. the detection phase is reversed for every other acquisition). Because the magnetization that occurs from polarization transfer grows up along the same direction as the spin-locking field of the source nucleus, alternate addition and subtraction of signals follows the growth of the cross-polarization magnetization. On the other hand, since experimental artifacts due only to the application of the spin-locking field on the observed nucleus are kept constant, they are effectively suppressed by alternate addition and subtraction of signals.
Since it involves a coherence-transfer step, the cross-polarization experiment can be extended into a two-dimensional heteronuclear correlation (HETCOR) experiment [11]. These experiments were performed by preparing the I spins with a 90° pulse, and then encoding their evolution frequencies in an initial (t₁) time period (see Figure 26b). The I spin polarization was subsequently transferred to the S spins with a spin-lock, and a free induction decay (the t₂ time domain) was accumulated from the S spins after each of a set of I spin evolution times. Two-dimensional Fourier transformation then provides a correlation spectrum. Note that the spin-locking pulse, due to its direction along one well-defined axis in the rotating frame, may only select one orthogonal component of the I spin magnetization in a particular experiment. This can be advantageous as the phase of the first pulse can be cycled using time proportional phase incrementation (TPPI) [12,13], which involves shifting the phase of the initial pulse by 90° each time the t₁ value is incremented. In this way, quadrature detection is simulated in t₁, and pure-absorption-phase lineshapes are obtained in both spectral dimensions.

The two-dimensional cross-polarization experiments were carried out with magnetization transfer from quadrupolar to spin-1/2 nuclei, as the short T₁ relaxation times for the quadrupolar spins aid in rapid signal averaging of the data. Reasonable experimental times could not be obtained with transfer in the other direction, that is from spin-1/2 to quadrupolar nuclei, due to the much longer spin-1/2 nucleus T₁ relaxation times.

(c) Dipolar-Dephasing Difference Experiments

The dipolar-dephasing difference MAS NMR experiments introduced by Veeman and co-workers [14] measure the difference between spin echoes for I nuclei obtained with and without irradiation of the S nuclei. The difference spectrum shows signals from only those I nuclei which are dipolar coupled (i.e. "connected") to S nuclei, and is thus a measure of the heteronuclear dipolar interactions between the I and S spins. Dipolar-
dephasing difference experiments under MAS conditions are analogous to the earlier SEDOR (spin-echo double-resonance) experiments [2,3] used for static samples.

The pulse sequence for the dipolar-dephasing difference experiments used in this thesis differs from that originally proposed [14]: rather than conducting two separate experiments, one with and one without irradiation of the S spins and then subtracting the spectra after Fourier transformation, the sequence was changed between successive scans and the signals alternately added and subtracted to give the FID corresponding to the difference spectrum directly. It was found that the signal-to-noise ratio (S/N) improved considerably, presumably by minimization of the effects of small variations in experimental conditions compared to running the experiments separately.

Ideally, the dipolar-dephasing difference experiment follows the pulse sequence shown in Figure 27a. In the first acquisition, a spin-echo from the I nuclei is acquired and stored in memory (denoted [acq]+), followed by a second acquisition where the S spins are also irradiated during the first half of the I spin echo, and this is subtracted from memory (shown as [acq]). The difference signal then directly reflects the interaction of these heterospins via the dipolar interaction between them, although the mechanism for this behaviour is complicated as will be addressed below.

Surprisingly, our attempts to acquire "null" signals in the dipolar-dephasing difference experiment by completely turning off or disconnecting the high-power amplifier for the S spins resulted in observation of a difference signal with no field applied to the S spins. A simulation of small (microsecond) timing errors during spin-echo cancellation experiments provided the reason for such a strange observation. The "hidden" switching times within the spectrometer (Bruker MSL 400) do not allow perfect difference experiments to be performed with pulses on the S channel in one-half of the echo sequence and not in the other. This may well be a general problem in performing these experiments, and should always be taken into account. It was necessary to always turn on pulses on the S channel during the first half of each echo experiment, with
Figure 27. Dipolar-dephasing difference experiments under MAS conditions with a rotational period of $\tau_r$:
(a) Difference experiment where a signal from a spin-echo is recorded first with no S spin irradiation. The experiment is immediately repeated with subtraction of the spin-echo signal obtained with irradiation of the S spins during the first half of the experiment. (b) Modification of (a) to take into account instrumental timing errors which occur when pulses are not applied during the first part of the experiment.
switching of the resonance frequency between positive ([acq]+) and negative ([acq]-) scans (Figure 27b). This was accomplished with a frequency offset list, with a resonance offset of 10 MHz to ensure that no r.f. power on the S channel was available during the accumulation of the normal spin-echo. Reasonable attenuation was provided by the tuning of the probe and the bandpass tuning of the final stage of the high-power amplifier. Null experiments were then accomplished by having no pulses on the S spin channel, by having off-resonance pulses in both parts of the difference experiment, or by having on-resonance pulses in both parts of the experiment. The number of rotor cycles between the initial 90° pulse and the refocusing pulse was usually five in each of these types of dipolar-dephasing difference experiment.

The mechanism of the effect leading to the observation of difference signals in these dipolar-dephasing difference MAS experiments is described by van Eck et al. [14] to be different from the mechanism operating in static SEDOR experiments. Through an array of experiments, they determined that the effect was not due to a change in evolution frequency with and without S spin irradiation, nor could it be described by a change in $T_2$ during the irradiation. They suggest a mechanism whereby some of the I spin-order is transferred to another spin reservoir and regained after the refocusing pulse. The irradiation on the S spins partly or fully destroys the transferred magnetization, which cannot then be regained. In light of the discussions by Vega [15,16] on the passage of quadrupolar satellite transitions through the resonance frequency, this is a distinct possibility for irreversible loss of magnetization during one or both halves of the spin-echo experiments.

These experiments might also be described in terms of adiabatic fast passage of the magnetization between the energy levels through the time-dependence during the sample rotation (e.g. MAS) of the $^{27}$Al first- or second-order quadrupolar interactions or the $^{31}$P chemical shift anisotropy. As the spinner completes one rotor cycle, the effective field (difference between the energy separation at a given instant in time and the
resonance energy separation $\Delta E = \hbar \omega_0 / 2\pi$ for some of the S spin transitions during the long dephasing pulses passes from negative to positive and back to negative again, either once or twice depending upon the orientation of the crystallite within the spinner. If this occurs on a time scale such that the S spin magnetization can adiabatically follow the effective field, the result is an adiabatic passage through resonance and an effective inversion of the magnetization either two or four times per rotor cycle. This modulates the sign of the dipolar coupling during a rotor cycle so that the coupling does not average to zero, similar in action to the dephasing pulses of a REDOR or TEDOR experiment (see next section). The reason that adiabatic rapid passage can be accomplished in both directions in these experiments is the relatively weak r.f. fields used. Independent confirmation of this mechanism could perhaps be accomplished with experiments on single crystals under MAS conditions.

(d) REDOR Experiments

To measure weaker $^{13}\text{C}^{15}\text{N}$ dipolar couplings in rotating solids, Gullion and Schaefer introduced the REDOR (rotational-echo double-resonance) experiment [17,18]. In the REDOR experiment, a spin echo for the I spins is measured under MAS conditions, and the I-S dipolar coupling is measured by the extent to which the spin echo is prevented from refocusing by dephasing S spin $\pi$ pulses. The spin pair investigated was $^{13}\text{C}^{15}\text{N}$, both introduced by isotopic enrichment. Because of this, they constitute an isolated spin pair, making a quantitative description of the experiment possible.

Figure 28a shows the basic pulse sequence used for the REDOR experiments. The format of the experiment is similar to that of the dipolar-dephasing difference experiment in that a spin echo sequence is used to form a signal for the I spins, and two experiments are carried out with and without perturbation of the S spins, the difference between the two signals reflecting the heteronuclear dipolar couplings. The difference between the two is that the application of the pulses in the REDOR sequence is gated
Figure 28. Pulse sequences for REDOR and TEDOR experiments: (a) REDOR experiment in which, in the first experiment, a conventional spin echo acquired after \( n \) rotor cycles provides the reference signal, \( S_0 \), and no pulses are applied on the S channel. In the second experiment, 180° pulses are applied to the S channel twice per rotor cycle, and the modified signal, \( S_f \), is recorded. The difference signal \( \Delta S \) is recorded directly by subtraction of the signals: \( \Delta S = S_0 - S_f \). (b) TEDOR experiment in which 180° pulses are applied for \( n \) rotor cycles to the S spins, shown here at \( \tau_r/4 \) and \( 3\tau_r/4 \) in each rotor cycle. Simultaneous 90° pulses then transfer the spin coherence from the I spins to the S spins, and further evolution for \( m \) rotor cycles under dipolar-dephasing produces observable signal, \( S_T \). (c) Two-dimensional heteronuclear correlation TEDOR experiment with preliminary evolution of I spin magnetization during the \( t_1 \) time period, and detection of S spin magnetization during the \( t_2 \) time period.
Figure 28
with the spinning rate and the pulses applied to the S spins are at specific points in a rotor
cycle and their effects are exactly understood, making the sequence one which, at least
for an isolated spin pair, can be described theoretically and the results interpreted
quantitatively.

In the REDOR experiment (Figure 28a), a 90° pulse is applied to the I spins to
begin I spin evolution. After an integral number of rotor cycles have passed \( t = n\tau_r/2, \)
with \( n \) even, a 180° refocusing pulse is applied to the I spins and a spin echo is formed at
time \( t = n\tau_r \). The amplitude of this spin echo is designated \( S_0 \), the full signal with no
dipolar dephasing. A second experiment is then carried out exactly as the first, but at half
integral multiples of the rotor cycles, a 180° pulse is applied to the S spins. The only
exception is at time \( n\tau_r/2 \) when the 180° pulse is applied to the I spins in order to form the
spin echo and no S spin pulse is applied. The outcome is a signal \( S_f \) that differs from the
\( S_0 \) signal due to dephasing caused by the non-zero average dipolar coupling. Retention
of the coupling is generated by a change of sign of the dipolar coupling every half rotor
cycle (at each 180° pulse). When the signal \( S_f \) is subtracted from the full echo intensity
\( S_0 \), the difference signal \( \Delta S = S_0 - S_f \) is due solely to spins that have I-S dipolar
interactions. In the experimental pulse sequences actually used, a direct difference
experiment was usually performed in order to obtain the \( \Delta S \) signal, while a normal spin-
echo experiment provided the \( S_0 \) signal used for normalization. The \( \Delta S \) signals were
compared with those obtained from separate \( S_0 \) and \( S_f \) experiments, with results agreeing
to within less than 1%, but the overall S/N ratio was better.

For an isolated pair of dipolar-coupled I-S heteronuclei, the expected difference
signal for the REDOR experiment can be calculated. Under magic angle spinning (MAS)
conditions, the evolution of the dipolar coupling is described by:

\[
\omega_D(\alpha, \beta; t_2) = \pm \pi D[\sin^2 \beta \cos(2(\alpha + \omega t_2) - \sqrt{2} \sin 2\beta \cos(\alpha + \omega t_2))]
\]  
(38)
where \( t_2 \) is the time, \( D = \gamma_1 \gamma_2 h/(2\pi \alpha^3) \) is the strength of the dipolar coupling, \( \omega_1 \) is the rotational frequency (in angular frequency units), and the azimuthal and polar angles \( \alpha \) and \( \beta \) describe the orientation of the internuclear vector in the reference frame of the MAS spinner (see Figure 29). For a given spin in the transverse plane, the average dipolar coupling evolution over a period \( t_2 \) is thus:

\[
\bar{\omega}_D(\alpha, \beta; t_2) = \frac{1}{t_2} \int_0^{t_2} \omega_D(\alpha, \beta; t) \, dt \\
= \pm \frac{\pi D}{2t_2 \omega_1} \{ \sin^2 \beta \left[ \sin^2(\alpha + \omega t_2) - \sin 2 \alpha \right] \\
- 2\sqrt{2} \sin 2 \beta \left[ \sin(\alpha + \omega t_2) - \sin \alpha \right] \} \quad (39)
\]

Over one complete rotor cycle \( \tau_r \), the evolution of the dipolar coupling averages to zero, i.e. \( \bar{\omega}_D(\alpha, \beta; \tau_r) = 0 \). Therefore, MAS averages away the evolution of the dipolar coupling, and with it any connectivity information that the dipolar coupling contains.

To re-introduce the dipolar couplings under MAS, the REDOR experiment involves the application of S-spin 180° pulses during each rotor cycle, and determines the effect on the observed I-spin magnetization. If an S-spin 180° pulse is applied at time \( t_1 \) after the start of each rotor cycle, the average dipolar coupling evolution over each rotor cycle becomes:

\[
\bar{\omega}_D(\alpha, \beta; t_1) = \frac{1}{\tau_r} \left[ \int_0^{t_1} \omega_D(\alpha, \beta; t) \, dt - \int_{t_1}^{\tau_r} \omega_D(\alpha, \beta; t) \, dt \right] \\
= \pm \frac{D}{2} \{ \sin^2 \beta \left[ \sin^2(\alpha + \omega t_1) - \sin 2 \alpha \right] \\
- 2\sqrt{2} \sin 2 \beta \left[ \sin(\alpha + \omega t_1) - \sin \alpha \right] \} \quad (40)
\]

In a normal REDOR experiment, the S-spin \( \pi \) pulses are applied at every half rotor cycle (i.e. \( t_1 = \tau_r/2 \)). Eq. (40) thus simplifies to:

\[
\bar{\omega}_D(\alpha, \beta; \tau_r/2) = \pm 4\sqrt{2} D \sin \alpha \sin \beta \cos \beta \quad (41)
\]
Figure 29. Diagram showing the relationship between the spinning axis, the external magnetic field $B_0$, and the I-S heteronuclear dipolar vector. For magic angle spinning, the spinning axis is inclined at an angle $\theta = 54.7^\circ$ with respect to the external field. The heteronuclear dipolar vector forms a polar angle $\beta$ and an azimuthal angle $\alpha$ with respect to the spinning axis.
If $n$ is the total number of dephasing rotor cycles, then the phase accumulation of each I-spin is:

$$
\Delta \Phi_{R,n} = \bar{\omega}_D(\alpha, \beta; \tau_f/2) \ n \tau_f
= 4\sqrt{2} \ n \ D \ \tau_f \ \sin \alpha \ \sin \beta \ \cos \beta
$$  \hspace{1cm} (42)

The expected difference signal, normalized to the full echo intensity, is calculated by averaging over all possible internuclear vector orientations (in a hemisphere):

$$
(\Delta S/S_0)_n = 1 - \frac{1}{2\pi} \int_{\alpha=0}^{2\pi} \int_{\beta=0}^{\pi/2} \cos(\Delta \Phi_{R,n}) \ \sin \beta \ d\beta \ d\alpha
$$  \hspace{1cm} (43)

where $\cos(\Delta \Phi_{R,n})$ represents each spin's contribution to the observed signal, and $\sin \beta$ is a weighting factor which is due to the distribution of spins about the spinning axis.

The Fourier transform of the time-domain signal collected from the top of the echo separates the intensities from each of the resolved resonances in the I spin spectrum. This was performed on a direct difference $\Delta S$ signal as well as on the full echo ($S_0$) signal, and values of $\Delta S/S_0$ were calculated for each resonance by the ratio of the peak areas of the $\Delta S$ and $S_0$ spectra, including peak intensities in the spinning sidebands when present. Null experiments were performed by removing all of the S spin 180° pulses during the experiments, or alternatively moving them all off-resonance by 10 MHz. Based on our discussion of small timing errors in the dipolar-dephasing difference experiment, we also performed the REDOR difference ($\Delta S$) experiment with S spin pulses on during both the $S_0$ and $S_f$ spin echoes. During the $S_f$ spin echo, the S spin pulses were applied on-resonance. During the $S_0$ spin echo, in which there should be no dephasing of the S nuclei, the S spin pulses were applied 10 MHz off-resonance. Again, the resonance frequency was switched between the $S_0$ and $S_f$ spin echoes using a frequency offset list.
(e) TEDOR Experiments

The extension of the REDOR technique to eliminate complications arising from natural abundance background signals led to the TEDOR (transferred-echo double-resonance) experiments [19,20]. The TEDOR experiment is designed to measure the weak I-S dipolar coupling of heteronuclear I-S pairs of spin-1/2 nuclei in the presence of a background of uncoupled I and S spins. In the first step of the TEDOR experiment, dephasing \( \pi \) pulses are introduced to prevent MAS refocusing of the I-S dipolar interaction. Once an effective I-S dipolar coupling (averaged over a rotor cycle) has been created by the dephasing \( \pi \) pulses, a coherence transfer is performed to select S spins dipolar-coupled to I spins from a sample that also contains uncoupled S spins. An observable signal arising from the selected S spins is then created and modulated by REDOR-type, dephasing \( \pi \) pulses. This allows the I-S dipolar coupling to be measured from the modulation pattern of the S spin signal. The TEDOR experiment is not complicated by the presence of signals from uncoupled S spins because the coherence transfer step gives rise to NMR spectra from only S spins that are dipolar-coupled to I spins. The S spin magnetization generated by the 90° S spin pulse in the transfer step is cancelled by phase cycling of the transfer pulses.

The beginning of the TEDOR experiment (Figure 28b) is much the same as in the REDOR experiment. The dephasing 180° pulses on the S channel are still one-half rotor cycle apart but are also now offset by \( \frac{\tau_r}{4} \), \( i.e. \) they occur at one-quarter and three-quarters of each cycle [19,20]. Movement of the 180° pulses by one-quarter of a rotor cycle makes certain versions of the TEDOR experiment possible (\( e.g. \) single-point acquisition) and only affects the trigonometric function present in the evolution of the dipolar-dephasing (see below). The desired goal of retaining terms involving the dipolar coupling is still accomplished. Now 180° pulses are necessary on both channels at \( t = n\frac{\tau_r}{2} \) in order to form the spin-echo while also preserving the sign of the dipolar coupling. At the maximum of the spin-echo (at the end of \( n\tau_r \)), the anti-phase magnetization which
has built up due to the retaining of dipolar interactions during \( n \) periods of dipolar dephasing is now transferred to the S spin system through a set of simultaneous 90° pulses on the I and S channels. After a further \( m \) rotor cycles with continued dephasing pulses on the S spins, the TEDOR signal (\( S_T \)) may be acquired directly. The placement of the dephasing pulses on the S channel after the coherence-transfer (differing from the scheme in references [19,20]) was chosen to minimize the number of pulses on the I nuclei (in our studies, exclusively the quadrupolar species).

The expected signal for the TEDOR experiment can be calculated in an analogous manner to the REDOR experiment. The dipolar dephasing in the first part of the TEDOR experiment evolves for \( n \) rotor periods as:

\[
\Delta \Phi_{T,n} = 4 \sqrt{2} n D \tau_T \cos \alpha \sin \beta \cos \beta
\]  

(44)

with similar dephasing (\( \Delta \Phi_{T,m} \)) during the \( m \) rotor periods of evolution after the coherence transfer. Comparing Eq. (44) to Eq. (42), it can be seen that the TEDOR dephasing now contains a \( \cos \alpha \) rather than the \( \sin \alpha \) dependence in the case of the REDOR signal due to the movement of the 180° pulses by one-quarter of a rotor cycle. The complete TEDOR signal (\( S_T \)) after \( n \) periods of preparative dephasing and \( m \) periods of evolution after the transfer is:

\[
(S_T)_{n,m} = \frac{1}{2\pi} \int_{\alpha=0}^{2\pi} \int_{\beta=0}^{\pi/2} \sin(\Delta \Phi_{T,n}) \sin(\Delta \Phi_{T,m}) \sin \beta \, d\beta \, d\alpha
\]  

(45)

Once again, null experiments were performed by removing the 180° pulses on the S channel which are necessary for the dipolar-dephasing.

Since it involves a coherence-transfer step, the TEDOR experiment can also be extended into a two-dimensional heteronuclear correlation (HETCOR) experiment. The two-dimensional TEDOR experiment involves an extra period of encoding of the I spin magnetization (Figure 28c). The experiments were performed by preparing the I spins with a 90° pulse, and then encoding their evolution frequencies in an initial \( t_1 \) time.
period. At the end of $t_1$, a second 90° pulse is used to remove one orthogonal component of the magnetization by returning it to the z-axis, effectively selecting only one component for the rest of the experiment and making possible the use of TPPI [12,13]. A TEDOR experiment is then begun for the magnetization that remains in the xy-plane. Proper phase cyclings to remove unwanted coherences and allow for TPPI accumulation of the data were employed (see Appendix). The S spin signal is acquired for each of a set of $t_1$ values, and the data array is subjected to a two-dimensional Fourier transform. As in the two-dimensional cross polarization experiment, the result is again a two-dimensional correlation spectrum of the dipolar connected spins in the sample.

The two-dimensional TEDOR experiments were carried out with magnetization transfer from the quadrupolar to the spin-1/2 nuclei (e.g. $^{27}$Al to $^{31}$P), since the short $T_1$ relaxation times for the quadrupolar spins aid in rapid signal averaging of the data. Reasonable experimental times could not be obtained with transfer in the other direction, e.g. from $^{31}$P to $^{27}$Al, due to the much longer $T_1$ relaxation times of the $^{31}$P spin-1/2 nucleus.

(f) $^{27}$Al and $^{31}$P MAS NMR Studies of VPI-5 and AIPO$_4$-8

The samples chosen for study were the aluminophosphate (AIPO$_4$) molecular sieves VPI-5 [21] and AIPO$_4$-8 [22]. The AIPO$_4$ molecular sieves are ideal candidates for the double-resonance NMR connectivity experiments: both $^{27}$Al and $^{31}$P nuclei are 100% abundant and have large magnetogyratic ratios ($\gamma$), giving substantial magnetizations and sensitivity. In addition, the large $\gamma$ values give relatively large dipolar couplings. Furthermore, the AIPO$_4$ molecular sieves are perfectly ordered systems, with exact alternation of $^{27}$Al and $^{31}$P nuclei, resulting in narrow resonances which enhance sensitivity as well as resolution.

VPI-5 was chosen as a representative example of three-dimensional inorganic framework structures, and the unit cell is of sufficient complexity that a number of
resonances are observed in the one-dimensional MAS spectra of both $^{27}$Al and $^{31}$P nuclei at 9.4 T (two for $^{27}$Al and three for $^{31}$P). The unit cell of the AIPO$_4$-8 is somewhat more complex, with at least five inequivalent T-sites for both $^{27}$Al and $^{31}$P in the dehydrated form. Since both systems contain more than one resonance in both of their $^{27}$Al and $^{31}$P MAS spectra, two-dimensional heteronuclear correlation (HETCOR) experiments can be used to provide the complete connectivity patterns among the resonances.

AIPO$_4$-8 was formed by thermal treatment of VPI-5 [23], which involved calcining the sample at 400°C overnight, and then rehydration by stirring in water overnight. The structure of AIPO$_4$-8 as well as the mechanism of its formation from VPI-5 are still a matter of debate [23]. Projections of the proposed structures for both aluminophosphates are reproduced in Figure 30. In both samples, the basic bonding unit is an Al-O-P linkage joining tetrahedrally-coordinated P sites with octahedral or tetrahedral Al sites. As prepared, both aluminophosphates contain water of hydration with two water molecules completing an asymmetric octahedral coordination at certain aluminum sites. Average distances between nearest-neighbour Al and P atoms are approximately 3.1 Å in both samples. Next nearest neighbours are approximately 5.5 Å with much smaller D values.

2.3. Results and Discussion

(a) $^{27}$Al and $^{31}$P MAS NMR Experiments

One-pulse MAS experiments with signal averaging over a number of free induction decays were acquired, yielding the $^{31}$P and $^{27}$Al MAS spectra shown in Figure 31. For the spin-1/2 $^{31}$P, MAS averages the chemical shift anisotropy to zero, and the resonances then appear at their isotropic shift values. Since the spinning frequency is smaller than the frequency spread of the anisotropy, a set of spinning sidebands is also observed at multiples of the spinning frequency. The sidebands contain information regarding the anisotropic interaction that may be recovered from an analysis of the
Figure 30. Projections ([001]) of layers in the framework structures for the two aluminophosphates, AlPO$_4$-8 and VPI-5. The unit cells are shown as dashed boxes. Each vertex in the framework represents a phosphorus or aluminum site, and the lines connecting the vertices are oxygen linkages between the strictly alternating aluminum and phosphorus atoms. Octahedral aluminum sites are formed by coordination of two water molecules at some of the tetrahedral sites.
Figure 31. One-dimensional MAS spectra of AlPO₄-8 and VPI-5. Spinning sidebands in the spectra are labelled with an asterisk (*). (a) $^{31}$P signal from AlPO₄-8 after 64 scans with a recycle delay of 30 s. (b) $^{31}$P signal from VPI-5 after 16 scans with a recycle delay of 30 s. (c) $^{27}$Al signal from AlPO₄-8 after 2048 scans with a recycle delay of 0.5 s. (d) $^{27}$Al signal from VPI-5 after 128 scans with a recycle delay of 0.5 s.
Figure 31

Frequency (ppm from $\text{Al(NO}_3\text{)}_3$)

tetrahedral

octahedral

Figure 31
moments of the sideband pattern [24], or from a comparison of relative sideband intensities [25]. For VPI-5, the \(^{31}\)P spectra reveal three crystallographically distinct phosphorus sites. For AlPO\(_4\)-8, three distinct resonances are also observed in an approximate ratio of 1:2:6. This indicates that there are at least three distinct \(^{31}\)P environments in the hydrated form of AlPO\(_4\)-8, most probably due to the water coordinated to neighbouring octahedral aluminum sites.

The \(^{27}\)Al MAS spectra, acquired after short excitation pulses (magnetization tip angles of less than 90°/(2I+1) = 15°) to ensure quantitative spectra [26], show resonances from both tetrahedrally- and octahedrally-coordinated aluminum atoms, the latter appearing at lower frequency in both cases (less than 0 ppm). For quadrupolar nuclei such as \(^{27}\)Al, MAS does not completely average the anisotropic second-order quadrupolar interaction in the central transition. For the tetrahedrally-coordinated aluminum atoms in VPI-5 and AlPO\(_4\)-8, the strength of the local electric field gradients are such that at 9.4 T, the resonance lines are broadened and shifted from their isotropic chemical shift, but the broadened lines do not show distinct quadrupolar powder patterns. The resonance for the octahedrally-coordinated sites in VPI-5 shows a distinct anisotropy pattern due to the enhanced second-order effects. Since the resonance from the octahedral site in VPI-5 is much broader than that from the tetrahedral site, the quadrupolar interaction must be stronger. In AlPO\(_4\)-8, on the other hand, nutation NMR and proton-decoupled MAS NMR measurements [27] have been interpreted with the quadrupolar coupling at the tetrahedral site being larger than that at the octahedral site, and neither resonance shows a distinct second-order powder pattern. The second-order effects may be further averaged using the techniques of dynamic-angle spinning or double rotation NMR, but these were not used in the present work due to the additional experimental complexity involved. It is important to note that the tetrahedral and octahedral sites can still be resolved from each other at high field without the use of DAS or DOR. As previously noted in the Introduction (Section 1.5d), the DOR technique has been applied previously to VPI-5
[28,29], and splitting of the tetrahedral resonance into two lines of equal intensity has been observed.

(b) One-Dimensional $^{27}\text{Al}/^{31}\text{P}$ Cross-Polarization NMR Experiments

As discussed previously, there have been no previous reports of cross-polarization in which quadrupolar nuclei were used as the magnetization source (i.e. transfer from quadrupolar to spin-1/2 nuclei). In this section, the development of $^{27}\text{Al}/^{31}\text{P}$ cross-polarization NMR experiments is described [30,31]. Cross-polarization is observed in both directions between $^{27}\text{Al}$ ($I=5/2$) and $^{31}\text{P}$ ($I=1/2$) nuclei in the aluminophosphate molecular sieves VPI-5 and AlPO4-8, and an experimental investigation of the parameters controlling the efficiency of the transfer is presented.

$^{27}\text{Al} \rightarrow ^{31}\text{P}$ and $^{31}\text{P} \rightarrow ^{27}\text{Al}$ cross-polarization experiments were performed on VPI-5 and AlPO4-8 as described in the Experimental section, using the pulse sequence in Figure 26a, and representative results are shown in Figure 32. The experiments show that cross-polarization is possible in both directions between quadrupolar and spin-1/2 nuclei. Because of the distance-dependence, the cross-polarization signal arises from nuclei which are close in space, or "connected" to each other. For each sample, therefore, the $^{27}\text{Al} \rightarrow ^{31}\text{P}$ CP experiments show as expected that all three $^{31}\text{P}$ resonances are connected to $^{27}\text{Al}$, while the $^{31}\text{P} \rightarrow ^{27}\text{Al}$ CP experiments show as expected that both the tetrahedral and octahedral $^{27}\text{Al}$ resonances are connected to $^{31}\text{P}$.

Null experiments were also carried out where one pulse or a set of pulses from the sequence in Figure 26a were removed, confirming that each signal arises from the cross-polarization process, and not as the result of direct irradiation of the observed nuclei with the spin-locking field.

