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Noise Reduction in Quadrupolar Echo Spectra at Short Echo Times

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The phase cycling scheme Exorcycle embedded into the quadrupolar echo pulse sequence is presented as a tool for reducing ringing effects in broad quadrupolar spectra. © 2001 Academic Press

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INTRODUCTION

The solid (*1*) or quadrupolar (*2*) echo pulse sequence 90°_x–τ-90°_y- τ-detection applied to spin $I = 1$ nuclei is a well-known tool (*3–5*) to provide undistorted powder spectra in systems with large ($\sim10^5$ Hz) static quadrupole splittings. Each shortcoming of the method calls for its specific remedy such as acquisition delay to compensate the effects of finite pulse length (*6*). One particular and annoying problem appears at τ values that are short enough to let NMR transients created by and phase coherent to the second pulse be detected. The remedy to this problem is to cycle the phase of the second pulse as 90°_x–τ-$90^\circ_{\pm y}$ (*4*); since the echo transient remains unchanged, adding signals from the two different scans cancels the transient from the second pulse. As an additional advantage, the technique also cancels the spurious signal that arises from the post-pulse ringing of the tank circuit. This latter benefit is a consequence of (most of) this electronic disturbance being phase coherent to the pulse that creates it (*7*). In this paper we call attention to the ringing signal that is induced by the first pulse of the quadrupolar echo sequence and makes itself visible at small τ values. We also present a way to cancel this disturbance. Our motivation stems from the necessity of obtaining ^{2}H NMR spectra that are sufficiently free of noise to allow spectral deconvolution.

THEORY

A phase cycle that would cancel the electronic ringing signal that is phase coherent with the first pulse in an echo sequence (i) must cycle the phase of the second pulse that alters the echo signal from nuclear spins and (ii) has to make use of the fact that the electronic ringing from the first pulse is independent of the phase of the second pulse. The conceptually simplest phase cycle that provides this is the Exorcycle (*8*), i.e.,

$$\begin{aligned}\phi_2 &= (x, y, -x, -y),\\ \text{Signal} &= (+, -, +, -),\end{aligned} \qquad [1]$$

where ϕ_2 is the phase of the second pulse (the phase of the first pulse is kept at x). In the quadrupolar echo, this phase cycle has been used (*9, 10*) to select coherence transfers by the second pulse with a change in the coherence order $|\Delta q| = 2, 4, 6, \ldots$. Hence, for a spin $I = 1$ nucleus this phase cycle applied with hard rf pulses selects the coherence transfer pathways $+1 \Rightarrow -1$ and $-1 \Rightarrow +1$ at the second pulse. It follows that the amplitude of the obtained echo is independent of the frequency offset which renders the measured transverse relaxation rate insensitive to magnetic field inhomogeneity. Note that this is not the case for the transverse relaxation rate measured by the conventional quadrupolar echo sequence (see (*10*) and references therein).

The effect of the echo on the ringing signal induced by the first pulse can be most easily illustrated if offset effects are assumed to be negligible. In this case, experiments with phases x and $-x$ for the second pulse do not provide any echo from the nuclear spins. Hence, it is only the scans with $\phi_2 = (y, -y)$ that provide the echo signal which reduces the NMR signal collected by the same number of scans by a factor of 2. The electronic ringing signal created by the second pulse is cancelled by pair-wise addition of the transients with opposite phases for the second pulse. The electronic ringing signal that is induced by the first pulse is constant throughout the phase cycle and, hence, is cancelled by adding and subtracting an equal number of scans. One can, of course, expand this phase cycle by cycling both the rf and receiver phases by the same amount. One should also note that there are other, conceptually more complex options (*11*) for phase cycles with equivalent effects on the ringing.

