

Advances and Applications of Dynamic-Angle Spinning
Nuclear Magnetic Resonance Spectroscopy

by

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Abstract

This dissertation describes nuclear magnetic resonance experiments and theory which have been developed to study quadrupolar nuclei (those nuclei with spin greater than one-half) in the solid state. Primarily, the technique of dynamic-angle spinning is extensively reviewed and expanded upon in this thesis. Specifically, the improvement in both the resolution (two-dimensional pure-absorptive phase methods and DAS angle choice) and sensitivity (pulse-sequence development), along with effective spinning speed enhancement (again through choice of DAS conditions or alternative multiple pulse schemes) of dynamic-angle spinning experiment were realized with both theory and experimental examples. The application of DAS to new types of nuclei (specifically the ^{87}Rb and ^{85}Rb nuclear spins) and materials (specifically amorphous solids) has also greatly expanded the possibilities of the use of DAS to study a larger range of materials. This dissertation is meant to demonstrate both recent advances and applications of the DAS technique and by no means represents a comprehensive study of any particular chemical problem.

dedicated to Julie, Mary and Richard

Table of Contents

Chapter 1	1
Introduction.....	1
Chapter 2	3
Theory of Nuclear Magnetic Resonance.....	3
Classical Magnetization Description	3
Quantum Mechanical Description	5
Rotations and Tensors.....	5
Perturbation Theory	7
Zeeman Interaction	11
Radio frequency irradiation	14
Chemical Shift Anisotropy.....	15
Quadrupolar Interaction	17
Dipole-Dipole Interaction	21
Truncation of RF Hamiltonian by the Quadrupolar Hamiltonian.....	22
Coherence Pathways	26
Eigenvalues from static samples	31
Eigenvalues from Rotating Samples	34
Lineshape simulations.....	38
Chapter 3	44
Dynamic-angle spinning DAS	44
History of DAS	44
Spinning Sidebands.....	52
Linewidths in DAS (Homonuclear Dipole-Dipole Interaction).....	69
Chapter 4	73
Pure Phase NMR.....	73
Pure-Absorption Mode Acquisition Methods	74
States Method.....	74
Time Proportional Phase Incrementation.....	76
Whole Echo Acquisition	77
Pure Phase DAS	79
Pulse Sequences	79
Experimental Examples	85
Signal-to-Noise Ratio Enhancements	88

Chapter 5	90
Cross Polarization	90
History.....	90
Spinning Effects on CP of Quadrupolar Nuclei.....	91
Theory	92
Experiments on Sodium Pyruvate and Sodium Hydroxide	105
Cross Polarization Results and Discussion	107
Chapter 6	112
Alternatives to DAS	112
Double Rotation (DOR)	112
Magic-Angle Hopping (MAH)	121
Dynamic-Angle Hopping (DAH).....	130
Chapter 7	137
Application of DAS to Inorganic Salts	137
Sodium	137
Rubidium Salts.....	137
Improvements from Multiple-Field DAS	145
Improvements from MAS-Detected DAS.....	147
Theory of Coupling Constants from Crystal Structure	150
Application of CPDAS to organic compounds	152
Chapter 8	156
Application of DAS to silicate materials	156
Crystalline Silicates.....	156
Amorphous Silicates	168
Experimental	172
Amorphous Silica	173
Tetrasilicates	180
Disilicates	184
Conclusions.....	187
References.....	189
Bibliography.....	189
Appendices.....	198
Computer programs.....	198
CQP - VAS Spectral Simulation Program	198
MINUITCQ - VAS Least Squares Fitting Program.....	210