The repeat time between acquisitions in these experiments was dictated by the $T_1$ relaxation time of the source nucleus for the polarization transfer. For VPI-5, the $T_1$ of
Figure 32. One-dimensional cross-polarization spectra of AlPO₄-8 and VPI-5: (a) $^{27}$Al → $^{31}$P cross-polarization spectrum of AlPO₄-8, with the null experiment shown below. Contact time was 1.6 ms, and 12800 scans were acquired with a recycle delay of 0.5 s. (b) $^{27}$Al → $^{31}$P cross-polarization spectrum of VPI-5, with the null experiment shown below. Contact time was 0.8 ms, and 16732 scans were acquired with a recycle delay of 0.5 s. (c) $^{31}$P → $^{27}$Al cross-polarization spectrum of AlPO₄-8, with the null experiment shown below. Contact time was 1.5 ms, and 512 scans were acquired with a recycle delay of 30 s. (d) $^{31}$P → $^{27}$Al cross-polarization spectrum of VPI-5, with the null experiment shown below. Contact time was 1.5 ms, and 512 scans were acquired with a recycle delay of 30 s.
Figure 32

(a)  

(b)  

(c)  

(d)  

Frequency (ppm from $\text{H}_3\text{PO}_4$)
the $^{27}$Al (less than 20 ms) is much shorter than that of $^{31}$P (approximately 15 s). For $^{27}$Al $\rightarrow^{31}$P CP, therefore, a short repeat time (100 ms $> 5T_1$ for $^{27}$Al) can be used to acquire the $^{31}$P signal. For $^{31}$P $\rightarrow^{27}$Al CP, on the other hand, a long repeat time (at least 30 s = $2T_1$ for $^{31}$P) is necessary. Therefore, the CP experiment from $^{27}$Al $\rightarrow^{31}$P will generally be preferable. This is a common feature of coherence transfer experiments from quadrupolar to spin-1/2 nuclei in general. The use of quadrupolar spins as a source of magnetization for slowly relaxing spin-1/2 species may therefore allow observation of the spin-1/2 nuclei in condensed solids such as minerals and ceramics, where their very long $T_1$ relaxation times could otherwise preclude their direct observation.

(c) $^{27}$Al $\rightarrow^{31}$P Cross-Polarization with Variation of $^{31}$P B$_1$ Field

The growth of the magnetization as a function of contact time is governed by the cross-polarization time constant ($T_{CP}$), while the decay of the total signal is affected by the efficiency of the spin-lock process (characterized by values for $T_{1P}$). For the VPI-5 sample, the growth of the $^{31}$P signal obtained from cross-polarization was studied as a function of contact time, and maxima were observed at approximately 1.5 ms for all three resonances. (See section 2.3d below for a detailed investigation of cross-polarization with variation of contact time.) Using this contact time and a fixed $^{27}$Al B$_1$ field, the magnitude of the $^{31}$P B$_1$ field was then varied and the $^{31}$P signal intensities measured as a function of field strength. The results are shown in Figure 33 for the three $^{31}$P peaks (numbered from high to low frequency). The maxima do not occur at the theoretical Hartmann-Hahn match for a static sample (from Eq. (35)), as indicated by the vertical arrows, but are offset by one rotor frequency in each direction. The spinning rate is $v_r = 3.0$ kHz, with $2v_r$ corresponding approximately to the 6.1 kHz separation observed between the maxima.
Figure 33. Variation of the $^{27}\text{Al} \rightarrow ^{31}\text{P}$ cross-polarization signal in VPI-5 as a function of the $^{31}\text{P}$ spin-locking $B_1$ field. The theoretical Hartmann-Hahn match for a static sample (from Eq. (35)) is indicated by the arrows. The horizontal bar showing a range of 6.1 kHz comes from a true measurement of 90° pulse lengths at those power settings.
These results are in accordance with the expected cross-polarization behaviour in the limit of fast spinning and weak r.f. field strength, in which the Hartmann-Hahn match condition is shifted by the rotor frequency [16], as shown in Eq. (46) for the present case:

$$\gamma_P B_{1,P} = 3 \gamma_{Al} B_{1,Al} \pm v_r$$

(46)

where the r.f. field strengths $\gamma_X B_{1,X}$ are in frequency units.

Therefore, the usual procedure to set up an $^{27}$Al $\rightarrow$ $^{31}$P cross-polarization experiment is as follows. On the solid sample itself, the 90° pulse is measured for the $^{27}$Al nuclei, and the power on the $^{27}$Al channel is then held fixed. The corresponding $^{27}$Al r.f. field strength is then determined from Eq. (37). Using this value, along with the spinning frequency, the desired $^{31}$P r.f. field strength is calculated from Eq. (46). The corresponding desired $^{31}$P 90° pulse is determined (Eq. (34)), and this pulse time is achieved by varying the power on the $^{31}$P channel. (Since the $^{27}$Al signal is not observed in this CP experiment, the external r.f. channel is used for $^{27}$Al, as the attenuation on the external channel can only be adjusted in relatively large, discrete steps. For the observed $^{31}$P nuclei, the normal X channel of the spectrometer is used, and its attenuation level can be varied in very small increments. It is easier, therefore, to fix the power level on the $^{27}$Al channel, and then make fine adjustments on the $^{31}$P channel.)

(d) $^{27}$Al $\rightarrow$ $^{31}$P Cross-Polarization with Variation of Contact Time

As stated earlier, certain complications may arise when studying cross-polarization in systems involving non-dilute pairs of nuclei, one or both of which is quadrupolar. The first complication involves the efficiency of the spin-locking process, leading to subsequent difficulties with cross-polarization. Vega [15,16] has shown that for quadrupolar nuclei, spin-locking of the central transition is a complex process due to the time-dependence of the first-order quadrupolar splitting in rotating samples. Spin-locking efficiency is greatly reduced in the intermediate region between adiabatic and
sudden passage of the zero-crossings for the first order quadrupolar splitting. Therefore the effective $T_{1p}$ for quadrupolar nuclei will be greatly reduced unless spinning is either very fast or very slow, and cross-polarization efficiency will subsequently diminish. Under the experimental conditions used in our studies, the measured $T_{1p}$ values for the $^{27}\text{Al}$ resonances in VPI-5 of 0.20 ms and 0.37 ms for the tetrahedral and octahedral resonances, respectively, are extremely short. For the spin-1/2 $^{31}\text{P}$ nuclei, the $T_{1p}$ values (from 21 - 31 ms), while still considered short, are much longer than those for $^{27}\text{Al}$ (see Table 5).

In the study of $^1\text{H}$ to $^{13}\text{C}$ cross-polarization, the dynamics of the buildup of $^{13}\text{C}$ signal intensity is usually modelled as:

$$S(t) = S_{\text{max}} \left(1 - \frac{T_{\text{CP}}}{T_{1p}^{\text{H}}}\right)^{-1} \left(\exp(-t/T_{1p}^{\text{H}}) - \exp(-t/T_{\text{CP}})\right)$$

where $T_{1p}^{\text{H}}$ is the time constant for spin-lattice relaxation of the protons in the rotating frame and $T_{\text{CP}}$ is the cross-polarization time constant which depends on the dipolar coupling and has a distance dependence of $1/r^6$. This model includes assumptions that $T_{1p}^{\text{C}}$ for the dilute $^{13}\text{C}$ nuclei is very long (i.e. $T_{1p}^{\text{C}} >> T_{1p}^{\text{H}}$ and $T_{1p}^{\text{C}} >> T_{\text{CP}}$), and that the number of protons is much greater than the number of dilute spins. Without these assumptions, which cannot be made for the study of $^{27}\text{Al}$ and $^{31}\text{P}$ in aluminophosphates, the equations for the dynamics of the cross-polarization process are more complicated and involve the $T_{1p}$ values of both sets of nuclei (Eq. (48)-(53)). For cross-polarization from I spins to S spins, a spin thermodynamic treatment gives [32,33]:

$$S(t) = S_{\text{max}} (a_+ - a_-)^{-1} \left(\exp(-a_+ t/T_{\text{CP}}) - \exp(-a_- t/T_{\text{CP}})\right)$$

where

$$a_+ = c \left[1 \pm \left(1 - \frac{b}{c^2}\right)^{1/2}\right]$$

$$b = \left(\frac{T_{\text{CP}}}{T_{1p}^{\text{I}}}\right) \left(1 + \frac{T_{\text{CP}}}{T_{1p}^{\text{S}}}\right) + \epsilon \alpha^2 \left(\frac{T_{\text{CP}}}{T_{1p}^{\text{S}}}\right)$$

$$c = 1/2 \left(1 + \epsilon \alpha^2 + \frac{T_{\text{CP}}}{T_{1p}^{\text{I}}} + \frac{T_{\text{CP}}}{T_{1p}^{\text{S}}}\right)$$

$$\epsilon = \frac{N_S}{N_I} \left[\frac{1}{(S+1/2)/(S+1/2)}\right]$$
\[ \alpha = \frac{(S + 1/2) \gamma S B_{1,S} \pm n \nu_r}{(I + 1/2) \gamma I B_{1,I}} \] with \( n = 1, 2 \) (53)

and \( N_X \) is the number of \( X \) nuclei present in the sample. The parameter \( \alpha \) is a measure of the modified Hartmann-Hahn matching condition, and is equal to one when the matching condition is satisfied. For strictly alternating aluminophosphate systems where the number of \( ^{27}\text{Al} \) and \( ^{31}\text{P} \) nuclei are equal, \( \varepsilon \alpha^2 \) is thus equal to 3 (\( ^{27}\text{Al} \rightarrow ^{31}\text{P} \) CP) or 1/3 (\( ^{31}\text{P} \rightarrow ^{27}\text{Al} \) CP).

For \( ^{27}\text{Al} \rightarrow ^{31}\text{P} \) cross-polarization, however, Eqs. (48)-(53) can be simplified considerably. Since \( ^{27}\text{Al} \) is a quadrupolar nucleus, its \( T_{1p} \) value is very small, i.e. \( T_{1p}^I \ll T_{1p}^S \) and \( T_{1p}^I \ll T_{CP} \). With this assumption, the CP process can be modelled as in Eq. (54).

\[ S(t) = S_{max} T_{1p}^I T_{CP} \left( \exp\left(-t \left( \frac{1}{T_{1p}^S} + \frac{1}{T_{CP}} \right) \right) - \exp\left(-t/T_{1p}^I \right) \right) \] (54)

It is interesting to note that because \( \varepsilon \alpha^2 \) is small, i.e. \( \varepsilon \alpha^2 \ll T_{CP}/T_{1p}^I \), Eq. (54) does not have any dependence on the value of \( \varepsilon \alpha^2 \).

Using the data in Figure 33, the \( ^{31}\text{P} \) r.f. field was set at the lower value where the signal is a maximum (\( \gamma P B_{1,P} = 18.8 \text{ kHz}, \ t_{90}^P = 13.3 \mu\text{s} \)), and a study of \( ^{27}\text{Al} \rightarrow ^{31}\text{P} \) cross-polarization with variation of contact time was performed on VPI-5. The results are shown in Figure 34 for the three \( ^{31}\text{P} \) resonances. The maxima in all three curves occur at approximately 1.5 ms. It is interesting to note that the signal maximum from the third \( ^{31}\text{P} \) peak (that at lowest frequency) did not reach as high of a value as those from the other two \( ^{31}\text{P} \) resonances.

It is possible to fit the behaviour of the curves in Figure 34 using Eqs. (48)-(53) for the general cross-polarization case, and also using Eq. (54) simplified for \( ^{27}\text{Al} \rightarrow ^{31}\text{P} \) cross-polarization. The parameters \( S_{max}, T_{CP}, T_{1p}^\text{Al}, \) and \( T_{1p}^\text{P} \) were fit with a non-linear least-squares routine in the Mathematica™ programming environment running on a Macintosh IIci computer. Initial estimates for the \( T_{1p} \) values were provided before the fit by averages of the measured \( T_{1p} \) values for the aluminum and phosphorus spins in VPI-5.
Figure 34. Variation of the $^{27}\text{Al} \rightarrow ^{31}\text{P}$ cross-polarization signal in VPI-5 as a function of contact time. The maxima occur at approximately 1.5 ms and the dashed lines are from a non-linear least squares fit to Eq. (54).
The results from the curve fits using the simplified Eq. (54) are the same as those using the general Eqs. (48)-(53), verifying that Eq. (54) is a valid model. The values for all of the relevant time constants appear in Table 5 (under "Direct CP"). The closeness of the fits may be judged by simulating the curves of Figures 34 with the parameters obtained, and these are shown as dashed lines on the graphs. It can be seen that the fits are all reasonably good.

Table 5. Experimentally determined parameters for the cross-polarization between $^{27}\text{Al}$ and $^{31}\text{P}$ nuclei in VPI-5.

<table>
<thead>
<tr>
<th>$^{31}\text{P}$ Site</th>
<th>Experiment</th>
<th>[ T_{\text{IP}} ] (ms)</th>
<th>[ T_{\text{IP}} ] (ms)</th>
<th>[ T_{\text{IP}} ] (ms)</th>
<th>[ T_{\text{CP}} ] (ms)</th>
<th>[ T_{\text{IP}} ] (ms)</th>
<th>[ T_{\text{CP}} ] (ms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1 (-23 ppm)</td>
<td>Spin-Lock</td>
<td>31</td>
<td>12</td>
<td>0.45</td>
<td>55</td>
<td>29</td>
<td>57</td>
</tr>
<tr>
<td></td>
<td>Direct CP</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Difference CP</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P2 (-27 ppm)</td>
<td>Spin-Lock</td>
<td>28</td>
<td>13</td>
<td>0.40</td>
<td>55</td>
<td>27</td>
<td>55</td>
</tr>
<tr>
<td></td>
<td>Direct CP</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Difference CP</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P3 (-33 ppm)</td>
<td>Spin-Lock</td>
<td>21</td>
<td>13</td>
<td>0.40</td>
<td>92</td>
<td>23</td>
<td>96</td>
</tr>
<tr>
<td></td>
<td>Direct CP</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Difference CP</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(a) Direct measurements of $T_{\text{IP}}$ values were 0.20 ms for the tetrahedral $^{27}\text{Al}$ resonance and 0.37 ms for the octahedral $^{27}\text{Al}$.

In addition, the parameters obtained may be compared to the measured $T_{\text{IP}}$ values in Table 5 (under "Spin-Lock"). It is observed that the $^{31}\text{P}$ $T_{\text{IP}}$ values are considerably lower from the fits, while the (average) $^{27}\text{Al}$ $T_{\text{IP}}$ values are higher. The $T_{\text{IP}}$ values calculated from the fits are similar for the three $^{31}\text{P}$ resonances, but they differ in the calculated values for $T_{\text{CP}}$. The third (lowest frequency) $^{31}\text{P}$ peak has a much larger value for $T_{\text{CP}}$ compared to the other two peaks, which have equal values for this parameter.

The $S_{\text{max}}$ values, which represent the normalized full intensities of the resonances, are found to be in a ratio of 1.0:1.0:1.2 for the $^{31}\text{P}$ sites 1, 2, and 3, respectively (from highest to lowest frequency), which is close to the expected 1:1:1 ratio for the three equally
occupied $^{31}$P sites. Since the $S_{\text{max}}$ values are similar, they cannot account for the lower signal maximum of the low frequency peak in the cross-polarization experiments (see Figure 34). Therefore, we attribute this difference to be mainly due to the difference in the $T_{\text{CP}}$ values. This cross-polarization time constant is related to the strength of the dipolar coupling, and hence the rate at which the cross-polarization signal is obtained. A longer time constant describes less efficient polarization transfer due to a weaker dipolar coupling between the nearby aluminum spins and the phosphorus spins contributing to this resonance. On this basis, we make a preliminary assignment of this $^{31}$P peak to the phosphorus site in VPI-5 that lies between two four-membered rings (P1 of reference [34]), since the other two phosphorus sites are more alike (shared between four- and six-membered rings) and are expected to show similar behaviour under cross-polarization compared to the other site. This assignment agrees with that of other authors [35-37].

Although calculated values of the second moments could be obtained from the x-ray structure parameters [34], we do not feel that the quantitative reliability of the $T_{\text{CP}}$ data justifies more than a qualitative interpretation.

(e) Cross-Polarization Difference Experiments

The cross-polarization difference experiment [8,9,38] is a further experiment of interest, in which the disappearance of the source (I) magnetization in the $I \rightarrow S$ cross-polarization process is studied. In this case, the magnetization is observed from the source I nuclei after the contact time with the target S nuclei, and this signal is subtracted from the signal obtained from a similar spin-lock on the I spins alone with no S spin irradiation. The observed difference signal reflects the depletion of the I spin signal due to polarization transfer to the S spins.

$^{31}$P $\rightarrow$ $^{27}$Al cross-polarization difference experiments on VPI-5 were performed using the pulse sequence in Figure 35. (The pulse program is given in Appendix 6.) In the first experiment (a), the $^{31}$P signal [acq]+ is obtained from a spin-lock on the $^{31}$P
Figure 35. Pulse sequence for $^{31}\text{P} \rightarrow ^{27}\text{Al}$ cross-polarization difference experiments, which measure the draining of the $^{31}\text{P}$ signal by contact with $^{27}\text{Al}$ spins. (a) In the first experiment, a spin locking pulse is applied to the $^{31}\text{P}$ nuclei, no pulse is applied to the $^{27}\text{Al}$ nuclei, and the $^{31}\text{P}$ signal is added to memory. (b) In the second experiment, the $^{27}\text{Al}$ nuclei are irradiated during the $^{31}\text{P}$ spin lock, and the $^{31}\text{P}$ signal is subtracted from memory.
spins alone with no $^{27}\text{Al}$ irradiation. In the second experiment (b), a spin-locking field is applied to the $^{27}\text{Al}$ nuclei, and the reduced $^{31}\text{P}$ signal [acq]- is subtracted from the [acq]+ signal. The resulting difference signal reflects the draining of the $^{31}\text{P}$ signal due to polarization transfer to the $^{27}\text{Al}$ nuclei. The magnitude of the difference signal for VPI-5 was studied as a function of contact time, and the behaviour of the signal for all three $^{31}\text{P}$ resonances is shown in Figure 36.

These experiments were performed to further understand the numerical values and relative importance of the $T_{1p}$ and $T_{CP}$ parameters in the CP process. It has been demonstrated that oscillations in CP signals between pairs of spins may be observed due to heteronuclear dipolar couplings, with reverse polarization transfer occurring as the magnetization is shuttled between the coupled nuclei. This has been reported for static single crystal samples [39], as well as for polycrystalline samples under MAS conditions [38,40]. Rapid phase modulation of the spin-locking field of the unobserved nucleus can quench reverse polarization transfer, effectively forcing a short $T_{1p}$ on the unobserved nucleus. The reverse transfer of polarization is quenched by rapid dephasing of the magnetization, and the direct difference signal does not show oscillations but continues to grow to a higher value than if reverse transfer were a dominant mechanism. Under these conditions, the difference magnetization, $S_{\text{diff}}(t)$, should grow as a function of the cross-polarization time constant, $T_{CP}$, while decaying due to the loss of $^{31}\text{P}$ (I) magnetization from the spin-lock (governed by $T_{1p}^I = T_{1p}^P$), so that [41]:

$$S_{\text{diff}} = S_{\text{max}} \exp(-t/T_{1p}^I) (1 - \exp(-t/T_{CP}))$$  (55)

Stejskal and co-workers have also shown that the dependence of the signal on $T_{1p}^I$ may also be removed by normalization of the difference signal with respect to the signal without draining from the unobserved ($^{27}\text{Al}$) nucleus [41]. However, we wanted to obtain another experimental estimate of the $T_{1p}^P$ values under cross-polarization conditions, and thus did not perform this normalization.
Figure 36. Variation of the $^{31}\text{P} \rightarrow ^{27}\text{Al}$ cross-polarization difference signal as a function of contact time in VPI-5. The dashed lines are from fits to Eq. (55).
The observation in Figure 36 that the signals continue to grow and do not show any oscillations is expected due to the short $T_{1p}$ values for the $^{27}$Al nuclei. The $T_{\text{CP}}$ and $T_{1pP}$ values were again estimated with a non-linear least squares analysis, fitting Eq. (55) to the data in Figure 36. The calculated results appear in Table 5 (under "Difference CP"), and these values were used for the simulations in Figure 36 (dashed lines). Here, the values for $T_{1pP}$ are very close to the directly-measured values, while the $T_{\text{CP}}$ values are almost identical to those from the fits of the full cross-polarization dynamics.

The $T_{1pP}$ data are consistent with the anticipated behaviour arising from the differences in the three experimental methods used for $T_{1p}$ determination. Thus, the results from the difference experiments are the same as those from the spin-lock measurements since the role of the aluminum nuclei in the difference experiments is only to remove $^{31}$P magnetization via the modified Hartmann-Hahn match. In the direct CP experiments, the total efficiency is determined by the effectiveness of both individual spin-locking processes, and, therefore, we obtain reduced $T_{1pP}$ values.

(f) Two-Dimensional Cross-Polarization Experiments

Resolving an NMR spectrum into two or more dimensions is helpful when one-dimensional spectra confirm that connectivities do exist between nuclei, yet direct connectivities between particular sites are still unknown or in question. For example, in the hydrated form of VPI-5, there are three phosphorous sites and three aluminum sites as deduced from MAS and DOR NMR results. Any proposed structures must contain three crystallographically inequivalent sites for both species to be consistent with these data. All of these sites are connected to each other (with only one oxygen atom between them) according to the proposed structure of McCusker and coworkers [34].

Since the cross-polarization experiment involves a transfer of magnetization from I to S nuclei, the experiment can be extended into a two-dimensional heteronuclear
Figure 37. Two-dimensional $^{27}\text{Al} \rightarrow ^{31}\text{P}$ cross-polarization experiment on VPI-5, with a contact time of 0.8 ms. A total of 640 scans were acquired for each of 256 experiments in $t_1$. The recycle delay of 0.5 s resulted in a total experimental time of 22.8 hours.
Figure 38. Two-dimensional $^{27}$Al $\rightarrow ^{31}$P cross-polarization experiment on AlPO$_4$-8, with a contact time of 1.6 ms. A total of 800 scans were acquired for each of 128 experiments in $t_1$. The recycle delay of 0.5 s resulted in a total experimental time of 14 h.
correlation experiment. Two-dimensional cross-polarization experiments were performed on both samples, with initial evolution of $^{27}$Al magnetization followed by polarization transfer to the $^{31}$P nuclei. For VPI-5, the two-dimensional spectrum of Figure 37 shows connectivities between all three $^{31}$P sites and both of the resolved $^{27}$Al sites (tetrahedral and octahedral). This is consistent with the proposed structure of ref. [34], as all connectivities are observed. For AlPO$_4$-8, the two-dimensional cross-polarization spectrum of Figure 38 again shows that both the tetrahedral and octahedral $^{27}$Al resonances are connected via dipolar couplings to each of the three resolved $^{31}$P sites in the second dimension.

(g) $^{27}$Al/$^{31}$P Dipolar-Dephasing Difference Experiments

As explained in the Experimental section earlier, dipolar-dephasing difference MAS NMR experiments are used to indicate connectivities between coupled heteronuclei through the dipolar interaction between them.

Dipolar-dephasing difference experiments were performed in both directions between the $^{27}$Al and $^{31}$P nuclei in VPI-5 using to the pulse sequence in Figure 27b, and the results [31] are shown in Figure 39. Here, the null experiments were carried out by moving all pulses applied to the S nuclei far off resonance, as described in the Experimental Section. Since signals are present only for those nuclei of one type (e.g. $^{27}$Al) which are dipolar coupled or "connected" to heteronuclei of another type (e.g. $^{31}$P), the appearance of signals in these experiments again establishes $^{27}$Al/$^{31}$P internuclear connectivities in the VPI-5 framework. This is the first time that these experiments have been used to show connectivities in molecular sieve systems with more than one tetrahedral site.

(h) $^{27}$Al/$^{31}$P REDOR Experiments on VPI-5 and AlPO$_4$-8

The REDOR experiment is a double-resonance solid-state NMR experiment that has been used to measure dipolar couplings, and hence internuclear distances, between
Figure 39. Dipolar-dephasing difference experiments on VPI-5. (a) $^{31}\text{P}$ dipolar-dephasing difference signal showing those resonances connected to the $^{27}\text{Al}$ spins. The null experiment is shown below. 32 scans were acquired with a recycle delay of 30 s. (b) $^{27}\text{Al}$ dipolar-dephasing difference signal showing that the resonances from both tetrahedral and octahedral aluminum sites are connected to the $^{31}\text{P}$ spins. The null experiment is shown below. 4096 scans were acquired with a recycle delay of 0.3 s.
isolated pairs of spin-1/2 heteronuclei. This section [31,42] describes the extension of the REDOR experiment to include quadrupolar nuclei and nonisolated spin pairs. The REDOR experiment was performed between $^{27}\text{Al}$ and $^{31}\text{P}$ nuclei in the aluminophosphate framework systems VPI-5 and AIPO$_4$-8.

In a REDOR experiment, dipolar-dephasing from 180° pulses during a spin-echo experiment is used to determine internuclear connectivities, or in ideal situations, internuclear distances. As discussed previously, in aluminophosphate framework systems with strictly alternating aluminum and phosphorus tetrahedra, the average distance between neighbouring tetrahedral sites is 3.1 Å. The second-nearest neighbour tetrahedral sites are populated by the same nuclear species due to the strictly alternating arrangement. Therefore, one must move to the third-nearest neighbour tetrahedral sites to reach the next heteronuclear species. Since the dipolar coupling drops off very steeply with increasing interatomic distance (magnitude proportional to $1/r^3$), these sites would provide a much smaller dipolar coupling than the nearest neighbours. The appearance of a difference signal in a REDOR spectrum, therefore, is assumed to arise only from nearest-neighbour tetrahedral sites.

The REDOR experiments were carried out in both directions between $^{27}\text{Al}$ and $^{31}\text{P}$ nuclei in VPI-5 and AIPO$_4$-8 using the pulse sequence in Figure 28a, and the difference spectra ($\Delta S$) are shown in Figure 40 with the experimental conditions as specified in the caption. In both directions, null experiments (not shown) were undertaken to ensure that the observed signal came from the dipolar-dephasing phenomenon and not from timing missets or experimental artifacts (see Experimental Section). The strong $\Delta S$ signals from both samples, with both types of nuclei being clearly observed, demonstrate the utility of these experiments for determining heteronuclear dipolar connectivities in solids.

Variation of the number of rotor cycles in the REDOR experiment leads to a
Figure 40. $^{27}\text{Al}^{31}\text{P}$ REDOR experiments in both directions for AlPO$_4$-8 and VPI-5. 
(a) $^{31}\text{P}(^{27}\text{Al}) \Delta S$ REDOR signal from AlPO$_4$-8 showing those resonances connected to $^{27}\text{Al}$ spins. 48 scans were acquired with a recycle delay of 90 s. (b) $^{31}\text{P}(^{27}\text{Al}) \Delta S$ REDOR signal from VPI-5 showing those resonances connected to $^{27}\text{Al}$ spins. 1536 scans were acquired with a recycle delay of 30 s. (c) $^{27}\text{Al}(^{31}\text{P}) \Delta S$ REDOR signal from AlPO$_4$-8 showing both resonances connected to $^{31}\text{P}$ spins. 4096 scans were acquired with a recycle delay of 0.5 s. (d) $^{27}\text{Al}(^{31}\text{P}) \Delta S$ REDOR signal from VPI-5 showing both resonances connected to $^{31}\text{P}$ spins. 4096 scans were acquired with a recycle delay of 0.5 s.
Figure 40

(a) Frequency (ppm from 85% H$_3$PO$_4$)

(b) Frequency (ppm from Al(NO$_3$)$_3$)
different amount of dipolar-dephasing which will accumulate with time as shown in Eqs. (42) and (43). For individual pairs of dipolar coupled nuclei, these equations may be used to generate the universal curve of Figure 41a which indicates the amount of REDOR signal scaled by the full (uncoupled) echo intensity. However, this curve is valid only for an isolated pair of spin-1/2 nuclei. In the aluminophosphate systems studied here, quadrupolar $^{27}$Al nuclei are involved, and there are four nearby heterospins contributing dipolar-dephasing to the signal of the observed spins. Therefore, the experimental curves are not expected to show the exact shape of the universal curve of Figure 41a (e.g. show an oscillation), but should qualitatively display the same behaviour.

Figures 41b,c show the evolution of the $^{27}$Al($^{31}$P) REDOR signals (i.e. $^{27}$Al observation with $^{31}$P decoupling) for both the tetrahedral and octahedral $^{27}$Al nuclei in VPI-5. As anticipated, the curves do not show an oscillation, rather they show a smooth approach towards full dephasing ($\Delta S/S = 1$). Computer modelling of the REDOR behaviour for a tetrahedron of $^{31}$P spins surrounding a central $^{27}$Al nucleus at an average internuclear distance of 3.1 Å also shows this behaviour, but the curves do not give a quantitative measure of the average bond distance.

Figure 42 shows the evolution of the $^{31}$P($^{27}$Al) REDOR intensities (i.e. $^{31}$P observation with $^{27}$Al decoupling) for the three resonances from VPI-5. Once again these curves show no oscillations as they approach $\Delta S/S = 1$. The study of these $^{31}$P($^{27}$Al) REDOR intensities is much more complex than the previous $^{27}$Al($^{31}$P) case, however, since each $^{27}$Al nucleus near to a $^{31}$P is not necessarily perturbed by the 180° pulses on the $^{27}$Al channel. Only a certain fraction (roughly one-third) of the $^{27}$Al nuclei have a spin energy level characterized as in the central transition (either in the +1/2 or -1/2 level), and only these (to a first approximation) will be flipped by the 180° pulses. The evolution of the $^{31}$P($^{27}$Al) REDOR signals (Figure 42), therefore, is slower than the $^{27}$Al($^{31}$P) REDOR signals (Figure 41b,c) since in the latter case, the dephasing 180°
Figure 41. Evolution of REDOR ($\Delta S/S_0$) signals: (a) Ideal evolution of the REDOR signal for $n$ rotor cycles of period $\tau_r$, assuming an isolated spin pair with dipolar coupling $D$. (b-c) Evolution of the $^{27}$Al($^{31}$P) REDOR signals in VPI-5, with $\tau_r = 322$ $\mu$s, for (b) the tetrahedral $^{27}$Al resonance and (c) the octahedral $^{27}$Al resonance.
Figure 42. Evolution of $^{31}\text{P}^{(27}\text{Al})$ REDOR signals for the $^{31}\text{P}$ peaks in VPI-5, with $\tau_r = 322$ µs, for: (a) the first (high frequency) $^{31}\text{P}$ peak, (b) the second $^{31}\text{P}$ peak, and (c) the third $^{31}\text{P}$ peak.
pulses affect all of the neighbouring spins, while in the former case, the 180° pulses affect only a fraction of the neighbouring spins. A complete analysis would have to take into account all spin levels of the $^{27}$Al nuclei and the effect of an on-resonance 180° pulse for the central transition. Qualitatively, however, the behaviour is as expected, and useful connectivity information can be obtained.

