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NMR Dipole–Dipole Refocusing with Shaped Pulses

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Sequences of shaped pulses have been successfully used in a number of applications of nuclear magnetic resonance and laser spectroscopy (*1*). These shaped pulses have been designed by analytic calculations, perturbative expansions, or simple computerized optimization. In all of the experimental applications published to date, however, the spin or molecular Hamiltonian could be accurately approximated by a distribution of uncoupled and unrelaxed two-level systems. This is, of course, a stringent assumption, and even in the most favorable cases (high-resolution NMR, magnetic resonance imaging) it provides an ultimate limitation to pulse sequence performance. We show here, for the first time, that shaped pulses provide improved performance in strongly coupled systems as well.

Multiple-pulse sequences have been used to eliminate magnetic dipole–dipole couplings in solids ever since the pioneering work of Waugh, Huber, and Haeberlen (*2*). The coherent averaging formalism they developed led directly to time-reversal (*3*) and two-quantum sequences (*4*) as well. We concentrate here on the two-quantum sequences shown in Fig. 1 for several reasons. They are purely amplitude modulated (pulse phases of 0 and π), which simplifies our calculations; Fig. 1A is a key building block of sequences to pump high-order multiple-quantum coherences (*4, 5*); and it is extraordinarily sensitive to errors because of convergence problems with the Magnus expansion. Typical applications have used peak Rabi frequencies an order of magnitude greater than thc largest couplings to produce successful refocusing.

We started with the simplest possible pulse sequence framework for such a sequence shown in Fig. 1B, and then used average Hamiltonian theory (*6*) to define the necessary constraints on pulse area and symmetry (*8*). The pulse shape was expanded in terms of Legendre polynomials, and then the coefficients of the polynomials were optimized so that the leading error terms appear in $\mathscr{H}^{(2)}$; the exact sequence propagator for two coupled spins was also calculated to check the validity of the Magnus expansion. Figure 1C shows the optimized sequence.

One way to characterize the quality of a two-quantum sequence is to see how phase shifts effect the time evolution. A two-quantum operator (such as $I_{1+}I_{2+} + I_{1-}I_{2-}$) is exactly inverted by a $\phi = \pi/2$ phase shift, since $(\exp(i\pi/2))^2 = -1$. Thus a hard $\pi/2$ pulse, followed by the refocusing sequence shown in Fig. 2A with rectangular or shaped pulses, produces the dipole-coupled equivalent of a Carr–Purcell echo train. For an ideal sequence there would be no time evolution. The exact theoretical perfor-

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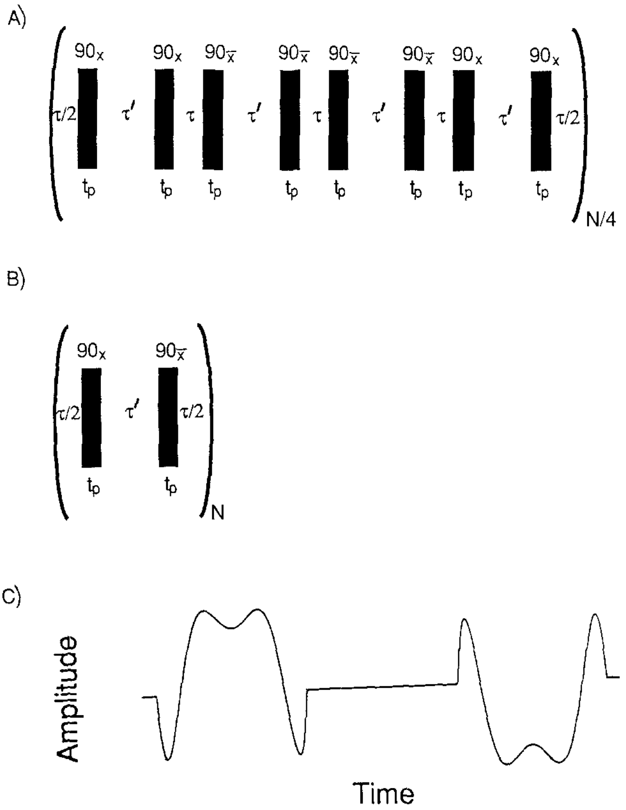

