Finite pulse width artifact suppression in spin-1 quadrupolar echo spectra by phase cycling

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Abstract 1

A phase cycling scheme for suppressing spectral artifacts introduced in quadrupolar echo spectroscopy of spin-1 nuclei due to finite pulse width effects is presented. The phase cycling scheme is developed using the formalism of average Hamiltonian theory and fictitious spin-1 operators. A simulation and experiment on deuterated polyethelene is performed highlighting the spectral artifact introduced by finite pulse widths and successful removal with the proposed phase cycling scheme.

The Quadrupolar Interaction in NMR 2

Due to nuclear magnetic moment interacting with electric field surrounding it. In general, this coupling is nonzero for spin greater than 1/2. In a large magnetic field the Hamiltonian is given by[1]:

$$H_{\omega Q} = \omega'_Q R_{2,0} \frac{1}{\sqrt{6}}[12 I_{z,1} I_{z,1} - II]$$

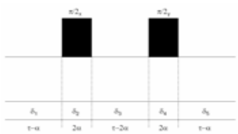
$$R_{2,0} = \sqrt{\tfrac{3}{2}}[P_2(cos(\theta)) + (\tfrac{\eta}{2})cos(2\theta)sin^2(\varphi)],\ P_2(cos(\theta))$$

$$\omega'_Q = \frac{e^2 qQ}{2I(2I-1)\hbar}$$

Spin Echo

The nuclear spin echo was first observed by E. Hahn [2] in the 1950's. The technique involves using two pulses that reverse the time evolution of a spin system. In practice, a spin echo is useful to acquire a signal free from artifacts introduced by the ring down of the RF coil.

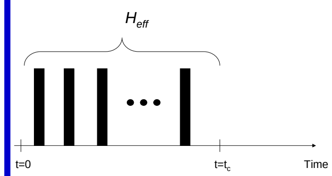
Pulse Sequence



Two pulse RF sequence for refocusing the quadrupolar Hamiltonian. In the figure, the two $\pi/2$ pulses have a width of 2α and the phases of the two pulses shown as x and y can be any combination of 90 degree phase shifted pulses[3].

[1] A. Jerschow, From nuclear structure to the quadrupolar NMR interaction and high-resolution spectroscopy, Prog. Nucl. Magn. Reson. Spectrosc. 46 (2005) 63-78.
[2] E. L. Hahn. Spin echoes. Phys. Rev. 80:580-94, 1950
[3] H.W. Speiss. Molecular dynamics of solid polymers as revealed by deuteron NMR, Colloids Polym. Sci. 261 (1983) 193-209

Average Hamiltonian Theory 3



The goal of average Hamiltonian theory, developed by J.S. Waugh and co-workers[4], is to replace a sequence of time-dependent perturbations (in NMR these are frequently in the form of RF pulses) and free evolution periods for which the system evolves under its internal Hamiltonian by an effective Hamiltonian H_{eff} which evolves the system from the state at time $t=0$ to $t=t_c$.

How to compute the effective Hamiltonian

$$\rho(t_c) = U_{RF} U_{int} \rho(0) U_{int}^{-1} U_{RF}^{-1} \qquad \overline{H}^0_{int} = \frac{1}{t_c}\int_0^{t_c} \widetilde{H}_{int}(\tau)dt$$

$$U_{RF} = \ldots U_3 U_2 U_1 U_0 \qquad \overline{H}^1_{int} = \frac{-i}{2t_c}\int_0^{t_c}[\widetilde{H}_{int}(\tau), \int_0^{\tau}\widetilde{H}_{int}(\phi)d\phi]d\tau$$

$$U_{int}(t,0) = exp[-it_c(\overline{H}^0_{int} + \overline{H}^1_{int} + \ldots] \qquad \overline{H}^2_{int} = \ldots$$

[4] U. Haeberlen, J.S. Waugh. Coherent averaging effects in magnetic resonance. Phys. Rev. 175 (1968) 453-467

Overview of the theoretical results 4
and how the phase cycling schemes were developed

For an x pulse followed by a y pulse the zeroth order term of the Magnus expansion is:

$$\overline{H}^0_{\omega Q} = \frac{4\alpha\omega_Q}{\pi\tau}[I_{x,2} - I_{z,2}]$$