(i) $^{27}$Al $\rightarrow$ $^{31}$P TEDOR Experiments on VPI-5 and AlPO$_4$-8

Like REDOR, the TEDOR experiment is a double-resonance solid-state NMR experiment that has been used to measure internuclear distances between isolated pairs of spin-1/2 heteronuclei. This section [31,42] describes the extension of the TEDOR experiment to include quadrupolar nuclei and nonisolated spin pairs. The TEDOR experiment was performed between $^{27}$Al and $^{31}$P nuclei in the aluminophosphate framework systems VPI-5 and AlPO$_4$-8.

As discussed previously, the TEDOR experiment was initially introduced to overcome the contributions of uncoupled natural abundance spins to the echo signal measured in a REDOR experiment. In the aluminophosphate systems studied here, there should be no uncoupled spins measured, but such contributions will be important when other spin-1/2 and quadrupolar systems are considered (e.g. $^{27}$Al/$^{29}$Si in zeolites). The use of coherence transfer also changes the experimental conditions in that the repeat time is determined by the $T_1$ relaxation times of the I spins which are not detected after the coherence transfer, and this will be an important advantage when considering aluminophosphates. The $^{27}$Al $T_1$ relaxation times are often of the order of tens of milliseconds or less, while the $^{31}$P spins have relaxation times of many seconds. Therefore, the $^{31}$P experiments may be repeated much faster if the relaxation time governing the experimental repetition is that of the $^{27}$Al. This will generally be true when other quadrupolar species are involved.

Figure 43 shows the $^{27}$Al $\rightarrow$ $^{31}$P TEDOR experiments performed on VPI-5 and
Figure 43. TEDOR signals from $^{27}\text{Al} \rightarrow ^{31}\text{P}$ coherence transfer in AlPO$_4$-8 and VPI-5, with $n = 2$ and $m = 1$. (a) Signal from AlPO$_4$-8 after 14400 scans with a recycle delay of 0.25 s. (b) Signal from VPI-5 after 9000 scans with a recycle delay of 1 s.
AIPO₄-8 using the pulse sequence in Figure 28b. In the TEDOR experiments, initial ²⁷Al antiphase magnetization was formed after two rotor cycles of preparative dephasing (n = 2). After coherence transfer of the antiphase magnetization (through simultaneous 90° pulses) and one additional rotor cycle of dipolar evolution (m = 1) in order to create observable spin coherence, the ³¹P signal was detected. Thus, coherence transfer from quadrupolar to spin-1/2 nuclei is feasible using the TEDOR experiment, as demonstrated previously for the cross polarization experiment.

The antiphase magnetization transfer (initially unobservable) evolves during this additional period into the in-phase magnetization which is detected. The evolution of the sidebands, however, is different from that of the isotropic peaks, and thus they are of different phase in the final spectra. Also important is proper phase cycling of the r.f. pulses to remove any signal arising from just the ³¹P 90° transfer pulse. As before, null experiments were performed and gave the expected null signals (not shown), confirming that the observed ³¹P signal is due only to coherence transfer from ²⁷Al nuclei.

Variation of the number of rotor cycles before or after the coherence transfer in the TEDOR experiment leads to differing amounts of dipolar-dephasing which will accumulate in time as shown in Eqs. (44) and (45). For individual pairs of dipolar coupled nuclei, these equations may again be used to generate a universal curve, shown in Figure 44a, which indicates the total amount of TEDOR signal obtained. As before, this curve is only strictly valid for an isolated pair of spin-1/2 nuclei. Thus, the theoretical analysis is complicated by the tetrahedral geometry of the ²⁷Al atoms surrounding the ³¹P nuclei. The ²⁷Al → ³¹P TEDOR curves for the three different ³¹P sites in VPI-5 are shown in Figures 44b,c and d, where the intensities plotted are those of the isotropic resonances alone, i.e. excluding the sidebands which have a different phase. Qualitatively, the expected rise at early numbers of rotor cycles is seen, with very quick damping of the signal as the number of rotor cycles is increased. As in the REDOR experiments, it is the qualitative connectivity information that can be obtained which
Figure 44. Evolution of TEDOR signals: (a) Ideal evolution of the TEDOR signal for $nD\tau_r = 1$ and assuming an isolated spin pair with dipolar coupling $D$. (b)-(d) Evolution of the $^{27}\text{Al} \rightarrow ^{31}\text{P}$ TEDOR signal for the three $^{31}\text{P}$ sites in VPI-5 with $\tau_r = 319$ $\mu$s and preparative dephasing for $n = 2$ rotor cycles. The number of rotor cycles after transfer $(m)$ was varied from 0 to 8. Since there is no $S_0$ experiment for reference, the peak heights are scaled in arbitrary units.
Figure 44
should be emphasized. The extension of this experiment into a second spectral dimension, discussed below, depends on observing qualitative connectivities as cross-peaks in the two-dimensional correlation plots.

The appearance of signals in both the one-dimensional REDOR and TEDOR spectra confirms that these experiments are useful for studying quadrupolar/spin-1/2 systems. The experiments are efficient enough with the moderate dipolar couplings in this system (approximately 400 Hz) that connectivities are observed in the Al-O-P linkages. When accumulating a $^{31}$P REDOR spectrum, the recycle time is dictated by the slow $^{31}$P relaxation rate, while the $^{27}$Al REDOR spectrum is acquired in less time due to the fast quadrupolar relaxation of the $^{27}$Al spins. However, the $^{31}$P TEDOR signal is accumulated quickly compared to the $^{31}$P REDOR signal since one must wait only for the relaxation of the quadrupolar $^{27}$Al spins. A similar situation is encountered when cross polarization experiments are performed from $^{27}$Al to $^{31}$P in VPI-5 [30,31]. The TEDOR experiment should therefore prove extremely useful for the observation of spin-1/2 nuclei with long spin-lattice relaxation times that are near to quadrupolar nuclei, as is often the case in dense inorganic systems such as minerals and ceramics.

(j) Two-dimensional TEDOR Experiments

The TEDOR experiment is also amenable to extension into a second spectral dimension since it involves coherence transfer to a heteronucleus, rather than spin-echo detection of dipolar decoupling in a difference experiment (as in the dipolar-dephasing or REDOR experiments). The two-dimensional $^{27}$Al $\rightarrow$ $^{31}$P TEDOR spectrum of VPI-5 is shown in Figure 45, acquired using the experimentally optimized conditions of two rotor cycles of preparative dephasing and one rotor cycle of anti-phase to in-phase evolution after the transfer ($n = 2$, $m = 1$). Figure 45 shows cross-peaks between all three $^{31}$P resonances and both tetrahedral and octahedral $^{27}$Al (the six resonances within the dashed box). Therefore, all of the expected connectivities are present between the observed
Figure 45. Two-dimensional $^{27}$Al $\rightarrow$ $^{31}$P TEDOR experiment on VPI-5, with $n = 2$ and $m = 1$. 3600 scans were acquired for each of 128 experiments in $t_1$. The recycle delay of 0.5 s resulted in a total experimental time of 64 h. The connected resonances are indicated by the dashed box.
resonances, in agreement with the proposed structure [34]. In addition, Figure 45 shows that the connectivities from the tetrahedral $^{27}$Al resonance to the $^{31}$P sites at -23 and -27 ppm (P1 and P2 sites, respectively) are slightly offset from one another. Since the tetrahedral $^{27}$Al resonance is due to two distinct tetrahedral aluminum environments, the offset between the connectivities to the P1 and P2 sites may be due to differences in the connectivities to the two tetrahedral aluminum sites. The two-dimensional TEDOR spectrum is pure-absorption-phase, with contours from both positive and negative intensities. The sidebands have some negative intensity as in the one-dimensional $^{27}$Al $\rightarrow ^{31}$P TEDOR spectrum (see Figure 43b), but the projections are absolute value mode due to the processing software of the spectrometer. A related two-dimensional coherence transfer experiment (using a different pulse sequence) was subsequently reported by van Eck and Veeman [43], and these authors obtained very similar results for the VPI-5 system.

Our new two-dimensional TEDOR experiment provides a qualitative picture of internuclear connectivities. However, the full assignment of peaks in these systems is not possible from qualitative connectivity data alone. Still, it is anticipated that there are many systems where the qualitative information alone will confirm, dispute, or suggest proposed structures or topologies in three-dimensional inorganic frameworks, particularly in cases where single crystal diffraction experiments are not possible.

A further extension of these experiments might help in the exact assignment of the resonances: Two-dimensional cross-polarization or TEDOR experiments which incorporate DOR or DAS techniques to obtain high-resolution of the quadrupolar $^{27}$Al nuclei might be able to resolve the connectivities to the two crystallographically inequivalent tetrahedral aluminum environments.
Spin diffusion [44] is a spin-lattice ($T_1$) relaxation phenomenon which occurs in the limit of "slow" molecular motion, i.e. $\omega_0 \tau_C >> 1$ where $\omega_0$ is the Larmor frequency and $\tau_C$ is the characteristic correlation time for the motion (see Section 1.2e). In this limit, the rate of transfer of spin energy between nuclei becomes much larger than the rate of transfer of energy to the lattice. In the double-resonance NMR experiments carried out in this thesis, spin diffusion could be an additional complicating factor by causing a widening of the connectivity networks, thereby making the results worthless for even qualitative information regarding molecular topology. To determine whether spin diffusion is occurring in these experiments, a number of $^{31}$P spin diffusion NMR experiments [45] were undertaken with various conditions during the mixing period (continuous r.f. irradiation on one or both nuclei as in the cross-polarization experiments, or the application of properly timed $^{27}$Al 180° r.f. pulses as in the REDOR and TEDOR experiments). No significant cross-peak intensity was observed in the two-dimensional spin diffusion spectra with mixing times of up to 25 ms, i.e. equal to or greater than the time scales of the one- and two-dimensional double-resonance experiments (approximately 1-5 ms). Therefore, the effect of spin diffusion has been discounted in the analysis. It is felt that these conclusions are valid for all AlPO$_4$ molecular sieves and other related systems since they are all perfectly alternating systems, and the $^{27}$Al-O-$^{31}$P distances (and thus the dipolar couplings) are all approximately the same. However, care should be taken to check this when new systems are being studied.
2.4. Conclusions

Cross-polarization and dipolar-dephasing experiments have been demonstrated and shown to be able to determine connectivities between quadrupolar and spin-1/2 nuclei in aluminophosphate molecular sieves. These experiments should also be more generally applicable to systems of quadrupolar and spin-1/2 nuclei such as $^{27}$Al/$^{29}$Si and $^{11}$B/$^{29}$Si. In the systems studied here, the cross-polarization experiments offer the advantage of selectivity rather than gains in signal-to-noise ratio. However, if the quickly relaxing quadrupolar spins are used as a polarization source, it may be possible to observe slowly relaxing spin-1/2 species in a much shorter time period, which will be important in condensed inorganic solids where the $T_1$ values of spin-1/2 nuclei may be as high as 1000 seconds.

In the case of cross-polarization involving less common spin pairs, many of the conventional ideas from $^1$H/$^13$C CP/MAS experiments are still useful, but they must be carefully re-evaluated. More general equations are needed for the cross-polarization dynamics, and an important role may often be played by quickly relaxing nuclei whose $T_{1p}$ values are shorter than $T_{CP}$. Measurement of all $T_{1p}$ values in the systems studied is necessary for a complete understanding of the cross-polarization dynamics. We have found internal consistencies among time constants calculated in these experiments for the behaviour of the spin-locked systems using conventional $T_{1p}$ measurements and a non-linear least squares analysis of direct cross-polarization and cross-polarization difference experiments.

Although not directly analogous to the cross-polarization experiments, the REDOR and TEDOR experiments also reveal connectivities via the dipolar interactions. Although not the case for the aluminophosphates studied here, if isolated pairs of spin-1/2 nuclei are involved, the REDOR and TEDOR data can provide important distance information. The spins considered could be selectively enriched to provide isolated spin
pairs (such as the $^{13}\text{C}/^{15}\text{N}$ spin pairs in biomolecules), or they might occur naturally (as in the $^{27}\text{Al}/^{31}\text{P}$ spin systems in aluminophosphates).

Due to the selectivity of the dipolar interactions exploited in these experiments, it is useful to design two-dimensional NMR correlation experiments based on these methods. Cross-polarization and TEDOR can be extended into two-dimensional experiments, and both corroborate the proposed structure of VPI-5 obtained from crystallographic measurements and refinement.

In subsequent chapters, the extension of this work to other pairs of nuclei will be demonstrated in zeolites and other molecular sieves, as well as in borosilicate glasses.
Chapter 2 References

Chapter 3. Increased Efficiency of Coherence-Transfer in Cross-Polarization from Quadrupolar Nuclei: Dynamic-Angle Cross-Polarization (DACP)

This chapter [1] describes an experiment which increases the efficiency obtained in cross-polarization (CP) experiments involving quadrupolar nuclei by carrying out the CP step while the sample is spinning parallel to the magnetic field. After the CP step, the spinning axis is rapidly switched to the magic angle for detection of the high-resolution signal. CP from $^{27}$Al to $^{31}$P nuclei in the aluminophosphate VPI-5 is used to illustrate this technique.

3.1. Introduction

An important step in the CP experiment is the spin-locking of magnetization along an axis in the rotating frame. For quadrupolar nuclei under MAS spin-locking conditions, there is a rapid loss of magnetization from the central transition due to the level crossings with satellite transitions which occur during sample rotation [2,3]. This severely limits the overall efficiency of the CP process when quadrupolar spins are involved [2,4,5]. Further, if the frequencies describing the strength of the homonuclear dipolar coupling between the source spins are small compared to the MAS rotational frequency, nuclear cross-relaxation (caused by mutual spin flips which allow the transfer of spin coherence) is modulated by the rotation and the CP efficiency may also decrease [6-8]. These problems may be overcome by performing the CP experiments with a stationary sample, or perhaps by spinning at some angle other than the magic angle. These options, however, sacrifice the high resolution available with MAS.

This chapter describes one method to improve the efficiency of the CP experiment by overcoming the loss of quadrupolar magnetization when spin-locking without degrading the spectral resolution: the use of CP experiments coupled with reorientation (Dynamic-Angle Spinning or DAS) of the spinning axis. This method has been used
previously for \(^1\)H/\(^13\)C and \(^1\)H/\(^1\)\(^{13}\)Cd CP in cases where the homonuclear dipolar couplings between the protons were weak [8]. The acceptable range of matching \(B_1\) r.f. field strengths in the rotating frame was narrowed, and the CP efficiency as a function of field strength broke into a centreband plus a set of sidebands [6]. We have observed similar behaviour in our CPMAS studies with quadrupolar nuclei (see Section 2.3c or ref [5]), and this is now taken into account in the experimental design and implementation. Here, however, we are investigating CP between quadrupolar and spin-\(1/2\) nuclei where the rapid loss of quadrupolar spin magnetization during spin-locking severely limits the overall CP efficiency.

In the dynamic-angle cross-polarization (DACP) experiment presented in this chapter, CP is performed from \(^{27}\)Al to \(^{31}\)P nuclei in the aluminophosphate VPI-5. The results indicate that the efficiency of the quadrupolar to spin-\(1/2\) CP process is increased due to a change in the apparent spin-lattice relaxation time in the rotating frame (\(T_{1p}\)) for the quadrupolar spins, accomplished by reorienting the spinning axis to be parallel to the \(B_0\) field for the CP step.

### 3.2. Experimental Section

One-dimensional cross-polarization experiments were carried out with coherence transfer from the central transition of the quadrupolar \(^{27}\)Al spins (\(I = 5/2\)) to the \(^{31}\)P spins (\(S = 1/2\)). The NMR pulse sequence for conventional spin-lock cross-polarization experiments [9,10] under MAS conditions is shown in Figure 46a. The rotor axis in these experiments is always at the magic angle of 54.74° in order to obtain high-resolution \(^{31}\)P spectra. The spin-locking (contact) pulses are applied simultaneously to the \(^{27}\)Al and \(^{31}\)P spins, and the r.f. field strengths \(\gamma_p B_{1,p} = 3 \gamma_{Al} B_{1,Al} \pm v_r\) are set to satisfy Eq. (56) [2]:

\[ \gamma_p B_{1,p} = 3 \gamma_{Al} B_{1,Al} \pm v_r \tag{56} \]

where \(v_r\) is the rotational frequency of the MAS spinner. This condition has been
Figure 46. (a) Conventional cross-polarization sequence used for CPMAS experiments. (b) Pulse sequence and rotor positioning for the dynamic-angle cross-polarization (DACP) experiment used for spinning samples. (c) Modified experiment for comparison of the CP efficiencies of the CPMAS and DACP experiments.
previously verified experimentally to produce the most efficient transfer of magnetization from the central transition of the quadrupolar spins to the spin-1/2 nuclei in CPMAS experiments (see Section 2.3c or reference [5]). The 90° pulse lengths were set to 12.5 µs and 15.0 µs for the $^{27}$Al and $^{31}$P spins respectively, and the rotational frequency was 3.0 kHz, approximately satisfying Eq. (56). Cross-polarization experiments were performed with a series of contact times, ranging from 0.333 to 10 ms.

The dynamic-angle cross-polarization (DACP) experiment is outlined in Figure 46b. (The spectrometer pulse program is given in Appendix 13.) This modification uses a home-built dynamic-angle spinning (DAS) probe with a fixed sample coil parallel to the axis of reorientation (perpendicular to the magnetic field) [11]. There is no effect on the matching and tuning of the coil when the sample axis is changed. However, it is important to note that the use of a fixed coil decreases the sensitivity (S/N ratio) due to a decrease in the filling factor (i.e. a smaller volume within the coil is occupied by the sample). This should be taken into account when choosing between a conventional CPMAS experiment and the DACP experiment for a particular sample, as one must weigh any gain in signal from the more efficient cross-polarization with the loss in signal due to the smaller sample size.

The radiofrequency coil in the DAS probe was double-tuned to 104.264 MHz and 161.977 MHz, the resonance frequencies for $^{27}$Al and $^{31}$P spins in the 9.4 T magnetic field. Chemical shifts are referenced to 85% H$_3$PO$_4$ for $^{31}$P and aqueous Al(NO$_3$)$_3$ for $^{27}$Al nuclei. The sample is initially moved into a position parallel to the magnetic field (an angle of 0°) where the 90° pulse is applied to the central transition of the $^{27}$Al spins, followed by the spin-locking fields. In this case, the Hartmann-Hahn matching condition (Eq. (57)) [12] is the same as for static samples:

$$3 \gamma_{Al} B_{1,Al} = \gamma_{P} B_{1,P}$$

(57)
and therefore the power of the pulses to the $^{27}$Al channel was modified so that the selective 90° pulse time was 15 μs for both the $^{27}$Al and $^{31}$P spins. After the transfer of coherence to $^{31}$P, the signal in the xy-plane is stored along the magnetic field direction with a 90° pulse so that the spinner axis can be switched to the magic angle. The hop time is approximately 50 ms, much shorter than the $T_1$ relaxation time for the $^{31}$P nuclei (approximately 15 s). Therefore, the $^{31}$P signal should not decay significantly during the hop. After the hop, the stored signal is returned to the xy-plane with another 90° pulse and a free induction decay is acquired. Proper phase-cycling includes a reversal of spin-temperature in the rotating frame to suppress artifacts [13], and additional cycling to remove any signal that might arise due to $T_1$ relaxation during the hop time.

To verify that a direct comparison of the relative efficiencies of the CPMAS and DACP experiments is meaningful, the modified CPMAS experiment shown in Figure 46c was used to obtain a cross-polarization signal under MAS conditions, but with the additional storage of the $^{31}$P signal for an appropriate time before detection. The signals obtained were essentially the same as from the direct CPMAS experiment, and the results shown below are from the cross-polarization experiments of Figure 46a. The long $T_1$ relaxation time of the $^{31}$P spins in VPI-5 is the reason that this additional consideration is unnecessary.

For each of the variations of the cross-polarization experiment shown in Figure 46, null experiments are essential verifications that the observed signal is real and due to the cross-polarization process. These were carried out by removing each of the first three pulses in an experiment, either one at a time or pairwise, and verifying that the signal disappeared [4,5].
3.3. Results and Discussion

The total $^{31}\text{P}$ signal obtained from the cross-polarization of magnetization from nearby $^{27}\text{Al}$ spins was measured as a function of contact time for the direct CPMAS experiment of Figure 46a and the DACP experiment of Figure 46b. The maximum signals were obtained with contact times of 1.3 ms for the CPMAS and 2.5 ms for the DACP experiments. The spectra from these two experiments are shown in Figure 47, with the total integrated DACP signal approximately 67% higher than the CPMAS signal. The behaviour of the signals from the two experiments as a function of contact time is presented in Figure 48. In the DACP experiment, the maximum signal intensity is higher and the maximum is shifted to longer contact time, as compared to the CPMAS experiment.

Spin thermodynamic arguments are a valuable tool for the understanding of cross-polarization of nuclear spins [14]. The equations describing the growth and decay of the transferred signal as a function of contact time show a complex dependence upon three relaxation time constants: $T_{\text{CP}}$, $T_{1\rho}^{\text{AI}}$, and $T_{1\rho}^{\text{P}}$. The growth of the signal depends on the cross-polarization transfer rate (or heteronuclear cross-relaxation rate), characterized by the time constant $T_{\text{CP}}$. The decay of the signal is determined by the relaxation rates of the spin-locked magnetizations in the rotating frame which are described by the $T_{1\rho}$ values for the different nuclei. The $T_{1\rho}$ relaxation times were measured independently for both sets of nuclei while spinning at 0° and at 54.74° and under the irradiation conditions of both experiments (note that the $^{27}\text{Al}$ field strength was changed between the CPMAS and DACP experiments in order to satisfy Eqs. (56) and (57) respectively). These results are given in Table 6, where the value for the $^{31}\text{P}$ nuclei while spinning at 0° ($T_{1\rho} = 20.4$ ms) is an average from the entire inhomogeneously-broadened lineshape which is not resolved into three resonances due to the chemical shift anisotropies. For the
Figure 47. (a) CPMAS spectrum of $^{31}$P in VPI-5. The spectrum was obtained with 4096 scans, a recycle delay of 0.5 s, and a contact time of 1.3 ms. (b) DACP spectrum of $^{31}$P in VPI-5. The spectrum was obtained with 4096 scans, a recycle delay of 0.5 s, and a contact time of 2.5 ms.
Figure 48. Total integrated cross-polarization signal from the $^{31}$P nuclei in VPI-5 as a function of contact time in (a) the CPMAS experiment and (b) the DACP experiment.
Table 6: Experimentally determined $T_{1p}$ parameters for $^{31}$P and $^{27}$Al nuclei in VPI-5.

<table>
<thead>
<tr>
<th>Nucleus</th>
<th>Site</th>
<th>$0^\circ$ spinning</th>
<th>MAS</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{31}$P</td>
<td>P1 (-23 ppm)</td>
<td>20.4 ms</td>
<td>19.7 ms</td>
</tr>
<tr>
<td>$^{31}$P</td>
<td>P2 (-27 ppm)</td>
<td>20.4 ms</td>
<td>16.8 ms</td>
</tr>
<tr>
<td>$^{31}$P</td>
<td>P3 (-33 ppm)</td>
<td>20.4 ms</td>
<td>13.2 ms</td>
</tr>
<tr>
<td>$^{27}$Al</td>
<td>tetrahedral (41 ppm)</td>
<td>2.78 ms</td>
<td>0.151 ms</td>
</tr>
<tr>
<td>$^{27}$Al</td>
<td>octahedral (-18 ppm)</td>
<td>2.93 ms</td>
<td>0.292 ms</td>
</tr>
</tbody>
</table>

$^{27}$Al resonances, one can still distinguish between the octahedral and tetrahedral sites while spinning at $0^\circ$. An increase in $T_{1p}$ for the $^{27}$Al nuclei from less than 0.3 ms to almost 3 ms is accomplished by changing the spinning angle from the magic angle to $0^\circ$, and this provides a qualitative thermodynamic argument for the observed behaviour. If the spin-locking in the rotating frame is more efficient while spinning at $0^\circ$, the target spins may be brought into thermal contact with the source spins for a longer period of time and more polarization-transfer will occur. The expressions describing the build-up and decay of observable signal were programmed in Mathematica, and the behaviour of the magnetization examined as a function of the relaxation parameters. Modeling of the appropriate equations bears out the fact that longer $T_{1p}$ values lead to higher maximum values at longer contact times, as shown in Figure 49, in qualitative agreement with the trend in the experimental data.

In our analysis [5] of the CPMAS experiment between $^{27}$Al and $^{31}$P in VPI-5, the difference in overall signal intensity for individual $^{31}$P resonances was also dependent on the cross-polarization rate ($1/T_{CP}$) which was found to be strongly site-dependent in the VPI-5 sample. It is also found through modeling that although an increase in this rate (i.e. a smaller $T_{CP}$ value) at $0^\circ$ would also lead to more magnetization transfer and thus a higher signal maximum, the maximum would occur at shorter contact times if the $T_{1p}$ values remain the same. In the experiments, however, the maximum occurs at longer
Figure 49. Simulations of cross-polarization dynamics with different relaxation parameters. For each curve, the $T_{1\rho}$ and $T_{1\rho}^I$ of the target nuclei were kept constant at 60 ms and 20 ms respectively, while the $T_{1\rho}$ of the source nucleus was varied as indicated.
contact times on going from CPMAS to DACP (Figure 48). Therefore, the major contributing factor to the increased signal maximum observed is an increase in the $T_{1p}$ value for the $^{27}$Al nuclei, and not a higher cross-polarization rate. It is possible, however, that a higher cross-polarization rate is a minor contributing factor to the increased signal maximum. Under MAS conditions, the cross-polarization rate depends on the modulation due to rotational motion, and movement of the Hartmann-Hahn matching condition by one rotational sideband is a reaction to the destructive effects of modulation. Therefore, spinning at $0^\circ$ should increase the cross-polarization rate since there are no longer any effects of modulation.

The overall gain in signal is still compromised by the fact that the $T_{1p}$ values of the $^{27}$Al nuclei are still very short even when spinning parallel to the magnetic field (less than 3 ms). However, it may be possible to improve this by using a stronger or more homogeneous spin-locking field, or by a phase-modulation of a lower power field [15]. The choice of a different field strength should be made with care, following the criteria presented by Vega [3] relating spinning speed, quadrupolar interaction strength, and the power of the spin-locking field.

The one-dimensional DACP experiment can be extended into a two-dimensional DAS/CP/MAS experiment to give a high-resolution connectivity map between the quadrupolar and spin-1/2 nuclei. This technique combines DAS to obtain a high-resolution spectrum of the quadrupolar nuclei, CP from the quadrupolar to spin-1/2 nuclei performed at $0^\circ$ for maximum efficiency, and MAS to obtain a high-resolution spectrum of the spin-1/2 nuclei. This experiment was tried for VPI-5 in an attempt to resolve the $^{31}$P connectivities to the two tetrahedral $^{27}$Al resonances which overlap in the $^{27}$Al MAS spectrum, but failed due to the very short $^{27}$Al $T_1$ relaxation times. Since the hop time of the DAS experiment (50 ms) is much longer than the $^{27}$Al $T_1$ relaxation times (approximately 20 ms), all of the $^{27}$Al magnetization decayed during the first part of the experiment.
Very recently, the viability of the DAS/CP/MAS experiment has been successfully demonstrated by Mueller and co-workers [16] for $^{23}$Na (I=$3/2$) and $^{31}$P (S=$1/2$) nuclei in polycrystalline sodium trimetaphosphate. The experiment clearly revealed connectivities between the two $^{31}$P and two $^{23}$Na resonances. In this case, the experiment was viable since the $^{23}$Na $T_1$ relaxation times were much longer than the hop time.

3.4. Conclusions

A more efficient cross-polarization experiment for quadrupolar nuclei that incorporates a flip of the spinning axis from a position parallel to the magnetic field to the magic angle for detection has been presented. This combines the spin-locking efficiency of stationary CP experiments with the high resolution of MAS detection. Using a DAS probe, which has a fixed irradiation and detection coil in the xy-plane, we are able to irradiate samples spinning parallel to the magnetic field and increase the spin-locking efficiency for the quadrupolar spins.

The experimental modification of the CPMAS to a DACP experiment provides an enhancement of signal that may significantly cut the experimental time necessary for observation of spin-1/2 nuclei in condensed phases. This gain in cross-polarization efficiency for acquisition of spectra from spin-1/2 nuclei near to quadrupolar spins may be used in combination with the rapid spin-lattice relaxation of quadrupolar nuclei to obtain signals from slowly relaxing spin-1/2 nuclei in condensed phases. In addition, the selective nature of the cross-polarization experiments will provide connectivity information in solid systems containing quadrupolar nuclei.

For VPI-5, the increase in $^{27}$Al $\rightarrow$ $^{31}$P cross-polarization efficiency using the DACP experiment is approximately 67%. This limited increase in cross-polarization efficiency must be weighed against the loss in signal due to the smaller sample size in the DAS probe used. In this case, therefore, if the sample size in an available CPMAS probe
is larger by more than 67%, then a CPMAS experiment will be more efficient than a DACP experiment. All of the cross-polarization experiments presented in the rest of this thesis are CPMAS experiments, since the available probes have sample sizes which are much larger (by factors of three to ten) than the DAS probe. However, the DACP experiments are still informative in that they demonstrate that an increase in the $T_{1\rho}$ value for the quadrupolar nuclei results in a greater cross-polarization efficiency.