EXPERIMENTAL RESULTS

In Figs. 1 and 2 we present four ^{2}H spectra obtained by the echo sequences 90°_x–τ-$90^\circ_{\pm y}$ (Figs. 1a and 2a) and 90°_x–τ-$90^\circ_{\text{Exorcycle}}$ (Figs. 1b and 2b). Both the rf and receiver phases were additionally cycled by 90° increments under which steps the relative phase of the first and the second pulses was kept as

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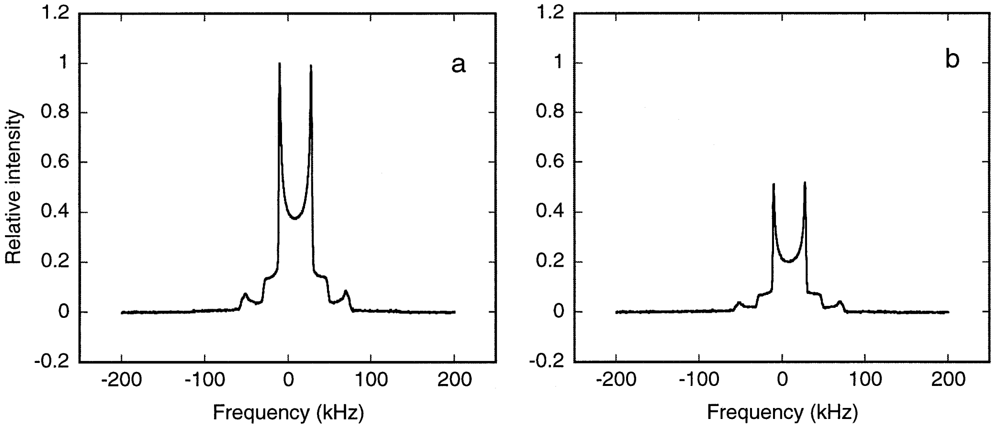

FIG. 1. ^{2}H NMR spectra of the solid powder of perdeuterated poly(methyl methacrylate). (a) Spectrum collected by the $90°_x$–τ-$90°_{\pm y}$ pulse sequence. (b) Spectrum collected by the $90°_x$–τ-$90°_{\mathrm{Exorcycle}}$ pulse sequence. The spectra have been acquired under identical experimental conditions with $\tau = 50\ \mu$s at 298 K. The spectra are normalized to the spectral maximum in (a).

specified above (for phase x of the first pulse). Hence, the full phase cycle consisted of eight steps for the spectra in Figs. 1a and 2a and 16 steps in Figs. 1b and 2b. With the exception of pulse spacing, the spectra were recorded under identical conditions on a Bruker AMX300 spectrometer equipped with an M3200 high-power (American Microwave Technology, 1 kW) transmitter that provided 2.0-μs long 90° pulses for the approximately 12-mm long samples located in a 5-mm solenoid probe. The rf coil of 6-mm i.d. and 18-mm length consisted of 24 turns yielding $Q \approx 65$.

The spectra in Fig. 1 were recorded by adding 1024 scans with $\tau = 50\ \mu$s in a sample of 36 mg perdeuterated (~98%, CIL) poly(methyl methacrylate). The start of the recording of the echo signal was set to $(\tau + \delta) = 53.2\ \mu$s after the second pulse where δ compensated for the cumulative effect of finite pulse lengths (*6*) and finite bandwidths of the probe and the transmitter (*12*). Because of the sufficiently large signal-to-noise ratio and sufficiently long delay time τ, spectra in Fig. 1a and 1b show no ringing artifacts. Hence, the effect of the phase cycle in Eq. [1] on the signal from the nuclear spins can be easily evaluated. In particular, the peak amplitude (measured on the inner powder peaks) in Fig. 1b is 0.52 ± 0.01 of that in Fig. 1a which agrees well with the theoretical prediction of 0.5 (see above).

The signal in Fig. 2 comes from the surfactant cetyltrimetylammonium bromide (CTAB) whose α-methylene group has been ~98% ^{2}H-enriched. The sample was approximately 80 mg of dry powder consisting of molecular complexes formed by CTAB (about 50 wt%) and a naturally occurring polyelectrolyte (partly sulfonated extracellular polysaccharide) (*13*). The transverse relaxation time, obtained from the τ-dependence of the signal, was about 50–60 μs across the spectra in Fig. 2. Since only a short delay time $\tau = 25\ \mu$s ($\delta = 3.2\ \mu$s as above) was allowed by the fast transverse relaxation and since the sample