List of Figures

Figure 2.1 Euler Angle Definitions	6
Figure 2.2 90-90 Echo Coherence Pathway	29
Figure 2.3 Zeeman and Quadrupolar Energy Splitting for $I = 3/2$ nucleus.....	32
Figure 2.4 PAS to ROTOR to LAB rotations	35
Figure 2.5 Static CSA (a), 1st Order (b) and 2nd Order (c) Quadrupolar Lineshapes	40
Figure 2.6 MAS CSA (a) and 2nd Order (b) Quadrupolar Lineshapes.....	41
Figure 2.7 Quadrupolar VAS Spectra	42
Figure 3.1 2nd and 4th Order Legendre Polynomials	45
Figure 3.2 DAS Experiment and Pulse Sequence	46
Figure 3.3 DAS Pulse Sequence Coherence Pathway.....	47
Figure 3.4 DAS Angle Pairs.....	49
Figure 3.5 Example 1D DAS Spectrum of Sodium Oxalate.....	50
Figure 3.6 Example 2D DAS Spectrum of Sodium Oxalate.....	51
Figure 3.7 Sidebands in MAS Spectra of CSA and Second-Order Quadrupolar Broadened Sites	52
Figure 3.8 Redefined DAS Pulse Sequence for Spinning Sideband Calculation.....	59
Figure 3.9 Sidebands in $k = 1$ DAS 2D Spectrum of RbClO_4 at 11.7T	60
Figure 3.11 $^{87}\text{RbClO}_4$ Sidebands in $k = 5$ DAS 2D Spectrum.....	65
Figure 3.12 $^{87}\text{RbClO}_4$ Sidebands in $k = 0.8$ DAS 2D Spectrum.....	66
Figure 3.13 All k values for fast spinning $^{87}\text{RbClO}_4$ DAS at 11.7T.....	67
Figure 3.14 Homonuclear Dipolar Linewidth versus Spinning Angle.....	70
Figure 3.15 Dynamic-Angle Spinning Linewidths as a function of k	72
Figure 4.1 Pure-Absorption mode and Mixed-Phase 2D NMR Spectra	74
Figure 4.2 Original DAS Experiment.....	80
Figure 4.3 Modified DAS Experiment	81
Figure 4.4 Hypercomplex DAS Experiment	82
Figure 4.5 Shifted-Echo DAS Experiment.....	83
Figure 4.6 Hypercomplex Shifted-Echo DAS Experiment	84
Figure 5.4 CP Efficiency versus Spinning Angle.....	107
Figure 5.5 Comparison of CPMAS, MAS and ZPMAS Experiments	109

Figure 5.6 Comparison of CPDAS versus DAS	110
Figure 6.1 DOR Rotor and Rotations.....	112
Figure 6.2 DOR of $^{87}\text{RbNO}_3$ at 9.4T	114
Figure 6.3 DOR of $^{23}\text{Na}_2\text{C}_2\text{O}_4$ at 9.4T.....	118
Figure 6.4 DOR of $^{23}\text{Na}_2\text{C}_2\text{O}_4$ at 9.4T.....	121
Figure 6.5 Magic-Angle Hopping Experiment.....	122
Figure 6.6 Magic-Angle Turning Experiment.....	125
Figure 6.7 Magic-Angle Turning Experiment with Pulses	127
Figure 6.8 MAS, MAT and MAT-180 Spectra of $^{207}\text{PbNO}_3$	129
Figure 6.9 DAS and DAH 1D spectra of $^{87}\text{Rb}_2\text{CrO}_4$	133
Figure 7.1 ^{87}Rb Salts 11.7T VAS Spectra	140
Figure 7.2 ^{87}Rb Salts 11.7T DAS Spectra	141
Figure 7.3 ^{87}Rb Salts 9.4T DAS Spectra	142
Figure 7.4 RbNO_3 Spectra at Four Field Strengths.....	145
Figure 7.5 RbNO_3 Linear Regression of Isotropic Shifts versus $1/B_0^2$	146
Figure 7.6 RbNO_3 9.4T 2D MAS detected DAS Contour Plot	148
Figure 7.7 RbNO_3 11.7T 2D MAS detected DAS Contour Plot	148
Figure 7.8 RbNO_3 Single Site MAS Slices and Simulations at 11.7T	149
Figure 7.9 ^1H Decoupled 2D ^{17}O CPDAS Spectrum of L-Alanine at 7.0T	153
Figure 7.10 Undecoupled ^{17}O MAS and DAS Spectra of L-Alanine at 11.7T.....	154
Figure 8.1 Crystal Structures of Some Pyroxene Silicate Minerals	159
Figure 8.2 Crystalline 9.4T DAS, DOR and MAS Spectra.....	161
Figure 8.3 Crystalline 11.7T DAS Spectra.....	162
Figure 8.4 Crystalline Diopside 9.4T and 11.7T MAS Spectra	165
Figure 8.5 Comparison of A_2O_3 Crystal and Glass Lattice Structures.....	169
Figure 8.6 Insertion of Modifying Cations into Silicate Glasses	170
Figure 8.7 2D DAS Spectrum of Amorphous SiO_2	173
Figure 8.8 SiO_2 Anisotropic Slices and Simulations	175
Figure 8.9 Electric Field Gradient Model Compound.....	176
Figure 8.10 Ab Initio Quadrupolar Parameters for $\text{H}_3\text{Si-O-SiH}_3$	177
Figure 8.11 Amorphous SiO_2 Bond Angle Distribution.....	178
Figure 8.12 2D DAS Spectra of Tetrasilicate Glasses	181

Figure 8.13 $K_2Si_4O_9$ Bond Angle Distribution.....	183
Figure 8.14 DAS Spectrum of $K_2Si_2O_5$ glass at 11.7T	185
Figure 8.15 $K_2Si_2O_5$ Bond Angle Distribution.....	186