The two-dimensional DAS/CP/MAS correlation experiment failed for VPI-5, but has recently been successfully demonstrated for a $^{23}\text{Na}/^{31}\text{P}$ system. Therefore, it is viable to combine quadrupolar line-narrowing with coherence-transfer techniques in some cases, with the limiting factor being the relaxation parameters of the quadrupolar spins.
Chapter 3 References

Chapter 4. $^{27}\text{Al}^{29}\text{Si}$ Connectivity Experiments in Zeolite Molecular Sieve Frameworks

This chapter [1] describes the extension of the $^{27}\text{Al}^{31}\text{P}$ coherence-transfer and dipolar-dephasing NMR connectivity experiments developed in Chapter 2 [2-4] to include the $^{27}\text{Al}^{29}\text{Si}$ spin pair. The results of a systematic investigation of a set of $^{27}\text{Al}^{29}\text{Si}$ connectivity experiments are presented for a series of representative zeolite molecular sieve frameworks. The success and utility of the experiments are demonstrated, and the optimum experimental conditions and the approximate experimental times which are involved for the different systems are reported.

4.1. Introduction

In Chapter 2, it was demonstrated that $^{27}\text{Al}^{31}\text{P}$ coherence-transfer and dipolar-dephasing connectivity experiments could be used in the AIPO$_4$ systems VPI-5 and AIPO$_4$-8 to successfully establish $^{27}\text{Al}$-$^{31}\text{P}$ connectivities, and that two-dimensional CP and TEDOR experiments could provide the three-dimensional heteronuclear bonding scheme. The AIPO$_4$ materials, however, are particularly attractive cases for these experiments: Both $^{27}\text{Al}$ and $^{31}\text{P}$ are 100% abundant isotopes and have large magnetogyric ratios, giving substantial magnetizations and sensitivity. In addition, the large magnetogyric ratios give relatively large $^{27}\text{Al}^{31}\text{P}$ dipolar couplings. Furthermore, as mentioned previously, the AIPO$_4$ molecular sieves are perfectly ordered systems and thus have narrow resonances enhancing sensitivity as well as resolution.

Low Si/Al ratio zeolites are more typical of molecular sieve systems. However, $^{27}\text{Al}^{29}\text{Si}$ connectivity experiments will predictably be much more difficult, mainly due to reduced sensitivity since the $^{29}\text{Si}$ nucleus is only 4.7% abundant. In addition, the lower magnetogyric ratio of $^{29}\text{Si}$ (approximately one-half that of $^{31}\text{P}$) means that the dipolar interaction in the $^{27}\text{Al}$-$^{29}\text{Si}$ unit will be proportionately smaller (approximately 210 Hz for $^{27}\text{Al}$-$^{29}\text{Si}$ where $r = 3.1$ Å). Furthermore, the zeolite systems are usually
not ordered, giving rise to a number of local environments whose resonances will each be relatively broad due to disordering over the tetrahedral sites, again reducing the sensitivity of the experiment. To overcome these obstacles, large sample sizes and long experimental times will be necessary.

4.2. Experimental Section

(a) Materials

A representative set of zeolite molecular sieves was chosen for study:

1. Zeolite A (Si/Al = 1), kindly provided by Dr. Y. Huang, was prepared by hydrothermal synthesis from a mixture of molar ratio $2.0 \text{SiO}_2 : \text{Al}_2\text{O}_3 : 5.0 \text{Na}_2\text{O} : 150 \text{H}_2\text{O}$ heated at 70°C for 3.5 hr.

2. Zeolite X (Si/Al = 1.75), kindly provided by Dr. W. Schwieger, was prepared by hydrothermal synthesis from a mixture of molar ratio $10 \text{SiO}_2 : \text{Al}_2\text{O}_3 : 6.5 \text{Na}_2\text{O} : 0.27 \text{Cs}_2\text{O} : 280 \text{H}_2\text{O}$ heated at 95 °C for 5 days.

3. Zeolite Y (Si/Al = 2.47) was obtained from the Linde company (LZY-52).

4. Zeolite omega (Si/Al = 4.2) was obtained from Union Carbide Corporation (ELZ-Ω-5).

In each case, the sample crystallinity and purity was checked by powder X-ray diffraction measurements (Rigaku rotating anode powder diffractometer).

(b) NMR Experiments

The $^{27}\text{Al}^{31}\text{P}$ experiments in Chapters 2 and 3 were performed on a Bruker MSL 400 spectrometer, where the $^{31}\text{P}$ channel was the normal X channel and the $^{27}\text{Al}$ channel was obtained by external modification (mixing, amplification, and remixing before detection) of the frequency from the $^1\text{H}$ channel. After these experiments were performed, a third r.f. channel was added to the spectrometer. Therefore, the $^{27}\text{Al}^{29}\text{Si}$ experiments in this chapter, and all subsequent experiments in this thesis, were performed
using the normal X channel for one nucleus and the third r.f. channel for the other. NMR resonance frequencies were 104.264 MHz for $^{27}\text{Al}$ and 79.495 MHz for $^{29}\text{Si}$. Initial studies were performed using a home-built double-tuned probe incorporating a 10 mm high-speed (Supersonic) spinner with an internal volume of 0.8 mL, supplied by Doty Scientific Inc. However, these experiments were limited by the S/N ratio obtainable in reasonable time periods. Therefore, all of the work presented here was carried out using a home-built double-tuned probe incorporating a larger 14 mm "Pencil Spinner" with an internal volume of 2.8 mL, supplied by Chemagnetics. Samples were spun at 2.2-2.9 kHz with the spinning rate monitored by an optical sensor unit. The $^{29}\text{Si} \, 90^\circ$ pulse and the $^{27}\text{Al} \, 90^\circ$ pulse (central transition only) were both in the range of 15-21 μs.

The four NMR connectivity experiments investigated all involved observation of $^{29}\text{Si}$, as the reverse experiments ($^{27}\text{Al}$ observation) are impractical due to the low natural abundance and long $T_1$ values of the $^{29}\text{Si}$ nuclei. The experiments were performed using the pulse sequences previously described in Chapter 2. The $^{27}\text{Al} \rightarrow ^{29}\text{Si}$ CP experiment was set up using zeolite A since the S/N ratio was good enough to observe an FID signal from a small number of scans, making experimental optimization of the $^{29}\text{Si}$ r.f. field strength and contact time possible.

4.3. Results and Discussion

A variety of zeolite molecular sieves have been investigated to evaluate the general applicability and relative efficiencies of the various experiments and the measurement times involved. The results will be presented in order of increasing difficulty of the experiments.

(a) Zeolite A

Zeolite A, whose structure [5,6] is shown inset in Figure 50, is the most straightforward case. The Si/Al ratio is unity, giving the highest concentration of Al
Figure 50. $^{27}\text{Al} \rightarrow ^{29}\text{Si}$ TEDOR experiment for zeolite A (structure shown inset), with $n = 2$ and $m = 1$. A total of 4133 scans were acquired with a recycle delay of 0.1 s, resulting in a total experimental time of 7 minutes.
possible for these systems. Further, there is only one lattice site in the structure and there
is exact alternation of Si and Al, thus resulting in a $^{29}$Si spectrum consisting of a single
sharp resonance. This system is optimum for these experiments and good spectra can be
obtained in very short periods of time, as illustrated by the $^{29}$Si TEDOR spectrum in
Figure 50 which was obtained by magnetization transfer from $^{27}$Al to $^{29}$Si in a total
measuring time of only seven minutes. For this reason, zeolite A was used to investigate
in detail the performance of the different experiments described in the Experimental
Section 4.2 to confirm the nature of the interactions involved from their general
adherence to the theoretically predicted behaviours. For comparison, the S/N obtained in
a fixed period of time (17 min) from the different experiments is given in Table 7
together with the experimental conditions. To aid in setting up the experiments and in the
interpretation of the resulting data, the $^{27}$Al and $^{29}$Si relaxation parameters in zeolite A
were measured. $^{27}$Al: $T_1 = 4.27$ ms, $T_2 = 1.23$ ms, $T_{1p} = 213 \mu$s; $^{29}$Si: $T_1 = 24.3$ s, $T_2 =
6.95$ ms, $T_{1p} = 405$ ms (77%) and 224 ms (23%). (In the case of $^{29}$Si, there were two
$T_{1p}$ relaxation times, perhaps due to variations in trace impurity levels within the sample
or within the individual crystals.)

Figure 51 shows the variation of the $^{29}$Si signal intensity as a function of the $^{29}$Si
spin-locking field strength for $^{27}$Al $\rightarrow$ $^{29}$Si cross-polarization measured at a contact time
of 2 ms, which as will be seen in Figure 52 corresponds approximately to the maximum
in the signal intensity as a function of the contact time. The figure shows that, in
accordance with the expected behaviour in the limit of fast spinning and weak r.f. field
strength, the Hartmann-Hahn match condition is shifted by the spinning frequency [7], or
in the present case,

$$\gamma_{Si} B_{1, Si} = 3 \gamma_{Al} B_{1, Al} \pm v_r$$

(58)

The $^{27}$Al 90° pulse length of 17 µs (measured for the central transition) corresponds to an
r.f. field strength of $3\gamma_{Al} B_{1, Al} = 14.7$ kHz, as indicated by the vertical arrow. The
Figure 51. Variation of the $^{29}$Si spin-locking r.f. field in the $^{27}$Al $\rightarrow$ $^{29}$Si cross-polarization experiment on zeolite A, measured with a contact time of 2 ms. The $^{27}$Al r.f. field strength of 14.7 kHz (measured for the central transition) is indicated by the vertical arrow.
Table 7. Results for $^{27}$Al/$^{29}$Si connectivity experiments on zeolite A.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Conditions</th>
<th>Number of Scans</th>
<th>Recycle Delay (s)</th>
<th>Acquisition Time (min)</th>
<th>S/N Ratio$^{(a)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cross-Polarization</td>
<td>2.0 ms contact time</td>
<td>10000</td>
<td>0.1</td>
<td>17</td>
<td>22.5</td>
</tr>
<tr>
<td>Dipolar-Dephasing</td>
<td>$5\tau_r = 2.0$ ms dephasing</td>
<td>100</td>
<td>10</td>
<td>17</td>
<td>26.2</td>
</tr>
<tr>
<td>REDOR</td>
<td>$n = 12$</td>
<td>100</td>
<td>10</td>
<td>17</td>
<td>21.2</td>
</tr>
<tr>
<td>TEDOR</td>
<td>$n = 2, m = 1$</td>
<td>10000</td>
<td>0.1</td>
<td>17</td>
<td>65.1</td>
</tr>
</tbody>
</table>

(a) The signal-to-noise ratio was calculated on the root-mean-square noise for a fixed region (-70 to -110 ppm) in each spectrum.

spinning rate is $v_r = 2.5$ kHz, with $2v_r$ corresponding approximately to the separation observed between the maxima.

Figure 52 shows the variation in $^{29}$Si signal intensity with contact time obtained for a matching condition corresponding to the maximum at lower $^{29}$Si r.f. frequency (12.7 kHz) in Figure 51. As discussed previously in the case of the $^{27}$Al/$^{31}$P CP experiments, the description of the dynamics of the cross-polarization process usually used for $^1$H(I) to $^{13}$C(S) cross-polarization is inadequate as it assumes that the $T_{1p}$ for the S nuclei is very long and that the number of I nuclei is much greater than the number of S nuclei. In the particular case where I is a quadrupolar nucleus, the efficiency of spin-locking the central transition is greatly reduced in the intermediate region between adiabatic and sudden passage of the zero energy crossings of the first order quadrupolar splitting, i.e. unless the spinning is very fast or very slow. In the present case, the $^{27}$Al $T_{1p}$ measured directly under MAS (2.5 kHz) is $213\mu$s, indicating that the spin-locking Hartmann-Hahn match condition will exist for only a very short period of time. Even though the dipolar coupling is small (210 Hz), it can be anticipated that the maximum in the curve will be at relatively short contact times.

Quantitatively, the equation for the dynamics of the cross-polarization process is complex and involves the $T_{1p}$ values of both sets of nuclei as well as the I/S cross-
Figure 52. Variation of the peak intensity as a function of contact time in the $^{27}$Al $\rightarrow ^{29}$Si cross-polarization experiment on zeolite A. The solid line is from a non-linear least squares fit to Eq. (54).
polarization time constant $T_{CP}$ which depends on the dipolar coupling [8,9]. The equations describing cross-polarization dynamics (Eqs. (48)-(54)) were previously presented in Chapter 2 for $^{27}\text{Al} \rightarrow ^{31}\text{P}$ cross-polarization. For $^{27}\text{Al} \rightarrow ^{29}\text{Si}$ cross-polarization in zeolite A where the Si environments are all Si[4Al], the equations are analogous to those for $^{27}\text{Al} \rightarrow ^{31}\text{P}$, except that the value of $\varepsilon_0 a^2$ is equal to 0.75 (using Eqs. (52) and (53)). (This assumes that $N_3/N_1 = 1/4$ since each of the four $^{27}\text{Al}$ nuclei surrounding a $^{29}\text{Si}$ nucleus is not likely to be coupled to any additional $^{29}\text{Si}$ nuclei due to the low natural abundance of $^{29}\text{Si}$.) The $^{27}\text{Al} \rightarrow ^{29}\text{Si}$ cross-polarization process can also be modelled using Eq. (54) simplified for the case of a very short $T_{1p}$ value for the source quadrupolar nuclei.

The solid line in Figure 52 is the theoretical curve obtained from a non-linear least squares fit of the data to Eq. (54), with the value of the $^{29}\text{Si} T_{1p}$ held fixed at its measured value of 405 ms, yielding the parameters $T_{CP} = 57$ ms and $^{27}\text{Al} T_{1p} = 355 \mu$s. If the $^{29}\text{Si} T_{1p}$ is not held fixed, the unrestrained non-linear least squares fit yields the parameters $T_{CP} = 96$ ms, $^{29}\text{Si} T_{1p} = 104$ ms, and $^{27}\text{Al} T_{1p} = 355 \mu$s, with the same closeness of the fit as from the former fit (Figure 52). We conclude that the former fit is more reliable since the $^{29}\text{Si} T_{1p}$ value is known from experiment, and that the difference in the fits is a measure of the width of the potential minimum of the fit. A note of caution, therefore, must be exercised with multi-variable non-linear least squares fits, and independent measurements of the parameters should be carried out. As seen previously in $^{27}\text{Al}/^{31}\text{P}$ CP experiments [4], the $^{27}\text{Al} T_{1p}$ from the fit is larger than that from direct measurement, but the general behaviour fits very well with that predicted.

The dipolar-dephasing difference experiment introduced by Veeman and co-workers is also efficient for zeolite A, with maximum signal intensity after five rotor periods of dephasing on $^{27}\text{Al}$ (Table 7). Although it is not possible to give an exact theoretical description of this experiment, the lack of signals in all of the null experiments clearly identifies the heteronuclear dipolar interactions as the important factor in the
dephasing process. Signals were also efficiently obtained in the $^{29}\text{Si}(^{27}\text{Al})$ REDOR experiment (Table 7).

The theoretical variation of the REDOR signal as a function of $n$ is a curve growing to a relative intensity of one, with a non-periodic oscillatory behaviour from which the dipolar coupling may be determined (Eqs. (42) and (43)). This is shown in Figure 53 (solid line) for $v_r = 2.5 \text{ kHz}$ ($\tau_r = 400 \mu\text{s}$) and an assumed $D$ value of 210 Hz.

As can be seen in the figure, the experimental data points (with error bars) follow a smooth curve as expected, but the growth is slower than the theoretical evolution. This arises because each $^{27}\text{Al}$ nucleus near to a $^{29}\text{Si}$ nucleus is not necessarily perturbed by the $180^\circ$ pulses on the $^{27}\text{Al}$ channel. Only a certain percentage of the nuclei (approximately one-third) have a spin energy level characterized as in the central transition (either in the $+1/2$ or $-1/2$ level), and only these (to a first approximation) will be flipped by the $180^\circ$ pulses. In addition, the effect of $T_2$ relaxation on the I nucleus magnetization is not included in the theoretical evolution, and there is substantial dephasing due to $T_2$ during formation of the echo whether or not pulses are applied to the S nucleus. Although the ratio $\Delta S/S_0$ tends to one as $n$ increases, the absolute values of both $\Delta S$ and $S_0$ die off with time (due to $T_2$) until the data become unreliable. This is indicated by the error bars in the figure which were calculated assuming errors in the intensities of $\pm 2\%$ for the largest measured signal ($S_0$ for $n = 2$). The $^{29}\text{Si} \ T_2$ value is 6.95 ms, and the maximum $\Delta S$ value is obtained after $n = 12$ rotor cycles. This was used in subsequent experiments as a working value for this variable at which reasonable S/N could be obtained (Table 7).

Because of the complexity of the current spin system involving quadrupolar nuclei and non-isolated spins compared to the isolated two spin-1/2 system for which the theory has been developed, it is unrealistic to try to interpret these data in more detail. However, it is felt that the general behaviour observed clearly indicates that the heteronuclear dipolar interactions are the basis for the observed effect.
Figure 53. Evolution of the $^{29}\text{Si}(^{27}\text{Al})$ REDOR signal in zeolite A, with $\tau_r = 400 \, \mu s$. For the experimental data points, the error bars were calculated assuming errors in the intensities of $\pm 2\%$ for the largest measured signal ($S_0$ for $n = 2$). The solid line shows the theoretical evolution of the REDOR signal for a single pair of spin-1/2 nuclei predicted from Eqs. (42) and (43) for $\tau_r = 400 \, \mu s$ and an assumed $D$ value of 210 Hz.
A similar situation exists for the TEDOR experiment. The signal is a predictable function of the numbers of rotor cycles $n$ and $m$ before and after the coherence transfer, respectively (Eqs. (44) and (45)). However, for values of $n$ greater than 2 while spinning at 2.5 kHz, the TEDOR signals subsequently observed as a function of $m$ were unacceptably small, presumably due to the $T_2$ decay in the $^{27}$Al spin-echo in the first part of the sequence (the $^{27}$Al $T_2$ is only 1.23 ms (for zeolite A), while $\tau_r$ is 0.40 ms). Thus all subsequent TEDOR experiments were carried out with $n = 2$ at this spinning rate. The expected variation of $S_{T,m}$ as a function of $\lambda = mD\tau_r$ is shown in Figure 54a, calculated for different placement of the $180^\circ$ pulses after the coherence transfer. For the standard pulse placement at $\tau_r/4$ and $3\tau_r/4$, the signal grows to a maximum value and then falls to a negative value and oscillates modulated by the dipolar coupling, ultimately becoming zero. The observed data for zeolite A show the correct general trend but show no evidence of oscillations (Figure 54b). Given the complexity of the current system, exact agreement is not expected and the data are taken as strong evidence for the general features assumed in the theoretical treatment being those in the present experiment.

There is, however, an additional test which can be applied in the case of TEDOR experiments. The placement of the $180^\circ$ pulses at $\tau_r/4$ and $3\tau_r/4$ was designed to facilitate single point acquisition, if desired, during each rotor period after the coherence transfer, as well as to minimize effects due to J couplings between the I and S spins [10]. However, $\tau_r/4$ and $3\tau_r/4$ also represent the most efficient points for the placement of the pulses. Symmetrical placement of the pulses about $\tau_r/6$ at longer intervals, e.g. $\tau_r/6$ and $5\tau_r/6$, will lead to a less efficient experiment with a lower maximum signal intensity and the maximum moved to larger $\lambda$ values (Figure 54a). (Placement of the $180^\circ$ pulses at $\tau_r/3$ and $2\tau_r/3$ produces the same evolution of the TEDOR signal, both theoretical and experimental, as placement at $\tau_r/6$ and $5\tau_r/6$.) The results of such a series of experiments are presented in Figures 54b-e and follow the trend predicted in Figure 54a, providing
Figure 54. Evolution of TEDOR signals: (a) Theoretical evolution of the TEDOR signal, assuming an isolated spin pair with dipolar coupling D, for a variation of 180° pulse placement during each rotor cycle after the coherence-transfer. (b-f) Evolution of the $^{27}$Al → $^{29}$Si TEDOR signals in zeolite A for a variation of 180° pulse placement during each rotor cycle after the coherence-transfer. In each case, $n = 2$, $\tau_r = 400 \mu s$, and the number of rotor cycles after transfer ($m$) was varied from 0 to 5.
additional support for the general correctness of the description of the present TEDOR experiment in terms of heteronuclear dipolar interactions.

From Table 7 which lists the $^{29}$Si S/N values for zeolite A obtained from the four different experiments under optimal conditions, it appears that the TEDOR experiment is the most efficient. Although it is not as easy to investigate this in detail in the more complex zeolite systems, it would appear that this is most often the case. The TEDOR experiment is a most forgiving one and, in addition, does not have the r.f. high-power and stability requirements of the spin-locking part of the CP experiment.

An additional advantage of both the CP and TEDOR experiments is that since they involve coherence-transfer, they can be performed as two-dimensional experiments yielding 2D heteronuclear correlation plots based on dipolar-couplings. Such experiments on pure zeolite A have been carried out and confirm these expectations. However, they are not presented here since they involve only a single correlation point, and are unrepresentative of zeolite systems in general in terms of the experimental times involved. An indication of the potential of such experiments is given in Figures 55 and 56. Figure 55 shows the results from a 2D TEDOR experiment performed on a small amount of zeolite A mixed with alumina (Woelm company, neutral) in a ratio of 7% NaA/93% Al$_2$O$_3$ (w/w). The 2D TEDOR spectrum clearly correlates the $^{29}$Si and $^{27}$Al resonances of zeolite A as indicated by the projections. However, the 2D TEDOR spectrum also cleanly removes the contribution of the Al$_2$O$_3$ to the $^{27}$Al one-dimensional spectrum as shown in Figure 56, which compares (a) the $^{27}$Al 2D TEDOR projection from Figure 55 with (b) the corresponding $^{27}$Al one-dimensional spectrum. The 2D TEDOR experiment removes not only the large broad peak from 40 to -20 ppm, but also the shoulder on the downfield side of the tetrahedral $^{27}$Al peak which is also due to Al$_2$O$_3$, as indicated by the arrow in Figure 56b. These two-dimensional experiments, therefore, may be useful in the characterization and identification of the different components in complex mixtures.
Figure 55. Two-dimensional $^{27}\text{Al} \rightarrow ^{29}\text{Si}$ TEDOR experiment on a zeolite A/alumina mixture (7%/93% w/w), with $n = 2$ and $m = 1$; 11104 scans were acquired for each of 48 experiments in $t_1$. The recycle delay of 0.1 s resulted in a total experimental time of 14.8 hr.
Figure 56. Zeolite A/alumina mixture (7%/93% w/w): (a) $^{27}$Al 2D TEDOR projection from Figure 55. (b) $^{27}$Al one-dimensional MAS spectrum after 256 scans with a recycle delay of 0.1 s. The arrow indicates the small tetrahedral $^{27}$Al peak due to the alumina.
Preliminary experiments were carried out on a commercial sample of zeolite X (molecular sieve 13X), but the low Si/Al ratio of 1.21 meant that the Si[4Al] resonance was very dominant in the $^{29}\text{Si}$ spectrum, and the results obtained were very similar to those of zeolite A. For this reason, these data are not presented here although they confirm in all cases the conclusions of the previous section.

In order to obtain a more representative material for study, a sample of zeolite X with a higher Si/Al ratio was synthesized. The $^{29}\text{Si}$ MAS NMR spectrum (Figure 57a), obtained under conditions which ensure the data are quantitatively reliable, now shows five signals corresponding to the five local environments Si[4Al] to Si[4Si] as indicated in the figure. The spectrum was deconvoluted as shown in Figure 57b, and the peak areas from the deconvolution are presented in Table 8. The Si/Al ratio was calculated from Eq. (32) to be 1.75. The establishment of heteronuclear connectivities will now be predictably much more difficult than for zeolite A. The $^{29}\text{Si}$ signal intensity is now spread over five resonances and each of these is broader than in the case of zeolite A, resulting in a very substantial loss in overall S/N. In addition, the Si/Al ratio has increased by almost a factor of two compared to zeolite A, so there are correspondingly fewer aluminum nuclei to act as magnetization sources. One simplification, however, remains. The framework structure of zeolite X, shown inset in Figure 57, has only one crystallographically inequivalent site in the asymmetric unit, as is the case for zeolite A. Therefore, there are no complications in the $^{29}\text{Si}$ MAS spectrum from different chemical shifts which would make the situation even worse.

In each of the $^{27}\text{Al}/^{29}\text{Si}$ connectivity experiments (CP, REDOR, TEDOR, and dipolar-dephasing difference experiments), the magnetization for each $^{29}\text{Si}$ resonance should arise only from the presence of the neighbouring $^{27}\text{Al}$ nuclei. It is predicted, therefore, that there will be a relative enhancement of each $^{29}\text{Si}$ resonance which is linear with the number of aluminum atoms in the neighbouring T-sites. (It should be noted that
Figure 57. Zeolite X (with structure shown inset): (a) $^{29}$Si MAS spectrum after 168 scans with a recycle delay of 20 s. (b) Deconvolution of $^{29}$Si MAS spectrum from (a). (c) Predicted deconvolution of $^{29}$Si spectrum for $^{27}$Al/$^{29}$Si connectivity experiments, assuming a relative enhancement for each peak which is linear with the number of aluminum atoms in neighbouring T-sites. (d) Predicted spectrum for $^{27}$Al/$^{29}$Si connectivity experiments from the summation of the curves in (c).
Table 8. Deconvolution of peaks in $^{27}$Al/$^{29}$Si connectivity experiments on zeolite X.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Fractional Areas</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$^\text{Si(4Al)}$</td>
</tr>
<tr>
<td>$^{29}\text{Si MAS}$</td>
<td>0.125</td>
</tr>
<tr>
<td>Predicted for $^{27}\text{Al}^{29}\text{Si}$ Experiments</td>
<td>0.219</td>
</tr>
<tr>
<td>REDOR</td>
<td>0.258</td>
</tr>
<tr>
<td>TEDOR</td>
<td>0.303</td>
</tr>
<tr>
<td>Dipolar-Dephasing</td>
<td>0.278</td>
</tr>
<tr>
<td>Cross-Polarization</td>
<td>0.242</td>
</tr>
</tbody>
</table>

In all zeolites, the $^{27}$Al-O-$^{29}$Si distances are almost constant, varying only between 3.0 and 3.2 Å, while the $^{27}$Al-O-Si-O-$^{29}$Si distances are in the range of 5.0 - 5.5 Å. Since the dipolar interaction is proportional to the inverse third power of the internuclear distance, this greatly weights the effect in favour of only the neighbouring T-site interactions.) By taking the deconvolution of the $^{29}$Si MAS spectrum (Figure 57b) and assuming a relative enhancement for each peak which is linear with the number of neighbouring aluminum nuclei, the predicted deconvolution of the $^{29}$Si spectrum for the dipolar-based experiments is calculated (Figure 57c). Summation of the curves in Figure 57c produces a predicted $^{29}$Si spectrum for the dipolar-based experiments (Figure 57d).

Using the experimental conditions optimized for zeolite A (Table 7), the CP, dipolar-dephasing difference, REDOR and TEDOR experiments were carried out giving the spectra shown in Figure 58. All the experiments took between eight and nine hours, considerably longer than zeolite A for the reasons given above, but still within a reasonable period of time. The spectra all show the expected trend, that there are relative enhancements of those signals corresponding to silicon local environments with higher aluminum contents, and the Si[4Si] resonance is absent since it has no surrounding
Figure 58. $^{27}\text{Al}^{29}\text{Si}$ connectivity experiments on zeolite X, with the predicted spectrum from Figure 57d shown as the dotted line in each spectrum. (a) $^{29}\text{Si}(^{27}\text{Al})$ REDOR experiment with $n = 12$. A total of 1600 scans were acquired with a recycle delay of 20 s, with a total experimental time of 8.9 hr. (b) $^{27}\text{Al} \rightarrow ^{29}\text{Si}$ TEDOR experiment with $n = 2$ and $m = 1$. A total of 300,000 scans were acquired with a recycle delay of 0.1 s, with a total experimental time of 8.3 hr. (c) $^{29}\text{Si}(^{27}\text{Al})$ dipolar-dephasing difference experiment with 5 rotor cycles (2.0 ms) of $^{27}\text{Al}$ dephasing. A total of 1500 scans were acquired with a recycle delay of 20 s, with a total experimental time of 8.3 hr. (d) $^{27}\text{Al} \rightarrow ^{29}\text{Si}$ cross-polarization experiment with a contact time of 1.5 ms. A total of 300,000 scans were acquired with a recycle delay of 0.1 s, with a total experimental time of 8.3 hr.
aluminum nuclei. In order to probe this more quantitatively, the spectra were all
deconvoluted and the peak areas compared with those predicted from the quantitative
$^{29}$Si MAS spectrum assuming a relative enhancement which is exactly linear with the
number of aluminum atoms in the neighbouring T-sites (Figures 57c, d). These data are
shown in Table 8 and in Figure 58 where the predicted spectrum (from Figure 57d) is
indicated by the dotted line in each spectrum. As can be seen, there is reasonable
agreement in all cases, with the CP experiment giving nearly an exact fit. Therefore, one
important use of these experiments will be the deduction of the nature of the local silicon
environment for different resonances in cases where the chemical shift data are
ambiguous.

It is also possible to establish the heteronuclear connectivities within a reasonable
period of time for this sample. Figure 59 shows the results of a 2D TEDOR experiment,
which involved a total experimental measuring time of 13.5 hr. Figure 60 shows the
corresponding 2D CP experiment which took 23.3 hr. Both of these 2D spectra show the
expected connectivities of tetrahedral $^{27}$Al to the Si[4Al], Si[3Al, 1Si] and Si[2Al, 2Si]
resonances (the connection to the Si[1Al, 3Si] resonance is too weak to be observed in
the 2D spectra). This range of times will be typical for systems of this Si/Al ratio and
complexity.