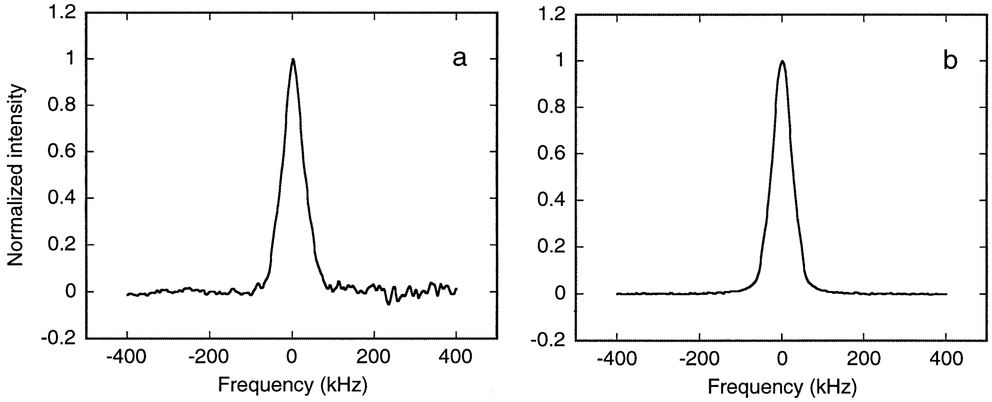

FIG. 2. ^{2}H NMR spectra of the solid powder of the complex created by the α-deuterated surfactant cetyltrimethylammonium bromide (CTAB) with a charged natural polyelectrolyte (*13*). (a) Spectrum collected by the $90°_x$– τ-$90°_{\pm y}$ pulse sequence. (b) Spectrum collected by the $90°_x$–τ-$90°_{\mathrm{Exorcycle}}$ pulse sequence. To allow a direct comparison of the signal-to-noise ratios, the spectra are shown with their peak intensities normalized to one. The absolute spectral intensity in (b) is half (within 2%) of that in (a). The spectra have been acquired under identical experimental conditions with $\tau = 25\ \mu$s at 298 K.

provided a low signal-to-noise ratio, the ringing affects the spectra in Fig. 2 more than in Fig. 1. Hence, the spectrum in Fig. 2a is of poor quality even after 256 k scans with the conventional phase cycle (*4*) that cancels ringing only from the second pulse are collected. In comparison, the signal-to-noise ratio in Fig. 2b is clearly higher despite the two-fold loss of the signal discussed above. This is a consequence of the Exorcycle that achieves a much more than two-fold reduction of the noise shown in Fig. 2a and dominated by electronic ringing induced by the first pulse. We have also found (spectra not shown) that the characteristic time for the decay of this noise component on increasing τ is on the order of 50–100 μs; since it decays slower than the signal from α-deuterated CTAB it cannot be cancelled by simply increasing τ.

CONCLUSION

Noise reduction in quadrupolar echo spectra is crucial if one attempts to deconvolute spectra into individual components. We have demonstrated that the shear increase in the number of scans may not be sufficient even when echo transients are collected instead of acquiring the signal after a single pulse. The underlying reasons are (i) the small signal and (ii) the long-lived electronic ringing that is phase coherent with the rf pulses. If the latter cannot be reduced by carefully adjusting the spectrometer hardware, it appears as extra noise illustrated in Fig. 2a. To further suppress this disturbance, one has to use a phase cycle where the created signal is invariant on changing the phase of the rf pulse that generated the phase-coherent ringing. While this has previously been accomplished for ringing induced by the second pulse in the quadrupolar echo sequence, this paper shows how to deal with the ringing that arises from the first pulse in this sequence. With the low-noise spectra achieved by inserting the Exorcycle into the quadrupolar echo sequence, one can deconvolute and analyze the obtained ^{2}H spectrum in terms of molecular order and disorder of the investigaed surfactant/polyelectrolyte complex (*13*). Note that the same benefit (without halving the net signal) also appears in 90°–τ-180°-τ-detection spin–echo experiments performed with short τ. Although the effect of Exorcycle in that pulse sequence has been investigated in detail (*14*), this point has seldom been appreciated (*15, 16*). On the other hand, one should note that the so-called “feed-through” signal (*12, 17, 18*), contibuted by the transverse magnetization that is not refocused by a second pulse either because the flip angle is mis-set to $\theta \neq 90^\circ$ or the pulse is not sufficiently nonselective, is not eliminated by the presented phase cycle in the case of a quadrupolar echo (*10, 11*).