FIG. 1. (A) The standard eight-pulse sequence for two-quantum excitation in dipole-coupled systems. To lowest order the sequence compensates for the errors linear in spin operators. (B) The two-pulse sequence is the simplest two-quantum sequence. However, it does not have compensating properties the eight-pulse sequence possesses. (C) Optimized shaped pulse sequence. The individual pulse is kept symmetric, so the overall sequence is antisymmetric. The sequence therefore makes all odd-order terms in the Magnus expansion vanish (*8*). In all above sequences the relation between the window lengths and the pulse width is given by $\tau' = t_p + 2\tau$.

mance of the shaped-pulse sequence on a two-spin system, compared to rectangular pulse sequences with the same peak power and duty cycle (δ), is shown in Fig. 2B. The peak Rabi frequency (ν_{peak}) was only three times larger than the dipole-coupling constant (D), so errors are obvious, but the pulse shaping provides dramatic improvement.

Figure 3 shows spectra of $\approx$5% CH_2Cl_2 dissolved in the liquid crystal nematic phase of Eastman 15320 at room temperature with acetone-d_6 as the internal lock. All spectra were obtained on a JEOL GX 270 MHz spectrometer with a standard 5 mm ^{1}H probe and with a sample spinning rate at 15 Hz to remove the inhomogeneity of the static field. A QuaTech WSB-10 synthesizer with an internal clocking rate of 200 ns/point was used to generate the nonsquare waveform with a 500 point approximation, as described in previous work (*7*). The top spectrum shows a Pake doublet

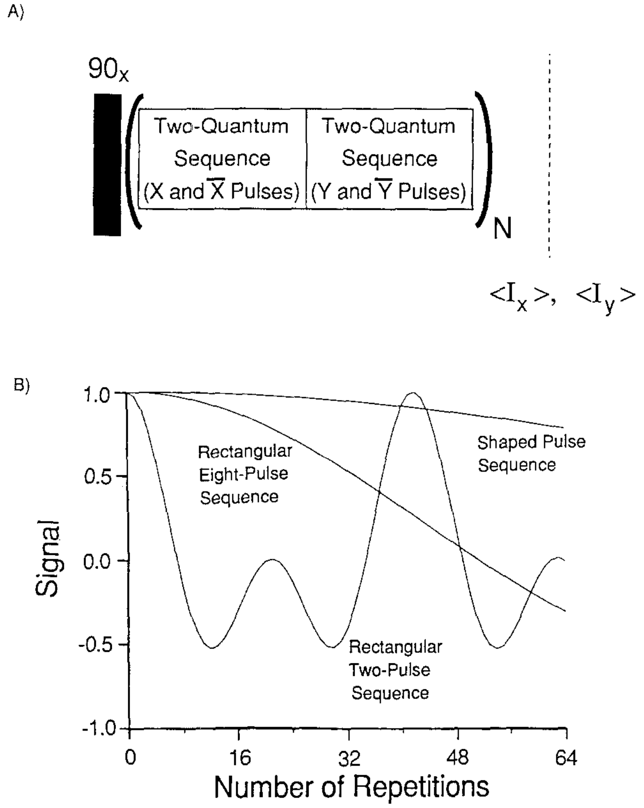

FIG. 2. (A) Schematic diagram for a dipole-coupled analog of the Carr–Purcell sequence. The first block following the prepulse is either the two- or the eight-pulse sequences. The second is the 90° phase-shifted version of the first. (B) Comparison of dipole refocusing performance of the shaped pulse sequence using the shape above with the rectangular two- and eight-pulse sequences for two-quantum excitation. The x magnetization is plotted against the number of repetitions N of the sequences. Parameters used are $\nu_{\text{peak}}/D \approx 2.8$; $\delta \approx 25.8\%$. See text for notation.

with the dipole-coupling constant $D \approx 1.1$ kHz, which results by applying a hard $\pi/2$ pulse followed by a Fourier transform of the free induction decay. The other two spectra result from the free evolution of the spins after one cycle of the sequence shown in Fig. 2A with shaped and rectangular pulses. If the refocusing was perfect, a normal-looking Pake doublet would result. However, both spectra display phase anomalies in the excited peaks due to spin operators such as $I_{1y}I_{2z}$, which are produced by the imperfect refocusing of the sequences. In order to make a fair comparison, we constrained the rectangular and shaped two-pulse sequences to the same peak power ($\approx$4 W) and same average power dissipation ($\delta \approx 25.8\%$); this makes the rectangular pulse sequence shorter than the shaped pulse sequence (545.2 μs for the rectangular pulse and 720 μs for the shaped pulse), which would normally tend to improve performance of the rectangular pulse sequence. With very high peak powers both sequences performed equivalently well; at the power shown here the shaped