And the density matrix at 3τ is given by:

$$\rho(3\tau) = \frac{\sin(\sqrt{2}w)}{\sqrt{2}} I_{x,2} + \frac{1}{2}[\cos(\frac{w}{\sqrt{2}}) + \cos(w\sqrt{2})]I_{y,1} - \frac{1}{2}[\cos(\frac{w}{\sqrt{2}}) - \cos(w\sqrt{2})]I_{z,1} + \frac{\sin(\sqrt{2}w)}{\sqrt{2}} I_{y,3} \frac{1}{4}[-2\sqrt{2}\sin(\frac{w}{\sqrt{2}}) + \sqrt{2}\sin(w\sqrt{2})]I_{x,3}$$

Where

$$w = \frac{12\alpha\omega_Q}{\pi}$$

The physics of these results show that the finite pulse widths contribute significantly to the system dynamics. When $\alpha=0$ we would have

$$\rho(3\tau) = I_{y,1}$$

corresponding to the case of ideal δ-function pulses.

In order to suppress the contribution of the finite pulse widths we calculated the effective Hamiltonians for the possible combinations of cycles that produce an echo. It can be shown that the following phase cycling schemes are robust in suppressing finite pulse width artifacts[5].

Phase cycling scheme I- is robust for removing the ringdown of the first pulse and finite pulse width artifacts for large τ.

$$\phi_1 = \{x,x,x,x,-x,-x,-x,-x,y,y,y,y,-y,-y,-y,-y\}$$

$$\phi_2 = \{x,y,-x,-y,y,x,-y,-x,y,x,-y,-x,x,y,-x,-y\}$$

$$RP = \{90,270,90,270,90,270,90,270,180,0,180,0,180,0,180,0\}$$

Phase cycling scheme II-completely suppresses finite pulse widths, to first order of the Magnus expansion

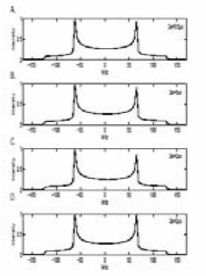
$$\phi_1 = \{x,x,-x,-x,y,y,-y,-y\}$$

$$\phi_2 = \{y,-y,y,-y,x,-x,x,-x\}$$

$$RP = \{270,270,90,90,180,180,0,0\}$$

[5] E. S. Mananga, Y. S. Rumala and G. S. Boutis "Finite pulseWidth artifact supression in spin-1 quadrupolar spectroscopy by phase cycling" submitted to the Journal of Magnetic Resonance

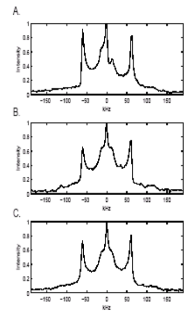
Simulation Results 5



Simulated quadrupolar echo spectra based on the two pulse sequence in Fig. 1, with a $\pi/2$ pulses about the x axis followed by a $\pi/2$ pulse about the y axis without any phase cycling. The figure highlights the spectral distortion introduced (skewed, asymmetric powder pattern) due to finite pulse widths of **A.** 0.5 μs, **B.** 1μs and **C.** 2 μs.

D. Simulated quadrupolar echo spectra, for 2 μs pulses with the phase cycling scheme II highlighting the finite pulse width artifact suppression.

Experimental Results



A. Normalized experimental quadrupolar echo spectra of deuterated polyethelene based on the two pulse sequence with $\pi/2$ pulse about the x axis followed by a $\pi/2$ pulse about the y axis without any phase cycling. The figure highlights the spectral distortion introduced (skewed, asymmetric powder pattern) due to finite pulse widths in agreement with our simulated result shown above. The peak in the middle of the powder pattern is due to a highly mobile group and has been observed by others in the same sample[6].
B. Normalized experimental quadrupolar echo spectra acquired on the same sample based on the two pulse sequence and phase cycling scheme I.
C. Normalized experimental quadrupolar echo spectra based on the two pulse sequence and phase cycling scheme II, highlighting the robust finite pulse width artifact suppression. In all of the experiments τ=40μs and 2α = 2µs.

[6] P. M. Henrichs, J. M. Hewitt and M. Linder, Experimental aspects of deuterium NMR of solids, J. Magn. Reson. 60 (1984) 280-298

Conclusions 6

Average Hamiltonian theory was applied for creating a phase cycling scheme that removes finite pulse width artifacts in the spectra of spin-1 nuclei acquired with the familiar two pulse echo experiment. Our results are verified both with a simulation tool written and experimentally on a sample of deuterated polyethelene. It is expected that a similar analysis can be performed on composite pulse cycles or other pulse sequences where finite pulse widths may introduce similar spectral distortions.

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