(c) Zeolite Y

This zeolite has exactly the same (Faujasite) structure as zeolite X but the Si/Al
ratio is higher (Si/Al = 2.5), considerably reducing the proportion of aluminum nuclei
available and correspondingly reducing the S/N in a given time period. Experiments
were again carried out using the experimental parameters of Table 7, and the resulting
$^{29}$Si spectra are shown together with the quantitative MAS spectrum in Figure 61. Again
there is an approximate proportionality with the number of Al atoms in adjacent T-sites,
as indicated by the dotted line spectra calculated as for zeolite X (Figures 57c, 57d and
Figure 59. Two-dimensional $^{27}$Al $\rightarrow$ $^{29}$Si TEDOR experiment on zeolite X, with $n = 2$ and $m = 1$; 17400 scans were acquired for each of 28 experiments in $t_1$. The recycle delay of 0.1 s resulted in a total experimental time of 13.5 hr.
Figure 60. Two-dimensional $^{27}\text{Al} \rightarrow ^{29}\text{Si}$ cross-polarization experiment on zeolite X, with a contact time of 1.5 ms; 52320 scans were acquired for each of 16 experiments in $t_1$. The recycle delay of 0.1 s resulted in a total experimental time of 23.3 hr.
Figure 61. $^{29}$Si spectra of zeolite Y. The predicted spectrum for the $^{27}$Al/$^{29}$Si connectivity experiments is shown as the dotted line in spectra b, c, and d. (a) $^{29}$Si MAS spectrum after 236 scans with a recycle delay of 20 s. (b) $^{27}$Al → $^{29}$Si cross-polarization experiment with a contact time of 1.25 ms. A total of 576,000 scans were acquired with a recycle delay of 0.1 s, with a total experimental time of 16.0 hr. (c) $^{29}$Si($^{27}$Al) dipolar-dephasing difference experiment with 4 rotor cycles (1.5 ms) of $^{27}$Al dephasing. A total of 2160 scans were acquired with a recycle delay of 30 s, with a total experimental time of 18.0 hr. (d) $^{27}$Al → $^{29}$Si TEDOR experiment with $n = 2$ and $m = 1$. A total of 532,047 scans were acquired with a recycle delay of 0.1 s, with a total experimental time of 14.8 hr.
Figure 62. Two-dimensional $^{27}\text{Al} \rightarrow ^{29}\text{Si}$ TEDOR experiment on zeolite Y, with $n = 2$ and $m = 1$; 35640 scans were acquired for each of 44 experiments in $t_1$. The recycle delay of 0.1 s resulted in a total experimental time of 43.6 hr.
58) and superimposed on the experimental spectra (Figures 61b,c, and d). The measurement times were now all considerably longer, between 16 and 18 hours. The two dimensional TEDOR experiment (Figure 62), which shows the expected connectivities, involved a total experimental time of 43.6 hr.

(d) Zeolite Omega

This system represents another level in difficulty. Firstly, the Si/Al ratio is even higher (Si/Al = 4.2), correspondingly reducing the S/N ratios of the \(^{27}\)Al/\(^{29}\)Si connectivity experiments obtained in a given time period. In addition, the framework structure [11], shown inset in Figure 63, contains two crystallographically inequivalent T-sites in the unit cell: one in the 4-ring (T\(_1\)) and the other in the 6-ring (T\(_2\)). The ratio between these T-sites is T\(_1\):T\(_2\) = 2:1. Furthermore, the differences in the local geometries of these two T-sites are significant and cause a chemical shift difference of several ppm, comparable to the effect on the chemical shift produced by changing Al for Si in an adjacent T-site. The situation is now quite complex, and the interpretation of the simple \(^{29}\)Si MAS spectrum (Figure 63a) is ambiguous. Two viable assignments have been proposed, as indicated in Table 9 [12,13], using quite different arguments. They agree in the assignment of all of the major resolved peaks, but differ in the assignment of the small signal due to the Si\(_2\)(2Al) site. This peak is expected to have only one-half the intensity of peak 5 (Si\(_1\)(2Al)), and should therefore lie hidden underneath the larger peaks. Assignment A assigns the Si\(_2\)(2Al) signal as contributing to peak 3, while assignment B assigns it to peak 4.

Figures 63b-d show the one-dimensional CP, dipolar-dephasing, and TEDOR spectra as indicated, obtained in measuring times of 19.4 hr. (The initial TEDOR experiment using the standard 180° pulse placement after coherence-transfer at \(\tau_r/4\) and \(3\tau_r/4\) resulted in a spectrum which could not be properly phased. Therefore, the 180° pulses after coherence-transfer were placed at \(\tau_r/3\) and \(2\tau_r/3\), and the resulting spectrum is
Figure 63. $^{29}$Si experiments on zeolite omega. The structure of zeolite omega is shown inset, with the two crystallographic sites $T_1$ and $T_2$ indicated. (a) $^{29}$Si MAS spectrum after 256 scans with a recycle delay of 10 s, with the assignment of the peaks given in Table 9. (b) $^{27}$Al $\rightarrow$ $^{29}$Si cross-polarization experiment with a contact time of 1.5 ms. A total of 700,000 scans were acquired with a recycle delay of 0.1 s, with a total experimental time of 19.4 hr. (c) $^{29}$Si($^{27}$Al) dipolar-dephasing difference experiment with 5 rotor cycles (2.0 ms) of $^{27}$Al dephasing. A total of 3500 scans were acquired with a recycle delay of 20 s, with a total experimental time of 19.4 hr. (d) $^{27}$Al $\rightarrow$ $^{29}$Si TEDOR experiment with $n = 2$ and $m = 1$. The 180° pulses after the coherence transfer were placed at $\tau_\gamma/3$ and $2\tau_\gamma/3$. A total of 700,000 scans were acquired with a recycle delay of 0.1 s, with a total experimental time of 19.4 hr.
Figure 63
Table 9. Peak assignment for the $^{29}$Si MAS spectrum of zeolite omega from Figure 63.

<table>
<thead>
<tr>
<th>Peak Number</th>
<th>Chemical Shift (ppm)</th>
<th>Assignment A (ref [12])</th>
<th>Assignment B (ref [13])</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-113.5</td>
<td>Si$_2$(0Al)</td>
<td>Si$_2$(0Al)</td>
</tr>
<tr>
<td>2</td>
<td>-107.1</td>
<td>Si$_2$(1Al)</td>
<td>Si$_2$(1Al)</td>
</tr>
<tr>
<td>3</td>
<td>-103.8</td>
<td>Si$_1$(0Al) + Si$_2$(2Al)</td>
<td>Si$_1$(0Al)</td>
</tr>
<tr>
<td>4</td>
<td>-98.6</td>
<td>Si$_1$(1Al)</td>
<td>Si$_1$(1Al) + Si$_2$(2Al)</td>
</tr>
<tr>
<td>5</td>
<td>-93.3</td>
<td>Si$_1$(2Al)</td>
<td>Si$_1$2Al</td>
</tr>
</tbody>
</table>

shown in Figure 63d.) In Figures 63b-d, peak 1 is missing as expected since it corresponds to Si$_2$(0Al), the intensity of peak 5 (Si$_1$(2Al)) is enhanced due to the two aluminum nuclei, and peaks 2 and 4 are relatively unaffected as they are (mainly) due to Si$_2$(1Al) environments. The intensity of peak 3, on the other hand, is sharply reduced due to the Si$_1$(0Al) environment which should not contribute any intensity. Thus, in general terms, the dipolar-based experiments confirm the general correctness of the two assignments in terms of the major contributions to peaks 1 - 5.

The assignment of the small peak due to the Si$_2$(2Al) site is different in the two assignments A and B, and the dipolar-based spectra are thought to show some contributions from this site as indicated by the vertical dashed line in the figure. In the TEDOR experiment (Figure 63d), there is a large shoulder (= -104 ppm) evident on the downfield side of peak 2. In the CP and dipolar-dephasing difference experiments (Figures 63b and c, respectively), there is a small shoulder (= -102 ppm) on the upfield side of peak 4, which makes peak 4 appear very broad. The $^{27}$Al/$^{29}$Si connectivity experiments thus suggest that the chemical shift of the Si$_2$(2Al) site lies in between peaks 3 and 4 (in the range of -102 to -104 ppm).
4.4. Conclusions

This chapter has demonstrated the development and feasibility of $^{27}\text{Al}^{29}\text{Si}$ dipolar-coupling based NMR connectivity experiments in zeolite molecular sieve frameworks. The spectra show relative enhancements of the $^{29}\text{Si}$ resonances approximately proportional to the number of aluminum atoms in the neighbouring T-sites, and may be used for spectral assignments, particularly in cases where there are contributions from both local geometries and also the number of aluminums, as in the case of zeolite omega. Two-dimensional CP and TEDOR versions of these experiments are possible, and will be of use in heteronuclear experiments on complex mixtures or where several resonances are observable in the one-dimensional spectra of the two nuclear species.
Chapter 4 References

Chapter 5. Structural Investigations of SAPO-37 Molecular Sieve by $^{27}$Al/$^{29}$Si and $^{27}$Al/$^{31}$P Coherence-Transfer and Dipolar-Dephasing Solid-State NMR Experiments

In this chapter [1], the results of $^{27}$Al/$^{29}$Si and $^{27}$Al/$^{31}$P coherence-transfer and dipolar-dephasing solid-state NMR experiments performed to investigate the structure of the silicoaluminophosphate molecular sieve SAPO-37 are described. The experiments presented here directly prove for the first time that silicon atoms substitute for phosphorus in the SAPO-37 framework, and also indicate the presence of three different aluminum environments.

5.1. Introduction

As described previously, zeolites are an important class of aluminosilicate open framework materials that are widely used as molecular sieves because of the selectivity of their channel systems towards the adsorption of organic molecules [2]. When combined with their acidic properties in the acid form, this gives them unique catalytic properties. Zeolites have been established industrial materials for thirty years, but recent years have seen the growth of a second class of related molecular sieves, namely the aluminophosphates (AlPO$_4$'s) [3]. Unlike most zeolites, the AlPO$_4$ structures are ordered, with an exact alternation of AlO$_4$ and PO$_4$ tetrahedra. The Al/P ratio, therefore, is always unity, and the system is neutral with no charge balancing extra-framework ions present. As a result, the AlPO$_4$'s cannot act as acid catalysts, although they have similar sieving properties as zeolites.

With the introduction of some silicon atoms into the AlPO$_4$ framework, however, the charge balance is altered, and acidity becomes possible. These silicoaluminophosphate molecular sieves (SAPO's) exhibit some properties characteristic of zeolites, and some unique properties that reflect their own chemical compositions [4]. SAPO-37, which has the faujasite framework, has been the subject of numerous investigations [5-12],
particularly to try to establish that the Si atoms are in the framework, and to determine the mechanism of silicon substitution. There are three possible mechanisms that can be envisaged for silicon substitution into an AlPO₄ framework: replacement of a single Al atom by Si (SM1 mechanism), replacement of single P atom by Si (SM2 mechanism), or the replacement of one P together with one Al atom by two Si atoms (SM3 mechanism). It is postulated that silicon substitution into the SAPO-37 framework proceeds via the SM2 and SM3 mechanisms, with the latter mechanism becoming more important for conditions of high silicon content (greater than 10% of the tetrahedral sites).

Over the last decade, high-resolution solid-state NMR spectroscopy [13] has emerged as a powerful technique for structural investigations of molecular sieves. In the previous chapters, double-resonance NMR connectivity experiments involving quadrupolar nuclei were developed and applied to aluminophosphate (²⁷Al/³¹P) [14-16] and zeolite molecular sieves (²⁷Al/²⁹Si) [17]. Specifically, the cross-polarization, TEDOR, REDOR, and dipolar-dephasing difference experiments were used to select ²⁷Al-O-³¹P and ²⁷Al-O-²⁹Si connectivities in these molecular sieve systems via the heteronuclear dipolar interactions between the pairs of nuclei. In this chapter, these experiments are utilized to select ²⁷Al-O-³¹P and ²⁷Al-O-²⁹Si connectivities in the silicoaluminophosphate molecular sieve SAPO-37.

5.2. Experimental Section

The sample of SAPO-37 was provided by W.R. Grace & Co. The sample was analysed by ICP-AES and found to have the T-atom composition (Si₀.₁₀ Al₀.₅₂ P₀.₃₈) O₂₋. A ¹H/¹³C CPMAS experiment confirmed that the sample contained tetramethylammonium (TMA) and tetrapropylammonium (TPA) ions as templates, and the sample was studied in the as-synthesized form. Powder x-ray diffraction measurements were performed using a Rigaku rotating anode powder diffractometer (Cu Kα radiation, λ = 1.5418 Å).
All NMR experiments were performed on a Bruker MSL 400 spectrometer modified to include a third radiofrequency channel. Resonance frequencies were 79.495 MHz for $^{29}\text{Si}$, 104.264 MHz for $^{27}\text{Al}$, and 161.977 MHz for $^{31}\text{P}$, and chemical shifts are reported with respect to tetramethylsilane (TMS), aqueous $\text{Al(NO}_3)_3$, and $\text{H}_3\text{PO}_4$, respectively. In all experiments, the magic angle was set using the $^{79}\text{Br}$ resonance of KBr. Due to the individual requirements of each experiment, three different NMR probes were used:

1. The $^{27}\text{Al}/^{29}\text{Si}$ connectivity experiments were performed using a home-built double-tuned probe incorporating a 14 mm "pencil spinner" supplied by Chemagnetics, with an internal volume of 2.8 mL. This large sample volume was necessary due to the low concentration of silicon in our sample of SAPO-37, coupled as usual with the low natural abundance of $^{29}\text{Si}$ (4.7%). Samples were spun at 2.2-2.5 kHz with the spinning rate monitored by an optical sensor unit. The $^{29}\text{Si} 90^\circ$ pulse and the $^{27}\text{Al} 90^\circ$ pulse (central transition only) were both in the range of 14.5-18.0 µs.

2. The $^{27}\text{Al}/^{31}\text{P}$ connectivity experiments were performed using a home-built double-tuned probe incorporating a 10 mm Supersonic spinner supplied by Doty Scientific Inc., with an internal volume of 1.0 mL. Samples were spun at 5.3-5.5 kHz with the spinning rate monitored by the spinning sidebands of the $^{79}\text{Br}$ MAS spectrum of KBr. The $^{31}\text{P} 90^\circ$ pulse and the $^{27}\text{Al} 90^\circ$ pulse (central transition only) were both 22.0 µs, respectively.

3. The $^{27}\text{Al}$ fast-spinning MAS experiments were performed using a home-built single-tuned probe incorporating a 5 mm high speed spinner supplied by Doty Scientific Inc., with an internal volume of 100 µL. Samples were spun at 4-12 kHz with the spinning rate monitored by the spinning sidebands in the $^{79}\text{Br}$ MAS spectrum of KBr. The $^{27}\text{Al} 90^\circ$ pulse (central transition only) was 1.5 µs.
The pulse sequences used for the cross-polarization (CP), TEDOR, dipolar-dephasing, and two-dimensional CP and TEDOR experiments were described in detail in Chapter 2. For the one- and two-dimensional TEDOR experiments, the numbers of rotor cycles before and after the coherence transfer \((n \text{ and } m, \text{ respectively})\) were optimized experimentally, and are indicated in each figure caption.

5.3. Results and Discussion

The powder x-ray diffraction spectrum (Figure 64) confirms the identity of the sample as SAPO-37, and shows that both the crystallinity and purity of the sample are high.

The \(^{29}\text{Si}\) NMR spectrum (Figure 65a) is in general agreement with those published previously [5-12]. The spectrum consists mainly of a sharp peak at -89.4 ppm (together with spinning sidebands as indicated in the figure), consistent with a single environment for Si. The nature of this environment, however, cannot be unambiguously assigned without further experiments, although the value of the chemical shift suggests that the environment could be Si[4Al]. The spectrum also shows a broad peak underneath the main sharp peak at around -90 ppm which may be due to aluminosilicate environments (e.g. Si[3Al, Si]), and a small sharp peak at -107.1 ppm which has been previously assigned as a Si[4Si] environment arising from small siliceous domains perhaps formed by the SM3 mechanism.

The \(^{31}\text{P}\) MAS spectrum (Figure 65b) also agrees with those published previously [5-9]. The spectrum consists of a sharp peak at -26.1 ppm, which can be assigned as P[4Al] from the expected P/Al alternation.

The nature of the silicon environment can be unambiguously assigned, however, through the \(^{27}\text{Al} \rightarrow ^{29}\text{Si}\) TEDOR spectrum (Figure 66). The TEDOR spectrum shows the same sharp peak as in the \(^{29}\text{Si}\) MAS spectrum, while the corresponding null experiment (not shown) shows no signal. Since \(^{27}\text{Al}\) is the only source of the coherence
Figure 65. (a) $^{29}\text{Si}$ MAS spectrum and (b) $^{31}\text{P}$ MAS spectrum of SAPO-37. Spinning sidebands are indicated with an asterisk.
Figure 66. $^{27}\text{Al} \rightarrow ^{29}\text{Si}$ TEDOR spectrum of SAPO-37, with $n = 2$ and $m = 1$. A total of 879897 scans were acquired with a recycle delay of 0.1 s, resulting in a total experimental time of 24.4 hr.
for the $^{29}\text{Si}$ signal, $^{27}\text{Al}-^{29}\text{Si}$ connectivities must exist, proving the silicon environment is Si[4Al]. This is consistent with Si substitution for P atoms via the SM2 mechanism.

The local environment of phosphorus can also be probed through the $^{27}\text{Al} \rightarrow ^{31}\text{P}$ TEDOR spectrum (Figure 67). As expected, the TEDOR spectrum shows the same single peak as in the $^{31}\text{P}$ MAS spectrum, verifying the P[4Al] environment. Again, a corresponding null experiment was performed (not shown), and showed no signal.

However, the situation for aluminum is not as straightforward as for silicon and phosphorus. The $^{27}\text{Al}$ MAS spectra obtained at different spinning rates (Figure 68) all show two sharp lines at 37.4 and 5.5 ppm, with evidence of a third very broad resonance lying underneath these two sharp peaks. The peak at 37.4 ppm can be assigned to tetrahedral Al. The peak at 5.5 ppm is typical of octahedral Al, and has previously been assigned to residual extra-lattice amorphous alumina [6,7]. The octahedral Al resonance has a much shorter $T_2$ value than the tetrahedral Al (approximately 1.0 and 9.0 ms, respectively). The spinning sidebands of the two sharp lines disappear when spinning faster that 6.4 kHz, while those of the third broad resonance are still seen when spinning at 12.1 kHz. This third broad resonance, therefore, has a much larger anisotropy (over 300 ppm) and a lower symmetry compared to the two sharp peaks. The chemical shift of the third broad resonance is difficult to measure directly since it is broad and lies underneath the two sharp signals. Figure 68 shows that as the spinning speed increases from 4.1 up to 12.1 kHz, the relative intensity of the octahedral Al peak seems to increase. Since the sidebands from the octahedral Al resonance disappear when spinning faster than 6.4 kHz, the increase in intensity of the octahedral Al resonance at higher spinning speeds must arise from another source. This increase is actually due to the third broad resonance, since its sidebands are still observable at high spinning rates. In addition, the resolution between the two sharp peaks decreases as the spinning speed increases. This implies that the isotropic chemical shift of the broad resonance is centred slightly downfield from the octahedral Al resonance, at around 10 ppm.
Figure 67. $^{27}\text{Al} \rightarrow ^{31}\text{P}$ TEDOR spectrum of SAPO-37, with $n = 4$ and $m = 1$. A total of 6400 scans were acquired with a recycle delay of 0.1 s, resulting in a total experimental time of only 11 min.
Figure 68. $^{27}$Al MAS spectra of SAPO-37 acquired at the different spinning rates indicated.
It was previously proposed [18] that the large anisotropies of both the tetrahedral and octahedral Al sites are evidence for asymmetrical environments such as Al[3P, Si]. However, when spinning faster that 6.4 kHz, the spinning sidebands of the two sharp lines (tetrahedral and octahedral Al) disappear, and only spinning sidebands from the third broad peak remain (Figure 68). Therefore, the large anisotropy observed must arise from the third broad peak, and not from the sharp tetrahedral or octahedral peak. In addition, in the 2D $^{27}$Al $\rightarrow$ $^{31}$P TEDOR experiment (see Figure 69 below), there is a large $^{27}$Al anisotropy observed, but no intense correlation with the sharp octahedral Al resonance. This provides additional support ruling out the octahedral Al peak as the source of the large anisotropy.

Further information regarding the nature of the three Al resonances can be obtained from the two-dimensional $^{27}$Al $\rightarrow$ $^{31}$P TEDOR experiment (Figure 69), which shows the individual $^{27}$Al-O-$^{31}$P connectivities in SAPO-37. The sharp tetrahedral $^{27}$Al site at 37.4 ppm shows a strong correlation to the single $^{31}$P site, as expected. There is also a set of lower intensity correlations over a range of about 300 ppm from the $^{27}$Al spectrum to the $^{31}$P site. The source of these correlations can be made clearer by comparing the $^{27}$Al 2D TEDOR projection (Figure 70a) with the corresponding one-dimensional $^{27}$Al MAS spectrum (Figure 70b). It can be seen that half of the set of smaller peaks in the $^{27}$Al 2D TEDOR projection (indicated by asterisks) are the sidebands of the sharp tetrahedral $^{27}$Al peak since they are separated by the rotational frequency around the isotropic shift of this resonance. However, the other half of the set of smaller peaks is due to the third broad resonance in the $^{27}$Al spectrum (isotropic peak and sidebands). (It should be noted that the contribution from spinning sidebands is enhanced in a TEDOR experiment.) A repeat of the 2D $^{27}$Al $\rightarrow$ $^{31}$P TEDOR experiment at a slower spinning speed (not shown) confirms that the isotropic shift of this third broad peak is centred at 7.4 ppm. This broad resonance has a large anisotropy (over 300 ppm), and is therefore likely due to an asymmetrical
Figure 69. Two-dimensional $^{27}$Al $\rightarrow$ $^{31}$P TEDOR experiment on SAPO-37, with $n = 4$, $m = 1$, and a spinning rate of 5.30 kHz. For each of the 128 experiments in $t_1$, 3584 scans were acquired. The recycle delay of 0.1 s resulted in a total experimental time of 12.7 hr.
Figure 70. $^{27}$Al experiments on SAPO-37. In both experiments, the spinning rate was 5.30 kHz. (a) $^{27}$Al 2D TEDOR projection from Figure 69, with spinning sidebands from the sharp tetrahedral peak at 37.4 ppm indicated (*). (b) $^{27}$Al one-dimensional MAS spectrum.
environment. Although it is possible that it could be due to an amorphous Al-O-P environment, the $^{31}$P MAS spectrum is sharp, making this possibility unlikely.

A 2D $^{27}$Al → $^{31}$P cross-polarization experiment (not shown) was also performed. This experiment gives the same correlation of the sharp tetrahedral $^{27}$Al site at 37.4 ppm to the single $^{31}$P site, as in the 2D TEDOR experiment. However, the sideband intensities are lower in the 2D CP experiment (as expected, since the contribution from spinning sidebands is enhanced in a TEDOR experiment), so the correlation to the third broad peak is not quite as clear.

The 2D $^{27}$Al → $^{31}$P TEDOR and CP experiments do not show any correlations to the octahedral Al site, consistent with the assignment of this site to extra-framework amorphous alumina. However, care must be taken in coming to this conclusion based on such a negative result. It is possible that the octahedral Al is in the framework, and correlations to this site may be missed as it has a very short $T_2$ value (approximately 1.0 ms), making it possible that the octahedral Al coherence might decay completely during the frequency encoding and echo periods of the two-dimensional experiments.

To eliminate this possible ambiguity, an $^{27}$Al($^{31}$P) dipolar-dephasing (DD) difference experiment was performed in which the $^{27}$Al spin echo was recorded first with $^{31}$P irradiation, and then without $^{31}$P irradiation. The difference between these two signals represents the $^{27}$Al sites which are connected to the $^{31}$P site. As can be seen from the pulse sequence in Figure 27a, since there is no frequency encoding period in the DD experiment, and the echo time can be made very short, the decay due to $T_2$ is minimized compared to the 2D TEDOR and CP experiments. In addition, since the $^{31}$P spectrum consists of only a single line, there is no loss of information in the DD experiment compared to possible 2D experiments.

The $^{27}$Al spin echo signal and the $^{27}$Al($^{31}$P) DD signal are compared in Figure 71. In each experiment, the total echo time was made as short as possible (two rotor cycles) in
Figure 71. $^{27}\text{Al}$ experiments on SAPO-37. In each experiment, the spinning rate was 5.65 kHz, and the total echo time was 2 rotor cycles ($n = 2$). (a) $^{27}\text{Al}$ spin echo spectrum (no $^{31}\text{P}$ dephasing) with the octahedral resonance indicated (*). (b) $^{27}\text{Al}^{(31}\text{P})$ dipolar-dephasing (DD) difference spectrum, with 1 rotor cycle of $^{31}\text{P}$ dephasing. A total of 116248 scans were acquired with a recycle delay of 0.5 s, resulting in a total experimental time of 16.1 hr.
order to minimize the effects of $T_2$ relaxation. The $^{27}$Al spin echo signal (Figure 71a) shows sharp resonances from tetrahedral and octahedral Al, and the third broad resonance underneath. In the $^{27}$Al($^{31}$P) DD experiment (Figure 71b), the octahedral Al peak is removed, and is thus due to Al which is not connected to P. Therefore, the octahedral Al atoms are not in the SAPO-37 framework. In addition, the presence of the third broad Al resonance in the DD experiment verifies that this Al site is connected to P in the lattice. A corresponding null DD experiment was performed (not shown), and this confirmed that no $^{27}$Al signals arose from imperfect subtraction in the difference experiment.

In an analogous manner, a $^{27}$Al($^{29}$Si) dipolar-dephasing difference experiment was performed to detect only those Al atoms with attached Si atoms. The $^{27}$Al spin echo signal (Figure 72a) shows a sharp resonance from tetrahedral Al and a broad resonance underneath. The $^{27}$Al($^{29}$Si) DD signal (Figure 72b) also shows a sharp tetrahedral Al peak and a broad resonance underneath. The presence of the sharp tetrahedral Al resonance in the $^{27}$Al($^{29}$Si) DD experiment suggests that this resonance contains contributions from Al nuclei with one or more Si nuclei as first-nearest neighbours. It is known that the Si sites in SAPO-37 tend to cluster together, rather than evenly distribute in the AlPO$_4$ framework [5-12]. Therefore, at 10% Si substitution for P, there should be detectable amounts of Al[4Si] environments. The chemical shift of the tetrahedral Al[4Si] environment in zeolite Y, which has the same topology as SAPO-37, is significantly higher than the tetrahedral Al peak observed in SAPO-37 (60 ppm versus 37 ppm at 9.4 T). However, it is felt that zeolite Y is not an appropriate chemical shift reference since at 10% Si incorporation, 90% of the SAPO-37 lattice is composed of Al and P tetrahedral sites, and the local geometries they impose may well determine the exact chemical shift.

Therefore, in the $^{27}$Al($^{29}$Si) DD experiment (Figure 72b), it is suggested that the environment of the nuclei which contribute to the sharp tetrahedral Al resonance at 37 ppm is Al[4Si], and that the deciding factor determining the appearance of the $^{27}$Al spectrum is
Figure 72. $^{27}$Al experiments on SAPO-37. In each experiment, the spinning rate was 2.36 kHz, and the total echo time was 2 rotor cycles ($n = 2$). (a) $^{27}$Al spin echo spectrum (no $^{29}$Si dephasing). (b) $^{27}$Al/$^{29}$Si dipolar-dephasing (DD) difference spectrum, with 1 rotor cycle of $^{29}$Si dephasing. A total of 275268 scans were acquired with a recycle delay of 0.5 s, resulting in a total experimental time of 38.2 hr.
the symmetry of the local Al environments. Thus, in the $^{27}$Al MAS spectra (Figure 68), the relatively narrow tetrahedral Al signal contains contributions from Al[4P] and Al[4Si], both of which are in symmetrical local environments. Furthermore, in a study [6] of SAPO-37 samples with 12, 16, and 21% Si incorporation, all of which contain some Al[4Si] environments, a sharp tetrahedral resonance was seen near 37 ppm, but no other sharp resonance was observed around 60 ppm (as in zeolite Y). This provides additional evidence that the Al[4Si] environments are contributing to the observed tetrahedral signal at 37 ppm. This resonance is relatively broad ($\Delta v_{1/2} = 2000$ Hz), and could accommodate two narrow resonances with somewhat different chemical shifts.

Although there is no AlPO$_4$-37 aluminophosphate analog of SAPO-37 available, a comparison of AlPO$_4$-5 [19] with SAPO-5 [20], and AlPO$_4$-11 [21] with SAPO-11 [22], shows that there is no noticeable change in the chemical shift of the sharp tetrahedral Al resonance when Si is incorporated into the lattice. This provides additional support for the argument that the chemical shift of the tetrahedral Al resonance does not change greatly on going from an Al[4P] to an Al[4Si] environment in SAPO molecular sieves.