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REFERENCES

1. J. G. Powles and J. H. Strange, Zero time resolution nuclear magnetic resonance transients in solids, *Proc. Phys. Soc*. **82,** 6–15 (1963).
2. J. H. Davis, K. R. Jeffrey, M. Bloom, M. I. Valic, and T. P. Higgs, Quadrupolar echo nuclear magnetic resonance spectroscopy in ordered hydrocarbon chains, *Chem. Phys. Lett*. **42,** 390–394 (1976).
3. J. H. Davis, The description of membrane lipid conformation, order, and dynamics by ^{2}H-NMR, *Biochim. Biophys. Acta* **737,** 117–171 (1983).
4. R. G. Griffin, Solid state nuclear magnetic resonance of lipid bilayers, *Methods. Enzymol*. **72,** 108–174 (1981).
5. K. Schmidt-Rohr and H. W. Spiess, “Multidimensional Solid-State NMR and Polymers,” Academic Press, London (1994).
6. M. Bloom, J. H. Davis, and M. I. Valic, Spectral distortion effects due to finite pulse widths in deuterium nuclear magnetic resonance spectroscopy, *Can. J. Phys*. **58,** 1510–1517 (1980).
7. I. P. Gerothanassis, Methods of avoiding the effects of acoustic ringing in pulsed Fourier transform nuclear magnetic resonance spectroscopy, *Prog. NMR Spectrosc*. **19,** 267–329 (1987).
8. G. Bodenhausen, R. Freeman, and D. L. Turner, Suppression of artifacts in two-dimensional J spectroscopy, *J. Magn. Reson*. **27,** 511–514 (1977).
9. R. L. Vold and R. R. Vold, Separation of single quantum spin echoes by two-dimensional Fourier transform techniques, *J. Magn. Reson*. **42,** 173–176 (1981).
10. I. Furó and B. Halle, 2D quadrupolar echo spectroscopy with coherence selection and optimized pulse angle, *J. Magn. Reson*. **98,** 388–407 (1992).
11. I. Furó, Accurate homogeneous linewidths for quadrupolar nuclei with 2D echo NMR experiments using soft pulses, *Chem. Phys. Lett*. **194,** 435–439 (1992).
12. P. M. Henrichs, J. M. Hewitt, and M. Linder, Experimental aspects of deuterium NMR in solids, *J. Magn. Reson*. **60,** 280–298 (1984).
13. N. Hedin, O. Regev, and I. Furó, Mesomorphic solid-like structures of sulfated extra-cellular polysaccharide-C$_n$TAB compounds, *Prog. Colloid Polym. Sci*. **112,** 140–145 (1999).
14. M. Rance and R. A. Byrd, Obtaining high-fidelity spin-1/2 powder spectra in anisotropic media: Phase-cycled Hahn echo spectroscopy, *J. Magn. Reson*. **52,** 221–240 (1983).
15. C. Brevard, Multinuclear instrumentation and observation, *in* “NMR of Newly Accessible Nuclei, Vol. 1” (P. Laszlo, Ed.), pp. 3–19, Academic Press, New York (1983).
16. A. C. Kunwar, G. L. Turner, and E. Oldfield, Solid-state spin-echo Fourier transform NMR of ^{39}K and ^{67}Zn salts at high field, *J. Magn. Reson*. **69,** 124–127 (1986).
17. H. W. Spiess, Deuteron spin alignment: A probe for studying ultraslow motions in solids and solid polymers, *J. Chem. Phys*. **72,** 6755–6762 (1980).
18. A. D. Ronemus, R. L. Vold, and R. R. Vold, Deuterium quadrupole echo NMR spectroscopy II. Artifact supression, *J. Magn. Reson*. **70,** 416–426 (1986).