List of Tables

Table 2.1	Second-rank reduced Wigner rotation matrix elements $d_{nm}^{(2)}(\beta)$	7
Table 2.2	Cosine Expansion Coefficients	34
Table 2.3	Coefficients in Anisotropic Cosine Expansion for the 2nd-Order Quadrupolar Correction Under Fast Spinning Conditions.	38
Table 4.1	Signal-to-Noise Ratio Enhancements For a Variety of Pulse Sequences	89
Table 5.1	Signal to Noise Ratios in CPDAS and Normal DAS	111
Table 6.1	Magic-Angle Hopping Experimental Phase Cycle	122
Table 7.1	^{87}Rb Isotropic Shifts and Coupling Products.....	143
Table 7.2	Previously Measured ^{87}Rb Isotropic Chemical Shifts and Quadrupolar Parameters.....	144
Table 7.3	$^{87}\text{RbNO}_3$ Multiple Field DAS Results.....	147
Table 7.4	^{87}Rb Isotropic Shifts from MAS Simulations.....	150
Table 7.5	$^{87}\text{RbNO}_3$ EFG Values From Crystal Structure	151
Table 8.1	Isotropic Chemical Shifts and Quadrupolar Coupling Products from Two Field Studies	164
Table 8.2	Diopside Quadrupolar Parameters	166
Table 8.3	SiO_2 Anisotropic Slice Fits	174
Table 8.4	$\text{K}_2\text{Si}_4\text{O}_9$ Anisotropic Slice Fits from 9.4T and 11.7T DAS Spectrum	182
Table 8.5	$\text{K}_2\text{Si}_2\text{O}_5$ Anisotropic Slice Fits.....	186

List of Symbols

Symbol	Description
$A_{lm}^\lambda, a_{lm}^\lambda, R_{lm}^\lambda, r_{lm}^\lambda, \rho_{lm}^\lambda, \sigma_{lm}^\lambda$	Spatial tensor operators for the λ interaction
A_N, S_N, S_{N_1, N_2}	Sideband amplitude functions
$(\alpha^\lambda, \beta^\lambda, \gamma^\lambda)$	Euler angles used in rotations between reference frames
B_0	Static magnetic field
CP	Cross polarization
CSA	Chemical shift anisotropy
C_Q	Quadrupolar coupling constant
$\langle L, M l, l, m, M - m \rangle$	Clebsch-Gordon Coefficient
DAS	Dynamic-angle spinning
DOR	Double rotation
$D_{m,n}^{(l)}(\alpha^\lambda, \beta^\lambda, \gamma^\lambda)$	Wigner rotation matrix element
D	Dipolar (either heteronuclear or homonuclear) interaction
$\delta(z)$	Dirac delta function
eQ	Nuclear quadrupolar moment
eq	Electric field gradient magnitude
FID	Free induction decay
γ	Nuclear gyromagnetic ratio
η_λ	Asymmetry parameter for the λ interaction
\hbar	Planck's constant
H_λ	Hamiltonian for λ interaction
\tilde{H}_λ	Rotating frame Hamiltonian for λ interaction
$ I, m\rangle$	Spin state ket for an I spin in state m

$\langle I, m $	Spin state bra for an I spin in state m
I_x, I_y, I_z	Cartesian spin operators
$I_0, I_{\pm 1}$	Spherical normalized spin operators
k	DAS time ratio constant
λ	Type of spin interaction (chemical shift anisotropy, quadrupolar, dipolar, etc.)
M_2	Second moment (from either dipolar or other interactions)
M_x, M_y, M_z	Cartesian sample magnetization components
p	Coherence level
$\Delta \mathbf{p} \quad (\Delta p_1, \Delta p_2, \dots, \Delta p_n)$	Coherence transfer pathway vector
$P_n [\cos \theta]$	Order- n Legendre polynomials of $\cos \theta$
PSD	Phase sensitive detection (or quadrature)
Q	Quadrupolar interaction
$1Q$	First-order quadrupolar interaction
$2Q$	Second-order quadrupolar interaction
θ_s	Shearing transformation shearing angle
ρ_0	Equilibrium density matrix describing spin system
$\rho_r(t)$	Reduced density matrix describing spin system
SEDAS	Shifted echo dynamic-angle spinning
$S(t), S(t_1, t_2)$	Time domain NMR signal (1 or 2 dimensional)
$S(\omega), S(\omega_1, \omega_2)$	Frequency domain NMR signal (1 or 2 dimensional)
T_1, T_2	Spin-lattice and spin-spin relaxation times
TPPI	Time proportional phase incrementation
T_{lm}^λ	Spin tensor operators for the λ interaction
$U(t), U^\dagger(t)$	Unitary time evolution operators
V	Perturbing Hamiltonian in perturbation theory

V_{xx}, V_{yy}, V_{zz}	Principal axes components of the electric field gradient
ω_1	Radiofrequency oscillating magnetic field
ω_l	Larmor precession frequency
ω_r	Sample spinning speed
ω_{rot}	Rotating frame precession frequency
ω_Q	Quadrupolar frequency

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