The observation of the third broad Al resonance in the $^{27}$Al($^{29}$Si) DD experiment (Figure 72b) shows that this Al site is connected to Si atoms in the lattice. This Al site is also connected to P, as indicated by the $^{27}$Al($^{31}$P) DD experiment (Figure 71b). The broad resonance, therefore, is assigned to tetrahedral Al surrounded by either [3P, Si], [2P, 2Si], or [P, 3Si]. These three Al environments are all asymmetrical since they contain a mixture of P and Si atoms, which gives rise to the large anisotropy observed. This is consistent with the known effect of symmetry on quadrupolar interactions. The investigation of other SAPO-37 materials with lower and higher degrees of Si incorporation would perhaps confirm these conclusions, and such experiments would be suggestions for future work in this area.
5.4. Conclusions

$^{27}\text{Al}/^{29}\text{Si}$ and $^{27}\text{Al}/^{31}\text{P}$ coherence-transfer and dipolar-dephasing solid-state NMR experiments provide structural information in the silicoaluminophosphate molecular sieve SAPO-37. The $^{27}\text{Al} \rightarrow^{29}\text{Si}$ TEDOR experiment unambiguously shows that the nature of the main Si environment is Si[4Al]. The $^{27}\text{Al} \rightarrow^{31}\text{P}$ TEDOR experiment shows that there is only a single P[4Al] environment. These experiments are consistent with Si substitution for P atoms via the SM2 mechanism. In addition, the $^{27}\text{Al}$ variable-speed MAS, 2D $^{27}\text{Al} \rightarrow^{31}\text{P}$ TEDOR, and $^{27}\text{Al}(^{31}\text{P})$ and $^{27}\text{Al}(^{29}\text{Si})$ dipolar-dephasing difference experiments indicate the presence of three types of Al environments in SAPO-37: (a) tetrahedral Al surrounded by symmetrical [4P] or [4Si] environments which give rise to a relatively sharp resonance at 37.4 ppm, (b) tetrahedral Al surrounded by asymmetrical [3P, Si], [2P, 2Si], or [P, 3Si] environments which give rise to a broad resonance with a large anisotropy (over 300 ppm), centred at 7.4 ppm, and (c) extra-framework octahedral Al which is not connected to either P or Si, which gives rise to a sharp resonance at 5.5 ppm.
Chapter 5 References


Chapter 6. $^{27}\text{Al}/^{31}\text{P}$ Solid-State NMR Structural Investigations of AlPO$_4$-5 Molecular Sieve

In this chapter, the results from $^{27}\text{Al}/^{31}\text{P}$ solid-state NMR connectivity experiments used to investigate the structure of the aluminophosphate molecular sieve AlPO$_4$-5 are reported [1]. The experiments show that both the tetrahedral aluminum and the octahedral aluminum formed upon hydration are connected to phosphorus in the framework, providing direct evidence that the AlPO$_4$-5 framework remains intact during the hydration process.

6.1. Introduction

AlPO$_4$-5 is a large-pore molecular sieve with a unidimensional pore system of diameter approximately 8 Å, and only one inequivalent tetrahedral site in its dehydrated framework [2]. AlPO$_4$-5 was the first novel framework of the AlPO$_4$-based molecular sieves whose structure was determined, although the more recently discovered zeolite SSZ-24 has the same topology [3]. AlPO$_4$-5 has a high water adsorption capacity (up to 28% of its dry weight), resulting in the conversion of up to 40% of the Al to octahedral coordination, as evidenced by $^{27}\text{Al}$ MAS NMR [4]. This structural transformation is readily reversible by dehydration over P$_2$O$_5$, as indicated by the loss of the octahedral $^{27}\text{Al}$ resonance. In addition, the X-ray diffraction pattern of hydrated AlPO$_4$-5 shows that the framework structure has not collapsed. These observations suggest that the octahedral Al observed is not extra-lattice, but is formed by hydration of a portion of the tetrahedral Al framework sites. This is in contrast to other systems, such as VPI-5 [5], where hydration (and tetrahedral to octahedral conversion) occurs, but at specific sites in the framework.

High-resolution solid-state NMR spectroscopy [6] has emerged as a powerful complementary technique to X-ray diffraction for structural investigations of molecular sieves [7,8]. In the previous chapters, double-resonance solid-state NMR connectivity experiments involving quadrupolar nuclei were developed and applied to AlPO$_4$ molecular
sieves ($^{27}$Al/$^{31}$P) [9-11], zeolites ($^{27}$Al/$^{29}$Si) [12], and SAPO-37 ($^{27}$Al/$^{31}$P and $^{27}$Al/$^{29}$Si) [13]. Specifically, cross-polarization, TEDOR, REDOR, and dipolar-dephasing difference experiments were used to select connectivities in these systems via the heteronuclear dipolar interactions between the pairs of nuclei. In this chapter, these techniques are applied to an investigation of the AlPO$_4$-5 system to try to obtain direct evidence that the framework remains intact during the hydration process.

6.2. Experimental Section

The sample of AlPO$_4$-5 was provided by Union Carbide Corporation. It was exchanged with D$_2$O by dehydrating at 70°C overnight, adding an excess of D$_2$O, exchanging with D$_2$O in a sealed vial for 5 h, removing the excess D$_2$O by absorption on filter paper, and finally packing and sealing the sample in a 10 mm rotor for NMR analysis.

The NMR experiments were performed using a Bruker MSL 400 spectrometer modified to include a third radiofrequency channel, with resonance frequencies of 104.264 and 161.977 MHz for $^{27}$Al and $^{31}$P, respectively. The $^{27}$Al and $^{31}$P chemical shifts are referenced to Al(NO$_3$)$_3$ and 85% H$_3$PO$_4$, respectively. A home-built double-tuned probe which incorporated a 10 mm supersonic spinner supplied by Doty Scientific Inc., with an internal volume of 0.8 mL, was used, and the 90° pulse lengths were 22.5 µs for both $^{31}$P and $^{27}$Al (central +1/2 ↔ −1/2 transition only). Spinning rates were between 4.9 and 5.2 kHz.

The pulse sequences used for the dipolar-dephasing (DD), cross-polarization (CP), TEDOR, and two-dimensional CP and TEDOR experiments were as described in Chapter 2. For the one- and two-dimensional TEDOR experiments, the number of rotor cycles before and after the coherence transfer ($n$ and $m$, respectively) were optimized experimentally, and are indicated in each figure caption.
6.3. Results and Discussion

The $^{27}$Al MAS spectrum of the hydrated AlPO$_4$-5 sample (Figure 73), acquired using a small pulse angle (less than 15°) to ensure a quantitative spectrum [14], shows sharp resonances from tetrahedral Al at 38 ppm and octahedral Al at -16 ppm. Integration of the peak areas shows that 38% of the Al sites have octahedral coordination, while 62% have tetrahedral coordination. This is in agreement with a previous study of hydrated AlPO$_4$-5 which found that up to 40% of the Al sites could be in an octahedral Al coordination [4]. The tetrahedral Al peak arises from the single Al[4P] environment in the framework, while the octahedral Al peak has been previously assigned [4] to an environment arising from the coordination of two water molecules to a tetrahedral Al site to give an octahedral coordination. Thus, the presence of the octahedral Al peak indicates that the sample is well hydrated. In addition, there is a very small sharp peak at 8 ppm (which is not a spinning sideband or due to the offset frequency) between the tetrahedral and octahedral Al resonances. This peak can be assigned to 5-coordinate Al arising from the coordination of one water molecule to a tetrahedral Al site in the framework. This environment is due to incomplete hydration, and may be an intermediary between tetrahedral and octahedral Al.

The $^{31}$P MAS spectrum (Figure 74) is similar to that previously presented [4] for fully hydrated AlPO$_4$-5, and shows a single broad asymmetric resonance centred at -26 ppm, with a small downfield shoulder in the region from -10 to -20 ppm. Careful inspection of the $^{31}$P MAS spectra of the hydrated and dehydrated samples presented in reference [4] indicates that in these also, upon hydration, the $^{31}$P resonance shifts downfield, broadens, and displays a small downfield shoulder.

The conventional $^{27}$Al spin-echo (SE) experiment (Figure 75a) shows resonances from tetrahedral and octahedral Al, and also a very small signal due to 5-coordinate Al. The T$_2$ relaxation times were determined to be 3.0 and 1.7 ms for the tetrahedral and
Figure 73. $^{27}$Al MAS spectrum of AlPO$_4$-5, acquired using a pulse angle of 11°. Spinning sidebands are indicated by an asterisk (*).
Figure 74. $^{31}$P MAS spectrum of AlPO$_4$-5, with spinning sidebands indicated (*).
Figure 75. $^{27}\text{Al}$ experiments on AlPO$_4$-5. In each experiment, the spinning rate was 4.88 kHz, and the total echo time was 2 rotor cycles ($n = 2$). (a) $^{27}\text{Al}$ spin echo signal (no $^{31}\text{P}$ dephasing), with spinning sidebands indicated (*). (b) $^{27}\text{Al}(^{31}\text{P})$ DD difference experiment, with 1 rotor cycle of $^{31}\text{P}$ dephasing. A total of 10528 scans were acquired with a recycle delay of 0.25 s. (c) $^{27}\text{Al}(^{31}\text{P})$ DD difference null experiment acquired under the same conditions as (b), except that the $^{31}\text{P}$ dephasing was kept on-resonance.
octahedral Al nuclei, respectively, and are therefore not short enough to cause problems in spin-echo type experiments over small to moderate numbers of rotor cycles. In the $^{27}\text{Al}(^{31}\text{P})$ dipolar-dephasing (DD) difference experiment, an $^{27}\text{Al}$ spin echo is recorded first with on-resonance $^{31}\text{P}$ dephasing, and then without $^{31}\text{P}$ dephasing (i.e. off-resonance). The difference between these two signals represents the $^{27}\text{Al}$ sites which are dipolar-coupled (i.e. close in space or "connected") to the $^{31}\text{P}$ site. The $^{27}\text{Al}(^{31}\text{P})$ DD experiment on AlPO$_4$-5 (Figure 75b) demonstrates that both tetrahedral and octahedral Al are connected to P, and thus both are in the framework. This confirms the previous suggestion [4] that octahedral Al is formed by coordination of two water molecules to an Al site. Since only a single tetrahedral Al site is observed, the octahedral Al must be formed at random sites in the framework. The corresponding $^{27}\text{Al}(^{31}\text{P})$ DD null experiment was performed (Figure 75c) in which the $^{31}\text{P}$ dephasing was kept on-resonance in all experiments. The null experiment confirmed that no $^{27}\text{Al}$ signals arose from imperfect subtraction in the difference experiment.

The one-dimensional $^{27}\text{Al} \rightarrow ^{31}\text{P}$ TEDOR and CP experiments involve coherence transfer from $^{27}\text{Al}$ to $^{31}\text{P}$, and thus show only signals from those $^{31}\text{P}$ sites which are dipolar-coupled to $^{27}\text{Al}$. In addition, since $^{27}\text{Al}$ is the source of the magnetization, the experiments can be repeated very quickly (0.1 s), thereby increasing the S/N ratio over a given time period. The CP experiment is shown in Figure 76a, using an optimized contact time of 2 ms, and the TEDOR experiment in Figure 76b, with the optimized conditions of $n = 4$ and $m = 1$ rotor cycle. The CP and TEDOR experiments both show as expected that the $^{31}\text{P}$ site, including the downfield shoulder, is connected to $^{27}\text{Al}$. Note that in the TEDOR experiment, the spinning sidebands (indicated by *) have a negative phase. This effect, observed previously in VPI-5 [10,11], arises because the evolution of the sidebands is different from that of the isotropic peaks. Using the optimized conditions for the 1D experiments, the TEDOR and CP experiments can be extended to two dimensions to map the individual connectivities.
Figure 76. $^{27}\text{Al} \rightarrow ^{31}\text{P}$ coherence-transfer experiments on AlPO$_4$-5, with spinning sidebands indicated (*). (a) $^{27}\text{Al} \rightarrow ^{31}\text{P}$ CP experiment, with a contact time of 2 ms. A total of 2400 scans were acquired with a recycle delay of 0.1 s. (b) $^{27}\text{Al} \rightarrow ^{31}\text{P}$ TEDOR experiment, with $n = 4$ and $m = 1$ rotor cycles. A total of 2048 scans were acquired with a recycle delay of 0.1 s.
A sample of AlPO$_4$-5 hydrated with H$_2$O was first used for the 2D $^{27}$Al $\rightarrow ^{31}$P TEDOR experiment. However, the correlation to octahedral Al was much weaker than expected, and could not be accounted for by the effects of $T_2$ relaxation alone. We feel that the presence of a third nucleus, namely $^1$H in the H$_2$O molecules coordinated to the octahedral Al, interferes with the reversal of the sign of the dipolar coupling in the TEDOR experiment, thereby reducing the efficiency of coherence transfer from octahedral Al to P. Therefore, the AlPO$_4$-5 was exchanged with D$_2$O (see Experimental Section 6.2) to reduce the interference from $^1$H in H$_2$O, and the D$_2$O-exchanged sample was used for all of the TEDOR and CP experiments presented in this work.

The 2D $^{27}$Al $\rightarrow ^{31}$P TEDOR experiment (Figure 77), acquired with $n = 4$ and $m = 1$ rotor cycle, shows clear correlations of both tetrahedral and octahedral Al to the P site, again confirming that octahedral Al is connected to P in the framework. The dashed lines show that the correlation of P to the tetrahedral Al resonance is centred at -26 ppm, while the correlation to octahedral Al is centred downfield at -22 ppm. The downfield offset of the octahedral Al cross-peak is consistent with growth of a downfield shoulder on the $^{31}$P resonance in the region from -10 to -20 ppm as water is incorporated. $T_2$ effects underestimate the intensity of the octahedral Al correlation ($T_2 = 1.7$ ms for octahedral Al versus 3.0 ms for tetrahedral Al), although the correlation to octahedral Al is still less intense than in the $^{27}$Al SE experiment (Figure 75a) which is itself subject to $T_2$ effects.

The 2D $^{27}$Al $\rightarrow ^{31}$P CP experiment (Figure 78), acquired with a contact time of 2 ms, also shows a clear correlation of P to both tetrahedral and octahedral Al. However, the correlation to octahedral Al is much stronger in the 2D CP experiment than in the 2D TEDOR experiment (Figure 77). In the $^{27}$Al projection of the 2D CP experiment, the intensity of the octahedral Al is approximately one-third that of the tetrahedral Al. Again, the dashed lines show that the correlation of P to tetrahedral Al is centred at -26 ppm, while the correlation to octahedral Al is centred downfield at -22 ppm. Interestingly, there is also
Figure 77. Two-dimensional $^{27}$Al $\rightarrow$ $^{31}$P TEDOR experiment on AlPO$_4$-5, with $n = 4$ and $m = 1$ rotor cycles. The dashed lines indicate the connected resonances. For each of the 128 experiments in $t_1$, 4096 scans were acquired. The recycle delay of 0.1 s resulted in a total experimental time of 14.6 hr.
Figure 78. Two-dimensional $^{27}\text{Al} \rightarrow ^{31}\text{P}$ CP experiment on AlPO$_4$-5, with a contact time of 2 ms. The dashed lines indicate the connected resonances, and the spinning sidebands are indicated (*). For each of the 128 experiments in t$_1$, 5600 scans were acquired. The recycle delay of 0.1 s resulted in a total experimental time of 19.9 hr.
a correlation of the previously assigned 5-coordinate Al resonance to P, which supports the assignment of this environment as arising from the coordination of one water molecule to an Al site in the framework. This correlation to 5-coordinate Al is also present in the 2D TEDOR experiment (Figure 77), although its intensity is much smaller than in the 2D CP experiment.

The two-dimensional CP and TEDOR experiments show correlations from tetrahedral Al to the large $^{31}$P peak (at -26 ppm), and from octahedral Al to the downfield shoulder (in the region from -10 to -20 ppm). This observation might suggest that there are only two P environments: one surrounded by tetrahedral Al, and one surrounded by octahedral Al. However, in this case, the resonances should be sharper than those observed. An alternative explanation can be formulated in terms of a random distribution. If the individual probabilities of finding tetrahedral and octahedral Al are approximately 62% and 38%, respectively, and the distribution is assumed to be random, there are actually five possible P environments surrounded by varying numbers of tetrahedral and octahedral Al as first nearest neighbours, as shown in Table 10. The broad $^{31}$P resonance, encompassing the large peak (-26 ppm) and the small shoulder (from -10 to -20 ppm), represents the distribution of the five possible P environments.

Table 10. Probabilities of the five possible phosphorus environments in AlPO$_4$-5.

<table>
<thead>
<tr>
<th>Phosphorus Environment (a)</th>
<th>Probability (%) (b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P[4 tet]</td>
<td>14.8</td>
</tr>
<tr>
<td>P[3 tet, 1 oct]</td>
<td>36.2</td>
</tr>
<tr>
<td>P[2 tet, 2 oct]</td>
<td>33.3</td>
</tr>
<tr>
<td>P[1 tet, 3 oct]</td>
<td>13.6</td>
</tr>
<tr>
<td>P[4 oct]</td>
<td>2.1</td>
</tr>
</tbody>
</table>

(a) "tet" and "oct" refer to tetrahedral and octahedral Al, respectively.
(b) The probabilities are calculated assuming that the individual probabilities of tetrahedral and octahedral Al are 62% and 38%, respectively, and that the distribution is random.
Figure 79 shows $^{31}$P rows of the 2D $^{27}$Al $\rightarrow$ $^{31}$P CP experiment (Figure 78) taken through the tetrahedral and octahedral $^{27}$Al resonances. Figure 7a shows that the correlation of P to octahedral Al is centred at -22 ppm, with a linewidth at half-height of 14 ppm. This distribution represents the four P environments which contain octahedral Al, i.e. from P[4 oct] to P[3 tet, 1 oct]. The centre of the distribution (-22 ppm) is likely due to P[2 tet, 2 oct] and not P[3 tet, 1 oct], even though the former has a lower probability than the latter. The reason is that there should be a relative enhancement of each of the four P resonances which is approximately proportional to the number of attached octahedral Al atoms, favouring those P environments with high Al content. Therefore, the intensity of the P[2 tet, 2 oct] site is enhanced relative to the P[3 tet, 1 oct] site. A similar behaviour was observed in dipolar-based $^{27}$Al $\rightarrow$ $^{29}$Si connectivity experiments on zeolites [12], in which there was a relative enhancement of a given resonance which was approximately linear with the number of Al atoms in the neighbouring tetrahedral sites. Figure 79b shows that the correlation to tetrahedral Al is centred at -26 ppm, with a linewidth at half-height of 12 ppm. This distribution represents the four P environments which contain tetrahedral Al, i.e. from P[1 tet, 3 oct] to P[4 tet]. Using the same arguments as for octahedral Al, the centre of the distribution (-26 ppm) is likely due to P[3 tet, 1 oct].

As a final check that the octahedral Al is in the framework, a 1D $^{31}$P $\rightarrow$ $^{27}$Al CP experiment was performed. The experiment (not shown) showed signals from both tetrahedral and octahedral Al, further confirming that both Al environments are connected to P in the framework, but was much less efficient than the $^{27}$Al $\rightarrow$ $^{31}$P CP experiment (Figure 76a), since the much longer $^{31}$P $T_1$ relaxation time now determines the recycle delay of the experiment.
Figure 79. $^{31}$P rows through octahedral Al (a) and tetrahedral Al (b), from the two-dimensional $^{27}$Al $\rightarrow$ $^{31}$P CP experiment on AIPO$_4$-5 (Figure 78). The spinning sidebands are indicated (*).
6.4. Conclusions

$^{27}$Al/$^{31}$P solid-state NMR experiments demonstrate directly that in hydrated AlPO$_4$-5, both tetrahedral and octahedral aluminum are connected to phosphorus in the framework. In addition, the two-dimensional $^{27}$Al $\rightarrow$ $^{31}$P TEDOR and CP experiments show a downfield offset of the octahedral $^{27}$Al correlation from the tetrahedral $^{27}$Al correlation, consistent with the growth of the downfield shoulder on the $^{31}$P resonance as water is incorporated. This observation can be interpreted in terms of a random distribution of tetrahedral and octahedral aluminum coordinations around the phosphorus sites. The two-dimensional $^{27}$Al $\rightarrow$ $^{31}$P CP experiment also shows that the small peak between the tetrahedral and octahedral $^{27}$Al resonances is connected to $^{31}$P, confirming the assignment of this site to 5-coordinate aluminum arising from the coordination of one water molecule to an aluminum site in the framework.

We observed an increased efficiency of coherence transfer from octahedral $^{27}$Al to $^{31}$P upon exchanging the sample with D$_2$O. This suggests that, in general, an abundant third nucleus (in this case, $^1$H in H$_2$O) may interfere with such coherence transfer experiments.
Chapter 6 References

Chapter 7. Coherence-Transfer and Dipolar-Dephasing Connectivity Experiments Involving $^{11}$B, $^{23}$Na and $^{29}$Si Nuclei in Borosilicate Glasses

7.1. Introduction

In this chapter, the $^{27}$Al/$^{31}$P and $^{27}$Al/$^{29}$Si connectivity experiments developed in Chapters 2 and 4 are extended to include $^{11}$B, $^{23}$Na and $^{29}$Si nuclei in two typical borosilicate glasses, Corning 7740 and soda glass. These techniques are shown to be feasible not only for selecting $^{11}$B/$^{29}$Si and $^{23}$Na/$^{29}$Si connectivities, but also for $^{11}$B/$^{23}$Na spin pairs where both nuclei involved are quadrupolar. Borosilicate glasses were chosen for study since they are representative of many dense inorganic materials such as minerals, glasses and ceramics. The purpose of this chapter is to evaluate the potential of the $^{11}$B/$^{23}$Na/$^{29}$Si connectivity experiments, rather than to provide new information on the structures of the glasses studied.

7.2. Experimental Section

(a) Materials

The borosilicate glasses studied were Pyrex (Corning 7740) and soda glass. The composition of Corning 7740 is 81% SiO$_2$, 13% B$_2$O$_3$, 4% Na$_2$O, and 2% Al$_2$O$_3$, and that of soda glass is 82% SiO$_2$, 12% B$_2$O$_3$, and 6% Na$_2$O.

(b) NMR Experiments

All experiments were carried out using a Bruker MSL 400 spectrometer modified to include a third r.f. channel. NMR resonance frequencies were 79.495 MHz for $^{29}$Si, 128.288 MHz for $^{11}$B, and 105.808 MHz for $^{23}$Na, and chemical shifts are reported with respect to the reference standards tetramethylsilane (TMS), BF$_3$Et$_2$O, and aqueous NaCl, respectively. The experiments were performed using a home-made double-tuned probe incorporating a 14 mm "pencil spinner" supplied by Chemagnetics which had an internal volume of 2.8 mL. The use of a large sample volume was necessary to obtain reasonable
S/N ratios for experiments involving $^{29}\text{Si}$ due to its low natural abundance. In all experiments, the magic angle was set using the $^{79}\text{Br}$ resonance of KBr. The spinning speeds in different experiments ranged from 2.1 to 2.5 kHz and were monitored by an optical sensor unit. The $^{11}\text{B}$ and $^{23}\text{Na}$ 90° pulses (central $\pm 1/2 \leftrightarrow -1/2$ transition only) and $^{29}\text{Si}$ 90° pulses were all in the range of 15-36 μs.

The pulse sequences for the CP, TEDOR, REDOR and dipolar-dephasing difference experiments were previously described in Chapter 2. To aid in setting up the experiments and in the interpretation of the resulting data, the $^{11}\text{B}$, $^{23}\text{Na}$, and $^{29}\text{Si}$ relaxation parameters in both glasses were first measured. These data are summarized in Table 11.

7.3. Results and Discussion

(a) One-Dimensional $^{29}\text{Si}$, $^{11}\text{B}$ and $^{23}\text{Na}$ MAS Spectra

The one-dimensional $^{29}\text{Si}$, $^{11}\text{B}$ and $^{23}\text{Na}$ MAS spectra of both glasses are shown in Figure 80. The $^{29}\text{Si}$ spectra of soda glass (Figure 80a) and Corning 7740 (Figure 80b) both contain a symmetrical peak which is centred at -105 and -110 ppm, respectively. The isotropic chemical shift values suggest that the predominant sites in these glasses are $Q^4$ units (a SiO$_4$ tetrahedron linked to four other such tetrahedra by sharing of oxygen atoms), with some of the Si-O-Si links being replaced by Si-O-B units. The lineshapes in Figures 80a and b are approximately Gaussian with linewidths of 1.2 and 1.5 kHz (15 and 19 ppm), respectively, indicating very substantial distributions of Si-O-Si and Si-O-B bond angles in these amorphous materials.

$^{11}\text{B}$ ($I = 3/2$) is a quadrupolar nucleus and MAS usually does not completely average the anisotropic second-order quadrupolar interaction in the central transition. For soda glass where a majority of the boron atoms have a tetrahedral coordination, the MAS spectrum (Figure 80c) shows mainly a single sharp line at about 0 ppm, since the near-
Table 11: Relaxation Parameters for the Nuclei in the Borosilicate Glasses Studied.

<table>
<thead>
<tr>
<th></th>
<th>$^{29}\text{Si}$</th>
<th></th>
<th>$^{11}\text{B}$</th>
<th></th>
<th>$^{23}\text{Na}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T_1$</td>
<td>$T_2$</td>
<td>$T_{1p}^{(a,b)}$</td>
<td>$T_1$</td>
<td>$T_2$</td>
</tr>
<tr>
<td>Corning 7740</td>
<td>260 s</td>
<td>120 ms</td>
<td>888 ms (72%) 15 ms (28%)</td>
<td>B3: 200 ms B4: 100 ms</td>
<td>B3: 32 ms B4: 17 ms</td>
</tr>
<tr>
<td>Soda Glass</td>
<td>174 s</td>
<td>56 ms</td>
<td></td>
<td>148 ms</td>
<td>20 ms</td>
</tr>
</tbody>
</table>

(a) non-exponential decays
(b) measured at same r.f. fields as experimental spectra
B3: trigonal boron
B4: tetrahedral boron
Figure 80. $^{29}\text{Si}$ MAS spectra of (a) soda glass and (b) Corning 7740. $^{11}\text{B}$ MAS spectra of (c) soda glass and (d) Corning 7740. $^{23}\text{Na}$ MAS spectra of (e) soda glass and (f) Corning 7740.
spherical symmetry produces a relatively small quadrupolar interaction. In the case of Corning 7740 (Figure 80d), the boron atoms have both trigonal and tetrahedral coordinations. The $^{11}$B resonance for trigonally-coordinated sites shows a "doublet" structure characteristic of a large quadrupolar coupling constant. Since the $^{11}$B chemical shift range is relatively small, the single absorption due to tetrahedral $^{11}$B overlaps on the high-field side with one of the maxima of the quadrupolar doublet of the trigonal $^{11}$B species at the applied field strength of 9.4 T. There is, however, enough resolution to differentiate the two coordinations. The $^{11}$B MAS spectra are consistent with those reported previously [1,2].

$^{23}$Na is also a quadrupolar nucleus with spin of 3/2. Ideally, the spectra should be able to distinguish between sodium ions which are thought to be associated with nonbridging oxygens and those which charge-compensate tetrahedral boron sites. However, only a broad, approximately symmetrical peak is observed for each glass due to the quadrupolar broadening and small $^{23}$Na chemical shift range. The resonances are centred at -19 ppm for soda glass (Figure 80e) and -23 ppm for Corning 7740 (Figure 80f).

(b) $^{11}$B/$^{29}$Si Connectivity Experiments

Figure 81 shows the one-dimensional $^{11}$B $\rightarrow$ $^{29}$Si TEDOR spectra of both glasses, demonstrating the viability of the experiment. Null experiments (not shown) were also performed by removing the $^{11}$B transfer pulse, and gave the expected null results. Since the TEDOR experiments involve coherence-transfer, the repeat time is determined by the $T_1$ relaxation times of the $^{11}$B nuclei which are not detected. This is an important advantage when considering dense inorganic materials such as minerals, ceramics and glasses. In the present cases, the $^{11}$B $T_1$ relaxation times are on the order of milliseconds, while the $^{29}$Si spins have relaxation times of hundreds of seconds, typical of many inorganic materials. Therefore, the experiments could be repeated relatively quickly.
Figure 81. (a) $^{11}\text{B} \rightarrow ^{29}\text{Si}$ TEDOR spectrum of soda glass, acquired with $n = 2$ and $m = 1$. A total of 25200 scans were acquired with a recycle delay of 2 s. (b) $^{11}\text{B} \rightarrow ^{29}\text{Si}$ TEDOR spectrum of Corning 7740, acquired with $n = 4$ and $m = 1$. A total of 1600 scans were acquired with a recycle delay of 1 s.
since the spin-lattice relaxation time governing the experimental repetition is that of the $^{11}\text{B}$ nuclei.

For individual pairs of dipolar-coupled nuclei, Eqs. (44) and (45) (in Chapter 2) may be used to generate a universal curve for the TEDOR experiment. The theoretical $^{11}\text{B} \rightarrow ^{29}\text{Si}$ TEDOR curve as a function of the number of rotor cycles before coherence-transfer ($n$) is shown in Figure 82a (solid line), assuming a dipolar-coupling constant of 280 Hz (calculated for $^{11}\text{B}-\text{O}^{29}\text{Si}$ with $r=3.0$ Å). The observed data points for Corning 7740 (Figure 82a) show the correct general trend, i.e. the signal rises quickly and reaches a maximum at $n = 4$, but dampens very slowly as the number of rotor periods is increased. Note that since the TEDOR signal is in arbitrary units (i.e. there is no reference signal), the experimental and theoretical curves do not have a common vertical axis. The theoretical curve is only strictly valid for an isolated pair of spin-1/2 nuclei. Given the complexity of the present systems, exact agreement is not expected and the comparison is presented only to demonstrate that qualitative information regarding the dipolar-couplings can be obtained using these experiments.