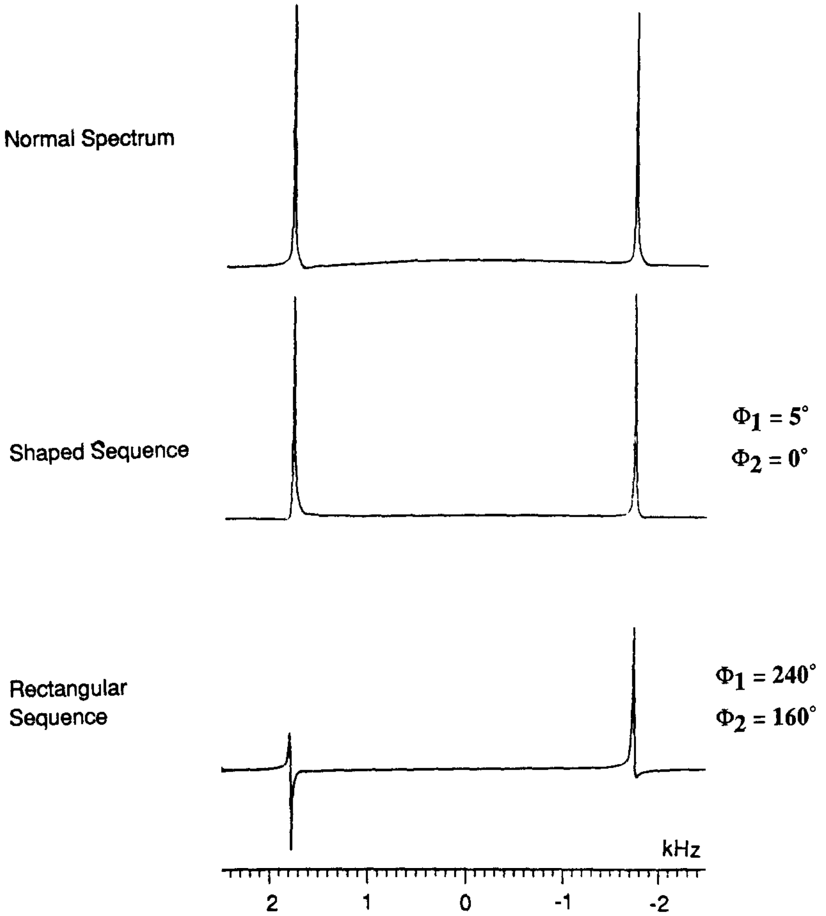

FIG. 3. Experimental verification of the peak power reduction with shaped two-quantum sequence. With a very low peak power ($\approx$4 W) the shaped pulse sequence maintains excellent dipolar refocusing, and thereby produces very small phase errors in the spectrum; the rectangular pulse sequence fails completely at the same peak power. ϕ_1 and ϕ_2 denote phase errors of the left and the right peaks, respectively.

pulse sequence gives rise to very small phase distortions and hence it maintains excellent refocusing (even after multiple repetitions), but the rectangular pulse sequence performs poorly.

In summary, we have shown that complex multiple-pulse sequences can be profitably replaced with shaped RF pulses. While this preliminary demonstration used only two coupled spins-$\frac{1}{2}$, the optimization procedure is valid for an arbitrarily large number of coupled spins. Further improvements are possible in several ways; for example, the two pulses can be made asymmetric if the second pulse is the time-reversed version of the first (*8*), and phase modulation is possible as well. The dimensionless ratio $\nu_{\text{peak}}/D \approx 2.8$ was intentionally made small here to demonstrate the limits of performance. This ratio was much larger (>15) in Ref. (*4*) to produce satisfactory refocusing with rectangular eight-pulse sequences. This implies a factor of 30 lower peak power here. The necessary time resolution to generate desired waveforms and necessary peak powers to work with state-of-the-art solid-state spectrometers can be obtained with commercially available components (*1*). Thus, we anticipate that pulse shaping will tremendously enhance capabilities for high-resolution NMR in solids.

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