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

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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
$\left(\alpha^{\lambda}, \beta^{\lambda}, \gamma^{\lambda}\right)$	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
$\langle L, M \mid l, l', m, M-m \rangle$	Clebsch-Gordon Coefficient
DAS	Dynamic-angle spinning
DOR	Double rotation
$D_{m,n}^{(l)}\left(\alpha^{\lambda}, \beta^{\lambda}, \gamma^{\lambda}\right)$	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
$\tilde{H}_{\lambda}$	Rotating frame Hamiltonian for λ interaction
$\lvert I, m \rangle$	Spin state **ket** for an *I* spin in state *m*

$\langle I, m \vert$	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
$\Delta\mathbf{p} \quad (\Delta p_1, \Delta p_2, \cdots, \Delta p_n)$	Coherence transfer pathway vector
$P_n[\cos\theta]$	Order-*n* Legendre polynomials of cosθ
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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