Resolving an NMR spectrum into two dimensions can be very useful when one-dimensional spectra confirm that heteronuclear connectivities do exist, but the exact connectivity relations between particular sites are still unknown. In the case of Corning 7740 where both trigonal and tetrahedral boron sites are present, one-dimensional TEDOR experiments indicate that the silicons are connected to boron. However, it is not clear whether the silicon is coupled to both boron sites as expected, or to just one of them. Figure 83 shows the results from a 2D TEDOR experiment performed on Corning 7740, which shows unambiguously that both the trigonal and tetrahedral $^{11}\text{B}$ resonances are connected to $^{29}\text{Si}$ sites. In the projection of the $^{11}\text{B}$ dimension, the intensity of tetrahedral $^{11}\text{B}$ is reduced relative to that of trigonal $^{11}\text{B}$. This is mainly due to the fact that the tetrahedral $^{11}\text{B}$ site has much shorter $T_2$ relaxation time than the trigonal site, and thus decays faster during the frequency encoding ($t_1$) and dipolar-dephasing ($n\tau_p$) periods.
Figure 82. Evolution of TEDOR and REDOR signals in Corning 7740. In each case, $\tau_r = 450 \mu$s, and the solid line shows the theoretical curve for an isolated pair of spin-1/2 nuclei with $D = 280$ Hz. (a) Evolution of $^{11}$B $\rightarrow$ $^{29}$Si TEDOR signal, with $m = 1$. Note that since the TEDOR signal is in arbitrary units, the experimental and theoretical curves do not have a common vertical axis. (b) Evolution of $^{11}$B REDOR signal with $^{29}$Si dephasing. The theoretical REDOR curve is calculated taking into account the natural abundance of $^{29}$Si.
Figure 83. Two-dimensional $^{11}\text{B} \rightarrow ^{29}\text{Si}$ TEDOR spectrum of Corning 7740, acquired with $n = 4$ and $m = 1$. A total of 2400 scans were acquired for each of the 24 experiments incrementing $t_1$, with a recycle delay of 1 s.
in the 2D TEDOR pulse sequence (see Figure 28c in Chapter 2).

Cross-polarization MAS experiments were also performed with polarization-transfer from $^{11}$B to $^{29}$Si. The Hartmann-Hahn match condition (from Eq. (33) in Chapter 2) is modified to take into account the excitation of only the central $^{11}$B transition and the expected shift by the spinning frequency [3], as in Eq. (59).

$$\gamma_{Si} B_{1, Si} = 2 \gamma_B B_{1, B} \pm \nu_r$$

The CP spectra (not shown) for both glasses are very similar to the TEDOR spectra (Figure 81), again indicating that boron and silicon sites are coupled to each other via heteronuclear dipolar interactions. Null experiments in which the $^{11}$B 90° pulse was removed from the sequence gave no significant observable magnetization.

The variation of $^{29}$Si signal intensity with contact time was also studied. The signal intensities reached maximum values at contact times of 5 and 1 ms for Corning 7740 and soda glass, respectively, and then decayed very slowly with increasing contact time. For both glasses under investigation, the $^{11}$B $T_{1p}$ values are very short at the spinning rates employed, indicating that the spin-locking will exist for only a very short period of time. Although the dipolar-coupling is small (280 Hz), it is thus expected that the maximum in signal intensity will appear at relatively short contact times, as observed experimentally. For Corning 7740, the $^{11}$B $T_{1p}$ values, especially for trigonal boron, are much longer than those for soda glass. This is likely the reason that the maximum CP signal intensity for Corning 7740 occurs at a longer contact time than for soda glass.

As in the TEDOR experiment, the repeat time between acquisitions in the CP experiment is determined by the $T_1$ relaxation time of the source nucleus for the polarization-transfer. In the case of the $^{11}$B $\rightarrow$ $^{29}$Si cross-polarization, the experiment can take advantage of the very short $T_1$ values of the $^{11}$B nuclei. Cross-polarization and TEDOR experiments in the opposite direction ($^{29}$Si $\rightarrow$ $^{11}$B) are precluded by the low natural abundance of $^{29}$Si (4.7%) and the extremely long $T_1$ of $^{29}$Si (hundreds of
11B(29Si) REDOR and dipolar-dephasing difference experiments were also carried out successfully by dephasing the 29Si nuclei and observing the 11B signals. The reverse experiments, i.e. observing the 29Si signal while dephasing 11B, are again not practical due to the very long 29Si T1. Figure 84 shows 11B(29Si) REDOR spectra for both glasses. These results confirm, once again, the existence of couplings between boron and silicon via dipolar interactions. For Corning 7740, both trigonal and tetrahedral 11B signals are observed (Figure 84b), consistent with the results of 11B → 29Si 2D TEDOR experiment (Figure 83). This example demonstrates that for systems where one nuclear spin species (S) has only one resonance signal while the other spin (I) has multiple sites, one-dimensional REDOR and dipolar-dephasing difference experiments are able to establish definite connectivities between I and S spin pairs by observing the I nuclei and dephasing the S nuclei. This can be advantageous in terms of saving instrument time, since two-dimensional experiments may be very time consuming.

Figure 82b shows the 11B REDOR signal with 29Si dephasing for Corning 7740 as a function of the number of rotor cycles, n. In this case, only 4.7% of the silicon sites coupled to 11B are 29Si. Thus, it can be anticipated that the REDOR signal will rise very slowly and never reach ΔS/S0 = 1 (i.e. full dephasing). The theoretical REDOR curve (solid line) is calculated using Eqs. (42) and (43) (in Chapter 2) for an isolated pair of spin-1/2 nuclei with a dipolar-coupling constant of 280 Hz, and taking into account the natural abundance of 29Si. Comparing the 11B → 29Si TEDOR and 11B(29Si) REDOR signals (Figures 82a and b, respectively), it can be seen that the experimental REDOR data is in closer agreement with its respective theoretical curve. This is because in the REDOR experiment, the spin pairs are more isolated than in the TEDOR experiment. (In each case, the theoretical curve is calculated for an isolated pair of spin-1/2 nuclei.) In the REDOR experiment, the spin pairs are reasonably isolated (i.e. only those 11B nuclei in the central transition are observed, and the natural abundance of the surrounding
Figure 84. (a) $^{11}$B($^{29}$Si) REDOR spectrum of soda glass, acquired with $n = 100$. A total of 3600 scans were acquired with a recycle delay of 1.5 s. (b) $^{11}$B($^{29}$Si) REDOR spectrum of Corning 7740, acquired with $n = 110$. A total of 7200 scans were acquired with a recycle delay of 1.5 s.
$^{29}$Si nuclei which are dephased is very low). In the TEDOR experiment, on the other hand, the spin pairs are not as isolated since many of the observed $^{29}$Si nuclei are surrounded by more than one $^{11}$B nucleus which is in the central transition.

(c) $^{23}$Na/$^{29}$Si Connectivity Experiments

The $^{23}$Na $\to$ $^{29}$Si TEDOR signals for both glasses were also observed (not shown), confirming that the sodium ions are connected to silicon through dipolar-couplings. For Corning 7740, the evolution of the $^{23}$Na $\to$ $^{29}$Si TEDOR signal was studied as a function of the number of rotor cycles before and after coherence-transfer ($n$ and $m$, respectively), with the maximum intensity appearing at $n = 10$ and $m = 1$. For a given number of rotor cycles after the coherence transfer ($m = 1$), the time period for maximum accumulated dipolar-dephasing for the $^{23}$Na $\to$ $^{29}$Si TEDOR ($n = 10$) is much longer than that for the $^{11}$B $\to$ $^{29}$Si experiment ($n = 4$, as shown in Figure 82a). Since the spinning rates used in both experiments were similar and the $^{23}$Na $T_2$ value is comparable to that of $^{11}$B (see Table 11), the longer period of preparative dephasing for the $^{23}$Na $\to$ $^{29}$Si TEDOR suggests that the dipolar-coupling between $^{23}$Na and $^{29}$Si is considerably weaker than that between $^{11}$B and $^{29}$Si, as would be expected.

$^{23}$Na $\to$ $^{29}$Si cross-polarization experiments were also attempted on Corning 7740 using several different contact times, but only a very small signal (not shown) was observed after 6 hours of signal accumulation. The glass has a relatively low sodium concentration, and thus the number of $^{23}$Na nuclei which can act as polarization sources is small. In addition, the dipolar-coupling between $^{23}$Na and $^{29}$Si is weak. However, since the $^{23}$Na $\to$ $^{29}$Si TEDOR experiments were successful, the poor CP signal is likely due to the difficulty in spin-locking the $^{23}$Na central transition [3,4]. This may also preclude efficient $^{23}$Na/$^{11}$B cross-polarization experiments which will be mentioned in next section. Therefore, in the situation where the polarization source is a quadrupolar nucleus in low concentration, the TEDOR experiment may be more efficient than CP.
(d) $^{23}$Na/$^{11}$B Connectivity Experiments

$^{23}$Na $\rightarrow$ $^{11}$B TEDOR experiments were performed for both glasses, and the spectra are shown in Figure 85. These results show that dipolar-couplings do exist between the sodium ions and boron sites. The spectrum of Corning 7740 (Figure 85b) contains mainly signal from tetrahedral $^{11}$B, suggesting a stronger dipolar interaction between sodium ions and this site. For Corning 7740, the evolution of the $^{23}$Na $\rightarrow$ $^{11}$B TEDOR signal was studied as a function of the number of rotor cycles, with the maximum intensity appearing at $n = 10$ and $m = 1$.

An attempt at $^{23}$Na $\rightarrow$ $^{11}$B cross-polarization was also made, but no observable signal was detected after 6 hours. In addition to the reasons discussed previously for the $^{23}$Na $\rightarrow$ $^{29}$Si CP experiments, a further complication arises from the fact that both the source ($^{23}$Na) and target ($^{11}$B) nuclei are quadrupolar and, therefore, both have very short "operational" T1p values under MAS, which further reduces the efficiency of the polarization transfer.

For both glasses, $^{11}$B($^{23}$Na) REDOR (Figure 86) and dipolar-dephasing difference experiments (not shown) were performed by observing $^{11}$B and dephasing the $^{23}$Na nuclei. Similar to the $^{11}$B($^{29}$Si) case described earlier, the evolution of the REDOR signal as a function of the number of rotor cycles (not shown) is slow. This results from the fact that each $^{23}$Na spin near $^{11}$B is not necessarily perturbed by the 180° dephasing pulses since only certain percentage (approximately one-half) of the $^{23}$Na spins are in either the +1/2 or -1/2 levels, and only these will be flipped by the 180° pulses.

These experiments can also be performed by observing $^{23}$Na and dephasing the $^{11}$B nuclei. Figure 87 shows the $^{23}$Na($^{11}$B) dipolar-dephasing difference spectrum of Corning 7740, demonstrating that these experiments can be performed in both directions provided that the T1 values of both nuclei involved are reasonably short and that the T2 values of the observed nucleus are reasonably long.
Figure 85. $^{23}\text{Na} \rightarrow ^{11}\text{B}$ TEDOR spectra of (a) soda glass and (b) Corning 7740. In each experiment, $n = 4$, $m = 1$, and a total of 3600 scans were acquired with a recycle delay of 1 s.
Figure 86. $^{11}\text{B}^{(23}\text{Na})$ REDOR spectra of (a) soda glass and (b) Corning 7740. In each experiment, $n = 28$, and a total of 3600 scans were acquired with a recycle delay of 1 s.
Figure 87. $^{23}\text{Na}(^{11}\text{B})$ dipolar-dephasing difference spectrum of Corning 7740, with 4 rotor cycles of $^{11}\text{B}$ dephasing. A total of 17000 scans were acquired with a recycle delay of 1 s.
7.4. Conclusions

The feasibility of performing coherence-transfer and dipolar-dephasing connectivity experiments involving $^{11}$B, $^{23}$Na, and $^{29}$Si nuclei has been demonstrated for the two borosilicate glasses Corning 7740 and soda glass. The results show that these experiments can be used not only for quadrupolar/spin-1/2 systems, but also for spin pairs where both nuclei involved are quadrupolar. The $^{11}$B/$^{29}$Si, $^{23}$Na/$^{29}$Si and $^{11}$B/$^{23}$Na spin pairs in borosilicate glasses are typical of those in dense inorganic solids, and the experiments are quite general in nature. The rapid spin-lattice relaxation of the quadrupolar $^{11}$B and $^{23}$Na nuclei can be used in coherence-transfer experiments (cross-polarization and TEDOR) to obtain spectra from the slowly relaxing $^{29}$Si nuclei in a relatively short period of time. For the coherence-transfer experiments, it is found experimentally that in the situation where the polarization source is a quadrupolar nucleus in low concentration, TEDOR experiments seem to be more efficient than cross-polarization. Two-dimensional TEDOR experiments are also possible, and can provide a qualitative picture of internuclear couplings between specific spin pairs. It is thought that these results will provide a basis for the application of these techniques to obtain local structural information on dense and amorphous inorganic materials for which there are only a limited number of applicable techniques.
Chapter 7 References


Chapter 8. INEPT Experiments in Solid State NMR

This chapter describes the first application of INEPT and DEPT experiments in solid state NMR [1]. These experiments utilize coherence-transfer based on heteronuclear J-couplings to detect through-bond connectivities under MAS conditions. Examples presented show that the experiments are applicable to both spin-1/2 and quadrupolar nuclei.

8.1. Introduction

Chapters 2 to 7 have described the development and application of double-resonance solid state NMR experiments based on the heteronuclear dipolar interaction. Cross-polarization, REDOR, TEDOR, and dipolar-dephasing difference experiments were used to determine internuclear connectivities via heteronuclear dipolar couplings in a variety of inorganic systems containing both quadrupolar and spin-1/2 nuclei [2-8].

J-couplings have also been used to establish internuclear connectivities in solids. For example, two-dimensional COSY and INADEQUATE experiments, which utilize homonuclear J-couplings, have been successfully used to establish $^{29}\text{Si}-\text{O}-^{29}\text{Si}$ through-bond connectivities in zeolites [9]. (For a review of these results, see Section 1.7c.) In the present chapter, it is demonstrated that heteronuclear through-bond connectivities can be detected under MAS conditions using INEPT (insensitive nuclei enhanced by polarization-transfer) [10] and DEPT (distortionless enhancement by polarization-transfer) [11] experiments which are based on heteronuclear J-couplings. These experiments were originally designed to enhance the solution state NMR spectra of insensitive nuclei (e.g. $^{13}\text{C}$) via polarization-transfer from abundant nuclei (e.g. $^{1}\text{H}$), and also to provide spectral editing features (e.g. discrimination of $^{13}\text{CH}$, $^{13}\text{CH}_2$, and $^{13}\text{CH}_3$ resonances).

As with the dipolar-coupling based CP, REDOR, TEDOR, and dipolar-dephasing difference experiments, the J-coupling based INEPT and DEPT experiments under MAS conditions should be applicable to both quadrupolar and spin-1/2 nuclei. In addition, they
should not suffer from the limitation of the dipolar-coupling based experiments that their success depends directly on the practical efficiency with which the averaging effect of MAS on the dipolar-coupling can be reduced or eliminated. Furthermore, in CP experiments involving quadrupolar nuclei, the efficiency is severely limited by short T_{1p} values. The J-coupling, however, is unaffected by the quadrupolar interaction and is not eliminated by MAS, both of which can greatly limit the efficiency of coherence-transfer involving quadrupolar nuclei.

8.2. Experimental Section

(a) NMR Experiments

All experiments were carried out using a Bruker MSL 400 spectrometer modified to include a third r.f. channel. Two double-tuned homebuilt probes were used: one with a 14 mm Chemagnetics pencil spinner stator (for the \(^{27}\text{Al} \rightarrow \^{29}\text{Si}\) and \(^{23}\text{Na} \rightarrow \^{29}\text{Si}\) experiments) and one with a 10 mm Doty Scientific supersonic stator (for the \(^{27}\text{Al} \rightarrow \^{31}\text{P}\) experiments). The pulse programs for the experiments are given in Appendices 14-17.

The basic pulse sequence used for I to S polarization transfer was the standard INEPT sequence [10] (shown in Figure 88a), where maximum signal intensity for two coupled spin-1/2 nuclei is obtained when \(\tau = 1/(4J)\), assuming \(T_2 >> 1/J\). The coherence-transfer is accomplished through the simultaneous 90° pulses on the I and S nuclei. Experiments were also performed using the refocused INEPT sequence [12] (shown in Figure 88b), where an additional echo sequence is added after the 90° transfer pulses. Here, \(\tau_1\) and \(\tau_2\) refer to two different delay times. The closely related DEPT sequence [11] (shown in Figure 88c), where maximum intensity for a pair of coupled spin-1/2 nuclei is obtained when \(\tau = 1/(2J)\) and the transfer pulse \(\theta = 90°\), was also investigated. For each pulse sequence, the \(\tau\) delays were set to integral numbers of rotor cycles.

Since it involves a coherence-transfer step, the INEPT experiment can be extended into a two-dimensional heteronuclear correlation experiment by adding an extra period of
Figure 88. Pulse sequences for INEPT and DEPT experiments, with the $\tau$ delays chosen to be integral numbers of rotor cycles to completely average the dipolar interaction:
(a) INEPT sequence in which the coherence-transfer is accomplished through the simultaneous 90° pulses on the I and S nuclei. (b) Refocused INEPT sequence, where an additional echo sequence is added after the 90° transfer pulses. (c) DEPT sequence, where $\theta$ is the tip angle of the I spin transfer pulse. (d) Two-dimensional INEPT experiment with preliminary evolution of I spin magnetization during the $t_1$ time period, and detection of S spin magnetization during the $t_2$ time period.
Figure 88

(a) I (90) (180) (90)

(b) I (90) (180) (90) (180)

(c) I (90) (180) (θ)

(d) I (90) (90) t₁ (180) (90) t₂

S \[\tau \quad \tau \quad \tau \quad \tau\]
encoding of the I spin magnetization (Figure 88d). The experiments were performed by preparing the I spins with a 90° pulse, and then encoding their evolution frequencies in an initial \((t_1)\) time period. At the end of \(t_1\), a second 90° pulse is used to remove one orthogonal component of the magnetization by returning it to the \(z\)-axis, effectively selecting only one component for the rest of the experiment and making possible the use of TPPI [13,14]. An INEPT experiment is then begun for the magnetization that remains in the \(xy\)-plane. (This is analogous to the strategy used in the two-dimensional TEDOR experiment (Section 2.2e).) Proper phase cyclings to remove unwanted coherences and allow for TPPI accumulation of the data were employed (see Appendix). The \(S\) spin signal is acquired for each of a set of \(t_1\) values, and the data array is subjected to a two-dimensional Fourier transform. The result is a two-dimensional correlation spectrum of the scalar-connected spins in the sample.

(b) Materials

The sample chosen for detailed study was the solid triphenylphosphine trichloroaluminum complex (1) where the phenyl groups were deuterated to simplify the experiment (i.e. eliminate the need for \(^1\text{H}\) decoupling and thus a triple-tuned \(^{27}\text{Al}^{31}\text{P}/^1\text{H}\) probe). This sample was kindly provided by Mr. G. Giesbrecht and Dr. M.D. Fryzuk of the Chemistry Department, UBC.

\[
\text{Ph}_3\text{P}−\text{AlCl}_3
\]

(1)

This sample was chosen for these experiments since the \(^{27}\text{Al}−^{31}\text{P}\) \(J\)-coupling is large (268 Hz) and the couplings are clearly observable in the \(^{31}\text{P}\) MAS spectrum. In addition, both \(^{27}\text{Al}\) and \(^{31}\text{P}\) are 100\% abundant isotopes, and thus sensitivity problems are reduced. Examples are also given using the aluminophosphates VPI-5 and AlPO\(_4\)-14 (\(^{27}\text{Al}^{31}\text{P}\)) and the feldspar minerals albite (\(^{23}\text{Na}/^{29}\text{Si}\)) and microcline (\(^{27}\text{Al}/^{29}\text{Si}\)).
8.3. Results and Discussion

Figure 89 shows (a) the $^{27}\text{Al} \rightarrow ^{29}\text{Si}$ INEPT spectrum of microcline, and (b) the $^{23}\text{Na} \rightarrow ^{29}\text{Si}$ refocused INEPT spectrum of albite, and Figure 90 shows the $^{27}\text{Al} \rightarrow ^{31}\text{P}$ refocused INEPT spectrum of VPI-5. The lineshapes are dispersive in Figure 89a since the magnetization is not refocused after coherence-transfer, and absorptive in Figures 89b and 90 since a refocused INEPT experiment is performed. In each case, a null signal is observed when the 90° transfer pulse from the source nucleus is removed, as indicated in the figures. Since the INEPT experiment involves a coherence-transfer step, it can be extended into a two-dimensional heteronuclear correlation experiment. Figure 91 shows the two-dimensional $^{27}\text{Al} \rightarrow ^{31}\text{P}$ INEPT spectrum of AlPO$_4$-14, in which the connectivities appear as dispersion signals (i.e. positive and negative intensities) since the $^{31}\text{P}$ magnetization is not refocused after coherence-transfer. This is illustrated in the $^{31}\text{P}$ spectrum at the top of Figure 91, which shows the positive and negative components of the $^{31}\text{P}$ magnetization.

Since the scalar J-coupling operates through "bonds" (i.e. by orbital overlap), bonding connectivities are obtained unambiguously. In this regard, the $^{23}\text{Na} \rightarrow ^{29}\text{Si}$ coherence-transfer of Figure 89b is of particular interest. The $^{23}\text{Na}$ nuclei are present in Na$^+$ ions and the interaction detected by the experiment indicates a degree of orbital overlap with other atoms, giving a direct confirmation and measure of the weak "bonds" often reported in X-ray diffraction derived solid state structures. In this regard, it is worth noting that in solution NMR spectroscopy, bonding interactions between ions in solution are not detected via J-couplings, and hence not considered. However, they are routinely detected by ESR spectroscopy when the spectra are run in poorly solvating solvents where ion-association is promoted [15-17].

In these experiments, we have assumed that the dipolar interactions are suppressed by the MAS since integral numbers of rotor cycles were used. However, the magnitudes
Figure 89. (a) $^{27}\text{Al} \rightarrow ^{29}\text{Si}$ INEPT spectrum of microcline, acquired using a delay of $\tau = 5$ ms. A total of 720 scans were acquired with a recycle delay of 20 s. (b) $^{23}\text{Na} \rightarrow ^{29}\text{Si}$ refocused INEPT spectrum of albite, acquired using delays of $\tau = 6.56$ ms and 6.15 ms in the first and second echo sequences, respectively. A total of 13296 scans were acquired with a recycle delay of 5 s. In each case, the null experiment is shown below.
Figure 90. $^{27}$Al $\rightarrow ^{31}$P refocused INEPT spectrum of VPI-5, acquired using delays of $\tau = 3.33$ ms in the first and second echo sequences, with the null experiment shown below. A total of 6400 scans were acquired with a recycle delay of 0.3 s.
Figure 91. Two-dimensional $^{27}\text{Al} \rightarrow ^{31}\text{P}$ INEPT spectrum of AlPO$_4$-14, acquired using a delay of $\tau = 1.642$ ms. A total of 8800 scans were acquired for each of the 64 experiments incrementing $t_1$, with a recycle delay of 0.1 s. The $^{27}\text{Al}$ projection is absolute value mode, while the $^{31}\text{P}$ spectrum (at top) was formed by summation of the $^{31}\text{P}$ rows through each of the three $^{27}\text{Al}$ resonances.
of the J-couplings involved in the above experiments are relatively small compared to the linewidths, and are not directly observable. For this reason, the solid triphenylphosphine trichloroaluminum complex (1), where the J-coupling is clearly observable, was investigated. Figure 92 shows various INEPT and related experiments on complex (1). The $^{31}\text{P}$ MAS spectrum (Figure 92a) shows clearly the multiplet structure of six lines due to the J-coupling of the $^{31}\text{P}$ nucleus to the six populated energy levels of $^{27}\text{Al}$. The INEPT, refocused INEPT and DEPT experiments (Figures 92b, c and d, respectively) each show only two peaks, corresponding to coupling to only the $\pm1/2$ $^{27}\text{Al}$ energy levels. This is because the initial 90° pulse on $^{27}\text{Al}$ activates coherence between only these levels, and it is this which is transferred to the $^{31}\text{P}$ nuclei. Any $^{27}\text{Al}$ nuclei where the $\pm1/2$ levels are not populated are not involved in this part of the experiment. Note that this observation is good, direct evidence that only the $\pm1/2$ central transition is excited, as is always assumed. Since the spin system consists of single pairs of $^{31}\text{P}$ and $^{27}\text{Al}$ nuclei, there is no interaction possible between the $^{31}\text{P}$ nuclei and any $^{27}\text{Al}$ nuclei not involved in the initiating pulse. Therefore, coupling to only the $\pm1/2$ $^{27}\text{Al}$ energy levels is observed in the final $^{31}\text{P}$ spectrum. This will not be the case in more complex systems.

Further evidence of the origin of the interaction is provided by the behaviour of the intensity of the detected $^{31}\text{P}$ signal as a function of the delays used in the INEPT experiment. The measured J-coupling is 268 Hz, and the maximum intensity in the INEPT experiment should be observed when the $\tau$ delay is $1/(4J) = 0.933$ ms. Figure 93a shows the intensities of the two peaks in the INEPT experiment (see Figure 92b) as a function of $\tau$, in which the $\tau$ delays were set to both integral and non-integral (i.e. 0.5, 1.5, 2.5, etc.) numbers of rotor cycles. The sinusoidal evolution of the magnetization is exactly that expected for a J-coupling mechanism. Based on the fact that both intensities pass through zero at $\tau = 3.778$ ms, the maxima should occur at 0.944 and 2.833 ms, while the zero points should occur at 1.889 and 3.778 ms (these $\tau$ values are indicated by arrows in Figure 93a). In fact, the first maximum of 0.944 ms is very close to the expected value of
Figure 92. $^{31}$P spectra of compound (1). (a) Simple $^{31}$P MAS spectrum. (b) $^{27}$Al $\rightarrow$ $^{31}$P INEPT spectrum, acquired using a delay of $\tau = 0.933$ ms. A total of 16 scans were acquired using a recycle delay of 5 s. (c) $^{27}$Al $\rightarrow$ $^{31}$P refocused INEPT spectrum, acquired using delays of $\tau = 0.933$ ms in both echo sequences. A total of 16 scans were acquired using a recycle delay of 5 s. (d) $^{27}$Al $\rightarrow$ $^{31}$P DEPT spectrum, acquired using a delay of $\tau = 1.866$ ms and a transfer pulse of $\theta = 90^\circ$. A total of 32 scans were acquired using a recycle delay of 5 s.
Figure 93. (a) Intensity evolution in the $^{27}\text{Al} \rightarrow ^{31}\text{P}$ INEPT spectrum of compound (1) as a function of $\tau$, in which the $\tau$ delays were set to both integral and non-integral numbers of rotor cycles. The maxima and zero points are indicated by the arrows. (Legend: downfield peak for integral (●) and non-integral (+) numbers of rotor cycles, and upfield peak for integral (■) and non-integral (×) numbers of rotor cycles.) (b) Intensity in the $^{27}\text{Al} \rightarrow ^{31}\text{P}$ DEPT spectrum of compound (1) as a function of the magnitude of the $^{27}\text{Al}$ transfer pulse $\theta$, with the maximum at 16 $\mu$s indicated by the arrow.
Figure 93
\( \tau = 1/(4J) = 0.933 \text{ ms} \).

Figure 93a shows that for this system, the amplitude of the intensity evolution in the INEPT experiment is slightly reduced when the \( \tau \) delay is set to non-integral numbers of rotor cycles. However, this had no effect on the period of the sinusoidal intensity evolution. This small reduction in intensity is expected since the anisotropic dipolar interaction is completely averaged only over a full rotor cycle.

In the DEPT experiment, the delay for maximum intensity is \( \tau = 1/(2J) = 1.866 \text{ ms} \) as expected, indicating that the determining factor is evolution under the influence of J-coupling. Figure 93b shows the evolution of the \( ^{31}\text{P} \) magnetization as a function of the magnitude (tip angle) of the \( ^{27}\text{Al} \) transfer pulse \( \theta \) in the DEPT sequence. The behaviour is again exactly that expected, with the maximum at a pulse length of 16 \( \mu \text{s} \) corresponding to a pulse angle of 90°, as indicated by the arrow in Figure 93b. This behaviour is strong additional evidence in favour of a J-coupling mechanism.

### 8.4. Conclusions

In summary, the INEPT and DEPT experiments based on heteronuclear J-couplings are viable in the solid state for both spin-1/2 and quadrupolar nuclei, and complement current approaches based on heteronuclear dipolar-couplings. The experiments have the advantage that because the J-coupling is not eliminated by MAS, they are straightforward compared to the dipolar-coupling based experiments whose success depends directly on the practical efficiency with which the averaging effect of MAS on the dipolar-coupling can be reduced or eliminated. In addition, since the J-coupling is unaffected by the quadrupolar interaction, the experiments are equally applicable to both spin-1/2 and quadrupolar nuclei. The experiments will not yield distance information, but will give unambiguous through-bond connectivities through orbital overlap, and may be of use in probing weak bonding interactions in solid-state structures.
Chapter 8 References

Chapter 9. Conclusions and Suggestions for Future Work

9.1. Conclusions

The work presented in this thesis has demonstrated that coherence-transfer and dipolar-dephasing double-resonance NMR experiments can be used to determine connectivities between quadrupolar and spin-1/2 nuclei in solids. The specific accomplishments were:

1. For the first time, cross-polarization and TEDOR experiments were performed in which quadrupolar nuclei were used as the magnetization source.

2. Cross-polarization, rotational-echo double-resonance (REDOR), transferred-echo double-resonance (TEDOR), and dipolar-dephasing difference experiments were used to determine connectivities via the heteronuclear dipolar-couplings between pairs of quadrupolar and spin-1/2 nuclei: $^{27}\text{Al} / ^{31}\text{P}$ in aluminophosphate molecular sieves, $^{27}\text{Al} / ^{29}\text{Si}$ in zeolites, and $^{11}\text{B} / ^{23}\text{Na} / ^{29}\text{Si}$ nuclei in borosilicate glasses. Two-dimensional extensions of the cross-polarization and TEDOR experiments were used to reveal connectivities between specific resonances in two-dimensional correlation spectra.

3. Increased efficiency of coherence-transfer from quadrupolar nuclei was observed in the dynamic-angle cross-polarization (DACP) experiment, in which the cross-polarization step is performed with the spinning axis parallel to the applied magnetic field, and then the spinning axis is hopped to the magic angle for detection of the high-resolution signal.

4. The $^{27}\text{Al} / ^{31}\text{P}$ and $^{27}\text{Al} / ^{29}\text{Si}$ connectivity experiments were used to determine the method of silicon substitution and reveal the presence of three types of aluminum environments in SAPO-37. The $^{27}\text{Al} / ^{31}\text{P}$ connectivity experiments were also used to
confirm that the octahedral aluminum formed upon the hydration of AIPO₄-5 remains bonded in the framework.

5. For the first time, INEPT and DEPT experiments were performed in the solid-state. These experiments utilize coherence-transfer based on the heteronuclear J-couplings, and were shown to be applicable to both quadrupolar and spin-1/2 nuclei.

The success of the experiments performed in this thesis should allow them to be applied with confidence in structural investigations of a range of important materials such as molecular sieves, minerals, ceramics, and glasses.

9.2. Suggestions for Future Work

The application of INEPT and DEPT experiments in solid state NMR should be investigated for a range of general systems, and their efficiencies compared to those of CP and TEDOR which are based on dipolar-couplings. In general, ¹H nuclei will be present, and thus ¹H decoupling and a triple-tuned probe will be required for these experiments. Although the lack of a triple-tuned probe has previously prevented such experiments from being performed, such a probe is now available in our laboratory.

Specifically, the INEPT and DEPT experiments should be investigated in systems such as [¹³C, ¹⁵N]-labelled amino acids in which a specific ¹³C-¹⁵N spin pair is labelled in isolation. (These experiments would require a ¹³C/¹⁵N/¹H triple-tuned probe since ¹H decoupling would be necessary.) Such systems were studied in the original REDOR [1,2] and TEDOR [3,4] experiments of Schaefer and co-workers. The results of the INEPT and DEPT experiments could then be compared to the results of the REDOR and TEDOR experiments to judge their relative efficiencies and confirm their different selectivities. The dependence of each experiment on factors such as the heteronuclear dipolar-coupling
constant (D), J-coupling constant, spinning speed, and relaxation times could then be used to choose the optimum experiment for a given system.

In addition, it should be possible to perform $^1\text{H} \rightarrow X$ (e.g. $^1\text{H} \rightarrow ^{13}\text{C}$) INEPT and DEPT experiments in the solid state if the strong $^1\text{H}$ homonuclear dipolar interactions can be efficiently suppressed by adding a multiple pulse line-narrowing scheme to the INEPT or DEPT pulse sequence. (These interactions can range up to 40 kHz and are thus too large to be completely averaged by MAS alone.) Using a series of r.f. pulses, multiple-pulse line-narrowing sequences average the homonuclear dipolar interactions to zero by orienting the spins (on average) along an axis inclined at the magic angle to the magnetic field in the rotating frame. Examples of such sequences are the original 4 pulse WAHUHA sequence [5] and the 8 pulse MREV-8 sequence [6-9] which uses two phase-alternated WAHUHA cycles to cancel errors from pulse imperfections.

$^1\text{H} \rightarrow X$ INEPT and DEPT experiments may be a complementary method to cross-polarization for both signal enhancements (for each experiment, the maximum enhancement is $\gamma_H/\gamma_X$) and for selectivity in solid state NMR experiments. In fact, the INEPT and DEPT experiments could have some distinct advantages over the CP experiments: Firstly, if the $^1\text{H}$ or $X \ T_{1p}$ values are short, the CP efficiency will be low, while the INEPT and DEPT experiments would be unaffected. Secondly, at very high spinning speeds, the CP efficiency is sharply reduced, while the INEPT and DEPT experiments may well be unaffected since the J-coupling is unaffected by MAS. Thirdly, the INEPT and DEPT experiments offer more selectivity than the CP experiments in that they are specific to through-bond interactions and are able to discriminate among different numbers of coupled nuclei (e.g. $^{13}\text{CH}$, $^{13}\text{CH}_2$, and $^{13}\text{CH}_3$ resonances). Potential disadvantages of the INEPT and DEPT experiments, however, are that their efficiencies are limited if the $T_2$ value of the source nuclei is short (i.e. if $T_2 \ll 1/J$), and that they will not yield distance information.
The INEPT experiments should also be used in conjunction with the dipolar-coupling based connectivity experiments in structural investigations of various materials. Preliminary results have been obtained on the feldspar minerals albite and microcline (see Figure 89, Section 8.3), both of which contain three distinct $^{29}$Si resonances. Preliminary results have also been obtained on the molecular sieves AlPO$_4$-14 (see Figure 91, Section 8.3) and AlPO$_4$-18, both of which contain multiple $^{27}$Al and $^{31}$P resonances which are not all interconnected. In each case, the results from the NMR connectivity experiments could be used together with x-ray powder diffraction data to provide a complete assignment of the NMR spectrum.

A possible new application of these experiments is in the study of adsorbed species in molecular sieves. For example, adsorbing $^{15}$NH$_3$ into dehydrated VPI-5 would result in the formation of octahedral aluminum sites by coordination to two $^{15}$NH$_3$ molecules. $^{15}$N/$^{31}$P connectivity experiments (CP, TEDOR and INEPT) could then be used to assign the $^{31}$P resonances based on their different $^{15}$N-$^{31}$P internuclear distances.

Another possible new application would be to incorporate double rotation (DOR) sample spinning into the connectivity experiments involving quadrupolar and spin-1/2 nuclei. (The concept of DOR is discussed in Section 1.5d.) For example, by incorporating DOR into a two-dimensional $^{27}$Al $\rightarrow$ $^{31}$P TEDOR experiment and synchronizing the pulses with the slower spinning outer rotor, the resolution of the $^{27}$Al dimension could be improved due to the second-order quadrupolar averaging of the DOR technique. This could possibly aid in the assignment of resonances in cases where quadrupolar broadening causes the resonances to overlap under MAS conditions.
Chapter 9 References

Appendices: Pulse Programs for NMR Experiments

The appendices list the pulse programs, written for the Bruker MSL 400 spectrometer, for the NMR experiments performed in this thesis. The command and programming structure are defined in the DISMSL (Version 911101) Manual.

BRUKER ANALYTISCHE MESSTECHNIK GMBH
Silberstreifen
D-7512 Rheinstetten 4
Germany

BRUKER INSTRUMENTS, INC.
Manning Park
Billerica, MA 01821
USA
Appendix 1. Pulse program to measure $T_1$ relaxation time by inversion-recovery

; KT1INVRC.PC

; INVERSION-RECOVERY $T_1$ PULSE SEQUENCE FOR F1 CHANNEL

START, D2 [F1 @PLS1]; 180° PULSE
VD
D1 [F1 @PLS2]; 90° PULSE
D3 [STA]; RINGDOWN AND TRIGGER
D0; RECYCLE DELAY
++PLS1
++PLS2
GOTO START
BEGIN LISTS
PLS1, +X -X +X -X +Y -Y +Y -Y
PLS2, +X +X -X -X +Y +Y -Y -Y
RLS, +X +X -X -X +Y +Y -Y -Y
END LISTS

; USE RPN
; DEFINE VDLIST BEFORE TONEAQ.AUM IS STARTED
; VD CAN BE SET FROM FOREGROUND AS "TAU"
; SEE OPERATORS MANUAL CHAPTER V.7
Appendix 2. Pulse program to measure $T_1$ relaxation time by saturation-recovery

; KSATRCF3.PC

; MEASURE $T_1$ BY SATURATION-RECOVERY FOR F3 CHANNEL
; ONE PULSE ACQUISITION WITH QUADRATURE PHASE CYCLE

PROT F1 F3
START, LOOP C7 TIMES ; TYPICALLY 50
   D1 [F3 +X]
   D22
   END LOOP
   D1 [F3 +X]
   LOOP C4 TIMES ; FOR VERY LONG $T_1$, SET C4 =1000 AND
   VD ; ENTER VD IN MS
   END LOOP
   D1 [F3 @PLS1 RGATE]
   D3 [STA] ; USE NT
   D0 [+PLS1] ; ACQUISITION

GOTO START

BEGIN LISTS
PLS1, +X -Y -X +Y
RLS, +X -Y -X +Y
END LISTS

; RECEIVER MODE: RPN OR QPN
; TRIGGER MODE: NT
; REC: F1 , DECOUPLER MODE: DO
Appendix 3. Pulse program to measure $T_2$ relaxation time

; HT2CPGM.PC

; CARR-PURCELL/GILL-MEIBOHM T2 SEQUENCE
; WITH TRIGGER ON TOP OF LAST ECHO
; TO EVALUATE MULTILINE SPECTRA AFTER FOURIER TRANSFORMATION

PROT ALL

START, D1 [F1 @PLS1 RGATE] ; 90 DEGREE PULSE
VD
D2 [F1 @PLS2 RGATE] ; 180 DEGREE REFOCUSING PULSE
VD
D3 [STA RGATE] ; TRIGGER ON TOP OF LAST ECHO
D0
++PLS1
++PLS2
GOTO START

BEGIN LISTS
PLS1, +X -Y -X +Y
PLS2, +Y +X
RLS, +X -Y -X +Y
END LISTS

; USE RPN
; USE TONEAQ.AU AND VDLIST TO RUN SERIES OF SPECTRA
Appendix 4. Pulse program to measure $T_{1\rho}$ relaxation time

; HT1RHO.PC
; MEASURE T1RHO FOR F1 CHANNEL

PROTXT

START, D1 [F1 @PLS1 RGATE] 
VD [F1 @PLS2 RGATE] ; CAREFUL: MAKE SURE
D3 [STA RGATE] ; VDLIST IS RIGHT!!
D0
++PLS1
++PLS2

GOTO START

BEGIN LISTS
PLS1, +X -Y -X +Y
PLS2, +Y +X -Y -X
RLS, -Y -X +Y +X
END LISTS

; USE RPN OR QPN FOR AQUISITION
Appendix 5. Pulse program for the cross-polarization experiment

; HCPF3F1.PC

; CROSS-POLARIZATION PULSE SEQUENCE WITH INVERSION OF
; SPIN TEMPERATURE

PROT XT

START, D11 [F3 PLS1^]
VD [F3 -Y F1 PLS2^]
D3 [RGATE STA] ; DEAD TIME DELAY
D0
GOTO START

BEGIN LISTS
PLS1, +X -X
PLS2, +X +X -X -X +Y +Y -Y -Y
RLS, +X -X -X +X +Y -Y -Y +Y
END LISTS

; RECEIVER MODE: RPN
; TRIGGER MODE: NT
; DECOUPLER MODE: DO
; NS=8*N
Appendix 6. Pulse program for the cross-polarization difference experiment

; KCPDIFFV.PC
; CROSS-POLARIZATION PULSE SEQUENCE WITH RPN
; ACCUMULATION OF DIFFERENCE
; FROM EXPTS WITH AND WITHOUT F3 PULSES

PROTXT

START, D1 [F1 @PLS1 RGATE]  ; CONTACT PULSE
VD [F1 @PLS2 F3 @PLS3 RGATE]  ; CONTACT PULSE
D3 [STA RGATE]  ; DEAD TIME DELAY
D0  ; DEAD TIME DELAY
D1 [F1 @PLS1 RGATE]
VD [F1 @PLS2 RGATE]
D3 [STA RGATE]
D0
++PLS1
++PLS2
++PLS3
GOTO START

BEGIN LISTS
PLS1, +X -Y -X +Y
PLS2, -Y -X +Y +X
PLS3, +X -Y -X +Y
RLS, +X -X -Y +Y -X +X +Y -Y
END LISTS

; RECEIVER MODE: QPN OR RPN
; TRIGGER MODE: NT
; DECOUPLER MODE: DO
; NS=8*N
Appendix 7. Pulse program for the two-dimensional cross-polarization experiment

; KCP2DF3.FC
;
; ********** SET IC1=4 FOR 2D-CP EXPERIMENT ************ ;
; CROSS-POLARIZATION PULSE SEQUENCE WITH INVERSION OF
; SPIN TEMPERATURE
; TWO DIMENSIONAL EXPT

PROT NONE

LOOP C1 TIMES
  3U
  ++PLS1
  3U
END LOOP

START, D11 [F3 @PLS1 RGATE]
D4
D5 [F3 @PLS3 F1 @PLS2 RGATE]
D3 [STA RGATE] ; DEAD TIME DELAY
D0
  ++PLS1
  ++PLS2
GOTO START

BEGIN LISTS
PLS1, +X +X +X +X +Y +Y +Y -X -X -X -X -Y -Y -Y
PLS3, -Y
RLS, +X -X +Y -Y +Y -Y -X +X
END LISTS

; RECEIVER MODE: RPN
; TRIGGER MODE: NT
; DECOUPLER MODE: DO
; NS=16*N
Appendix 8. Automation program for the two-dimensional cross-polarization, TEDOR and INEPT experiments

; KTPPI4.AUM
; TO BE USED WITH KCP2DF3.PC, HTED2DC4.PC OR KINEPT2D.PC

C1 = 0 ; SET IC1 = 2 FOR 2D-TEDOR OR 2D-INEPT
D4 = 3U ; IC1 = 4 FOR 2D-CP

1  ZE
2  GO
3  WR #1
4  IF #1
5  IC1
6  I4
7  IN=1

EXIT
Appendix 9.  (a) Pulse program for the dipolar-dephasing difference experiment

; KVEEMRF3.PC

PROT NONE
START,  D10 [SYN3=SYN^]
   D1  [F1 @PLS1 RGATE]   ; PULSE WITH PHASE LIST 1
   D23 [F3 @PLS3 RGATE]
   D2  [F1 @PLS2 RGATE]
   D23 [STA RGATE]
   D0
   D10 [SYN3=SYN^]
   D1  [F1 @PLS1 RGATE]
   D23 [F3 @PLS3 RGATE]
   D2  [F1 @PLS2 RGATE]
   D23 [STA RGATE]   ; NEGATIVE TRIGGER!!!
   D0
++PLS1
++PLS2
++PLS3
GOTO START

BEGIN LISTS
PLS1, +X -Y -X +Y
PLS2, +Y +X -Y -X
PLS3, +X
RLS, +X -X -Y +Y -X +X +Y -Y
SYN, (161.977) (171.977)
END LISTS

; RECEIVER MODE: RPN
; TRIGGER MODE: NT

(b) Program to calculate the delay in the dipolar-dephasing difference experiment

; VEEMNCAL.AUM

D21 = 1M
D22 = D21/K3   ; K3 = SPINNING SPEED IN KHZ
D24 = D22*C1   ; C1 = NUMBER OF ROTOR CYCLES
D23 = D24 - D1

EXIT
Appendix 10. (a) Pulse program for the REDOR experiment

; HREDORF3.PC
; PERFORMS SUBTRACTION

PROT F1
START, D10 [SYN3=SYN^]
   D1 [SYN3=SYN^] [F1 @PLS1 RGATE]
   D2 [F3 @PLS2 RGATE]
   D12 [F3 @PLS2 RGATE]
   LOOP C1 TIMES ; N = 2*C1 + 2
      D23
      D12 [F3 @PLS3 RGATE]
      D23 [F3 @PLS2 RGATE]
      D12 [F3 @PLS2 RGATE]
   END LOOP
   D23 [F1 @PLS4 RGATE]
   D2 [F1 @PLS4 RGATE]
END LOOP
D12 [F3 @PLS2 RGATE]
D22 [F3 @PLS2 RGATE]
D3 [STA RGATE] ; SET D3=D1/2 AND USE NT
D0
D10 [SYN3=SYN^]
D1 [F1 @PLS1 RGATE]
D22 [F3 @PLS2 RGATE]
D12 [F3 @PLS2 RGATE]
LOOP C1 TIMES
   D23
   D12 [F3 @PLS3 RGATE]
   D23 [F3 @PLS2 RGATE]
   D12 [F3 @PLS2 RGATE]
END LOOP
D23 [F1 @PLS4 RGATE]
D2 [F1 @PLS4 RGATE]
D23 [F1 @PLS4 RGATE]
LOOP C1 TIMES
   D12 [F3 @PLS2 RGATE]
   D23 [F3 @PLS2 RGATE]
continued next page
D12 [F3 @PLS3 RGATE]
D23
END LOOP
D12 [F3 @PLS2 RGATE]
D22
D3 [STA RGATE] ; SET D3=(D1)/2 AND USE NT
D0
++PLS1
++PLS2
++PLS3
++PLS4
GOTO START

BEGIN LISTS
PLS1, +X -Y -X +Y
PLS2, +X
PLS3, +Y
PLS4, +Y +X -Y -X
RLS, +X -X -Y +Y +X +Y -Y
SYN, (79.495) (89.495)
END LISTS

; RECEIVER MODE: RPN
; TRIGGER MODE: NT
; D23 = [T(ROT)-2*D12]/2
; D22 = [T(ROT)-D1-D12]/2

(b) Program to calculate the delays in the REDOR experiment

; REDORCAL.AUM
; MICROPROGRAM TO CALCULATE DELAYS FOR REDOR EXPERIMENT
; TO BE USED IN CONNECTION WITH HREDORF3.PC
; ENTER D1, D12 AND SPINNING FREQUENCY BEFORE RUNNING THIS!!!

C2 = 2
D13 = 1M
D14 = D13/K3 ; K3 IS THE SPINNING FREQUENCY IN KHZ!
D15 = D1+D12
D16 = D15/C2
D18 = D14/C2 ; 1/2 OF ROTATIONAL PERIOD
D22 = D18 -D16
D23 = D18 -D12
EXIT
Appendix 11. (a) Pulse program for the TEDOR experiment

; HTEDN MV.PC
; USE WITH KTEDOR.AUM FOR VARIATION OF PULSE POSITION
; TRANSFER FROM F3 TO F1
; ALTERNATES +X AND +Y 180 DEG PULSES ON F1
; 90 DEGREE TIMES MUST BE EQUAL

PROT F1
START,   D1 [F3 @PLS1 RGATE]
         D23
         D2 [F1 @PLS2 RGATE]
LOOP C1 TIMES ; N = 2C1+2
         D24
         D2 [F1 @PLS6 RGATE]
         D24
         D2 [F1 @PLS2 RGATE]
END LOOP
         D24
         D2 [F1 @PLS6 RGATE]
         D25
         D2 [F3 @PLS3 F1 @PLS2 RGATE]
         D25
         D2 [F1 @PLS2 RGATE]
LOOP C1 TIMES
         D24
         D2 [F1 @PLS6 RGATE]
         D24
         D2 [F1 @PLS2 RGATE]
END LOOP
         D24
         D2 [F1 @PLS6 RGATE]
         D23
         D1 [F3 @PLS5 F1 @PLS4 RGATE] ; TRANSFER PULSE
LOOP C4 TIMES ; M = C4
         D23
         D2 [F1 @PLS2 RGATE]
         D24
         D2 [F1 @PLS6 RGATE]
         D23
END LOOP
         D3 [STA RGATE] ; SET D3=D1/2
         D0 ; AND USE NT
         ++PLS1
         ++PLS2

continued next page
++PLS3
++PLS4
++PLS5
++PLS6
GOTO START

BEGIN LISTS
PLS1, +X +X -Y -Y -X -X +Y +Y
PLS2, +X
PLS3, +Y +Y +X +X -Y -Y -X -X
PLS4, +X +X -Y -Y -X -X +Y +Y
PLS5, -Y +Y -X +X +Y -Y +X -X
PLS6, +Y
RLS, +X -X -Y +Y -X +X +Y -Y
END LISTS

; RECEIVER MODE: RPN
; TRIGGER MODE: NT
; NS = 8*N
; D3 = D1/2
; D23 = T(ROT)/4 - D2/2 - D1/2
; D24 = T(ROT)/2 - D2
; D25 = T(ROT)/4 - D2

(b) Program to calculate the delays in the TEDOR experiment

; TEDORCAL.AUM
; MICROPROGRAM TO CALCULATE DELAYS FOR TEDOR EXPERIMENT
; TO BE USED IN CONNECTION WITH KTEDORS2.PC OR HTEDNMV.PC
; ENTER D1, D2 AND K3 = SPINNING FREQUENCY BEFORE RUNNING THIS

C5 = 2
C2 = 4
C3 = 3
D13 = 1M
D14 = D13/K3 ; K3 IS THE SPINNING FREQUENCY IN KHZ
D15 = D1+D2
D16 = D15/C5 ; D16 IS 3/2 OF D1
D17 = D14/C2 ; 1/4 OF ROTATIONAL PERIOD
D18 = D14/C5 ; 1/2 OF ROTATIONAL PERIOD

D3 = D1/C5
D23 = D17 - D16
D24 = D18 - D2
D25 = D17 - D2
EXIT
Appendix 12. Pulse program for the two-dimensional TEDOR experiment

; HTED2DC4.PC

; ??? DID YOU SET IC1=2 ???

; TWO DIMENSIONAL TEDOR EXPT
; TRANSFER FROM F3 TO F1
; 90 DEGREE TIMES MUST BE EQUAL
; USE KTPPI4.AUM FOR AUTOMATION

LOOP C1 TIMES
    3U
    ++PLS1
    3U
END LOOP

START, 10U
D1 [F3 @PLS1 RGATE]
D4
D1 [F3 @PLS6 RGATE]
D23
LOOP C4 TIMES ; N = 2 + 2*C4
    D2 [F1 @PLS2 RGATE]
    D24
    D2 [F1 @PLS7 RGATE]
    D24
END LOOP
D2 [F1 @PLS2 RGATE]
D24
D2 [F1 @PLS7 RGATE]
D25
D2 [F3 @PLS3 F1 @PLS2 RGATE]
D25
LOOP C4 TIMES
    D2 [F1 @PLS2 RGATE]
    D24
    D2 [F1 @PLS7 RGATE]
    D24
END LOOP
D2 [F1 @PLS2 RGATE]
D24
D2 [F1 @PLS7 RGATE]
D23
D1 [F3 @PLS5 F1 @PLS4 RGATE] ; TRANSFER PULSE

continued next page
D23 ; M = 1
D2 [F1 @PLS2 RGATE]
D24
D2 [F1 @PLS7 RGATE]
D23
D3 [STA RGATE] ; D3 = (D1)/2
D0
++PLS3
++PLS4
++PLS5
++PLS6
++PLS1
GOTO START

BEGIN LISTS
PLS1, +X +X -Y -Y -X -X +Y +Y
PLS2, +X
PLS3, +Y +Y +X +X -Y -Y -X -X
PLS4, +X +X -Y -Y -X -X +Y +Y
PLS5, -Y +Y -X +X +Y -Y +X -X
PLS6, -Y -Y -X -X +Y +Y +X +X
PLS7, +Y
RLS, +X -X -Y +Y -X +X +Y -Y
END LISTS

; RECEIVER MODE: RPN
; TRIGGER MODE: NT
; NS = 8*N
; D3 = (D1)/2
; D22 = D23 + D1
; D23 = T(ROT)/4 - D2/2 - D1/2
; D24 = T(ROT)/2 - D2
; D25 = T(ROT)/4 - D2
Appendix 13. Pulse program for the dynamic-angle cross-polarization (DACP) experiment

; KCPHOPVC.PC
; CROSS POLARIZATION PULSE SEQUENCE WITH QPN AND INVERSION OF SPIN TEMPERATURE
; USING F3 AND F1 AND HOPPING FROM 0 DEG TO MAGIC ANGLE
; ALLOWS VARIABLE CONTACT TIME

PROT NONE

START, D10 [XT +X] ; TRIG PROFILE AND FIRST HOP
D14 ; SETTLING TIME
D11 [F3 @PLS1 RGATE] ; 90 DEG PREPARATION FOR CP
VD [F1 @PLS2 F3 -Y RGATE]
D1 [F1 @PLS3 RGATE] ; STORE MAGNETIZATION
D10 [XT +Y] ; TRIG HOP TO MAGIC ANGLE
D13 ; HOP TIME
D1 [F1 @PLS4 RGATE] ; F1 90 DEG PULSE
D3 [RGATE STA] ; DEAD TIME
D0 ++PLS1
++PLS2
++PLS3
++PLS4
GOTO START

BEGIN LISTS
PLS1, 8(+X) 8(-X)
PLS2, -X +Y +X -Y
PLS3, +Y +X -Y -X -Y +X
PLS4, +Y +X -Y -X -Y +X
-Y -X +Y +X +Y +X -Y -X
RLS, +X -Y -X +Y
END LISTS

; RECEIVER MODE: QPN OR RPN
; TRIGGER MODE: NT
; NS=16*N
Appendix 14. Pulse program for the INEPT experiment

; KINEPT.PC
; INEPT BASIC PULSE SEQUENCE FOR J-COUPLED SPECTRA
; TRANSFER FROM F3 TO F1
; USE WHEN T2 IS SHORT
; 90 DEG TIMES MUST BE EQUAL

PROT ALL

START,  D11 [F3 @PLS1] ; 90 DEG PULSE
         VD ; 1/4J DELAY
         D12 [F3 @PLS2 F1 @PLS3] ; 180 DEG PULSES
         VD ; 1/4J DELAY
         D11 [F3 @PLS4 F1 @PLS5] ; 90 DEG PULSES
         D3 [STA RGATE] ; RINGDOWN AND TRIGGER
         D0
         ++PLS1
         ++PLS2
         ++PLS3
         ++PLS4
         ++PLS5
GOTO START

BEGIN LISTS
PLS1,  8(+X) 8(-X)
PLS2,  +X -X
PLS3,  +X -X
PLS4,  +Y +Y -Y -Y
PLS5,  4(+X) 4(+Y) 4(-X) 4(-Y)
RLS,  +X +X -X -X +Y +Y -Y -Y
END LISTS

; REMEMBER TO TYPE RP
; RPN, NT
; D24 = D2 - D12
; D25 = D1 - D11
; NS = 16 * N
Appendix 15. Pulse program for the refocused INEPT experiment

; HINEPTR.PC
; INEPT PULSE SEQUENCE FOR J-COUPLED SPECTRA
; TRANSFER FROM F3 TO F1 WITH REFOCUSING
; USE WHEN T2 IS SHORT
; 90 DEG TIMES MUST BE EQUAL

PROT ALL

START, D1 [F3 @PLS1] ; 90 DEG PULSE
   D6 ; 1/4J DELAY
   D2 [F3 @PLS2 F1 @PLS3] ; 180 DEG PULSES
   D6 ; 1/4J DELAY
   D1 [F3 @PLS4 F1 @PLS5] ; 90 DEG PULSES
   VD ; 1/(8J) FOR POSITIVE DOUBLET,
   D2 [F3 @PLS2 F1 @PLS6] ; TRIPLET AND QUARTET
   VD
   D3 [STA RGATE] ; RINGDOWN AND TRIGGER
D0
   ++PLS1
   ++PLS2
   ++PLS3
   ++PLS4
   ++PLS5
   ++PLS6
GOTO START

BEGIN LISTS
PLS1, 8(+X) 8(-X)
PLS2, +X -X
PLS3, +X -X
PLS4, +Y +Y -Y -Y
PLS5, 4(+X) 4(+Y) 4(-X) 4(-Y)
PLS6, +X -X +X -X +Y -Y +Y -Y
RLS, +X +X -X -X +Y +Y -Y -Y
END LISTS

; REMEMBER TO TYPE RP
; RPN, NT
; D24 = D2 - D12
; D25 = D1 - D11
; NS = 16 * N
Appendix 16. Pulse program for the DEPT experiment

; HDEPTF3.PC
; DEPT PULSE SEQUENCE FOR J-COUPLED SPECTRA
; TRANSFER FROM F3 TO F1 WITH REFOCUSBING

PROT ALL
START, D11 [F3 +X] ; 90 DEG PULSE
VD ; 1/2J DELAY
D12 [F3 @PLS2] ; 180 DEG PULSES
D1 [F1 @PLS4]
VD ; 1/2J DELAY
D10 [F3 @PLS3] ; 45 DEG < D10 < 135 DEG
D2 [F1 @PLS5]
VD
D3 [START GATE] ; RINGDOWN AND TRIGGER
D0
++PLS2
++PLS3
++PLS4
++PLS5
GOTO START

BEGIN LISTS
PLS2, +X -X +Y -Y
PLS3, 4(+Y) 4(-Y)
PLS4, 8(+X) 8(+Y) 8(-X) 8(-Y)
PLS5, +X -X +X -X +X -X +X -X
       +Y -Y +Y -Y +Y -Y +Y -Y
RLS, +X +X -X -X -X +X +X
       +Y +Y -Y -Y +Y +Y +Y +Y
       -X -X +X +X +X +X -X -X
       -Y -Y +Y +Y +Y +Y -Y -Y
END LISTS

; REMEMBER TO TYPE RP
; RPN, NT
; NS = 32 * N
; D10 45 DEG FOR ALL MULTIPLECTIES
; D10 90 DEG FOR DOUBLETS ONLY
; D10 135 DEG FOR DOUBLETS AND QUARTETS UP, AND TRIPLETCS
; (AND QUINTETS?) DOWN
Appendix 17. Pulse program for the two-dimensional INEPT experiment

; KINEPT2D.PC
; INEPT BASIC PULSE SEQUENCE FOR J-COUPLED SPECTRA
; TRANSFER FROM F3 TO F1
; USE WHEN T2 IS SHORT
; 90 DEG TIMES MUST BE EQUAL

; SET IC1=2 AND C1=0 TO START

PROT ALL
LOOP C1 TIMES
  3U
  ++PLS1
  3U
END LOOP

START, D1 [F3 @PLS1] ; 90 DEG PULSE
D4
D1 [F3 @PLS6]
D6
D2 [F3 @PLS2 F1 @PLS3] ; 1/4J DELAY
D6
D1 [F3 @PLS4 F1 @PLS5] ; 180 DEG PULSES
D6
D3 [STAGATE] ; 1/4J DELAY
DO
++PLS1
++PLS2
++PLS3
++PLS4
++PLS5
++PLS6
GOTO START

BEGIN LISTS
PLS1, +X +X -Y -Y -X -X +Y +Y
PLS2, +Y +Y +X +X -Y -Y -X -X
PLS3, +X -X -Y +Y
PLS4, -Y +Y -X +X +Y -Y +X -X
PLS5, +X +X -Y -X -X +Y +Y
PLS6, -Y -Y -X -X +Y +Y +X +X
RLS, +X -X -Y +Y -X +X +Y -Y
END LISTS

; REMEMBER TO TYPE RP
; RPN, NT
; NS = 8*N