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New, Compensated Carr–Purcell Sequences

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New, compensated Carr–Purcell pulse sequences are reported, all based on x and y phase alternation of the π pulses. The sequences compensate cumulative pulse errors for all three components of magnetization. Applications include the measurement of homonuclear dipole coupling in the presence of chemical shifts and the measurement of heteronuclear dipole coupling in magic-angle spinning experiments (REDOR). The performance of the new pulse sequences is compared experimentally to previously reported schemes.

The Carr–Purcell pulse sequence is the original repetitive pulse train in magnetic resonance (*1*). For the measurement of T_2 from the envelope of echo peaks, Meiboom and Gill showed that the cumulative effects of π pulse errors can be removed by phase shifting the initial $\pi/2$ pulse (*2*). That is, π pulses along the x axis preserve the x component of magnetization M_x despite pulse imperfections. However, M_y and M_z are rotated about the x axis by the CPMG pulse train and rapidly dephase from the effects of H_1 inhomogeneity and resonance offsets.

There are several applications for Carr–Purcell-like sequences which preserve all three components of magnetization (*3*). Exact π pulses leave the homonuclear dipole interaction unchanged but refocus chemical shifts. Therefore, the envelope of the Carr-Purcell echo peaks of a system with homonuclear dipole and chemical-shift interactions is simply the homonuclear dipole free-induction decay, just as though the chemical shift were absent (*4*). This simple result allows distances to be determined, despite the presence of chemical shifts.

However, there are restrictions to the experiment. The effects of the chemical shift must be removed at *all* times, not just at the echo peaks, because the chemical shift and dipolar Hamiltonians do not commute [a similar effect occurs for J couplings in liquids (*5*)]. Satisfaction of this requirement implies the echo spacing 2τ must be small compared to the chemical-shift dephasing time: $\Delta\omega_{cs}2\tau \ll 1$. Also, the dipole interaction involves all three components of magnetization (*5, 6*).

$$\mathscr{H}_D \sim I_{z1}I_{z2} - I_{x1}I_{x2}/2 - I_{y1}I_{y2}/2. \qquad [1]$$

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Imperfect π_x pulses will scramble I_y and I_z. Because the spin coordinates are weighted differently, $\mathscr{H}_D$ will be affected by the pulse errors. The condition $\Delta\omega_{cs}2\tau \ll 1$ requires a large number of pulses, causing a potentially large cumulative effect of pulse errors on the dipole interaction. Engelsberg and Yannoni have reported very successful experimental determinations of dipole interactions using CPMG pulse sequences (*4*). There, pulse errors are eliminated by using a specially designed NMR coil with a highly homogeneous H_1.

A second application is the determination of heteronuclear dipole couplings (I_zS_z) in solids while magic-angle spinning. Ordinarily, this interaction is averaged to zero by the spinning. Application of π pulses to one or both spins, synchronous with the spinning, returns the dipole interaction. The experiments are REDOR, rotational echo double resonance (*7, 8*). One of us (T.G.) has performed REDOR experiments with a train of π pulses applied to each of the nuclei. The pulse train on the observe nucleus (e.g., ^{13}C) must compensate the transverse components of the magnetization. The pulse train on the unobserved nucleus (e.g., ^{15}N) must compensate the respective z component of magnetization. With uncompensated pulse sequences, large offset dependences have been observed in such REDOR spectra. These REDOR experiments are an application of π pulse trains that compensate all three components of magnetization.

Maudsley has previously noted that certain imaging experiments could benefit from a Carr–Purcell type of pulse sequence (*9*). Because precessional phase carries spatial information, it is important that the π pulse train be equally effective for M_x and M_y.

With these applications in mind, we report new, Carr–Purcell pulse sequences which are compensated for all three components of magnetization. We note that all rotations leave the magnitude of magnetization unchanged. So, any pulse sequence that preserves two components must also preserve the third.

EXPERIMENTAL

The experiments reported here were performed at 53.14 MHz on a water sample lightly doped with Cu^{2+}. The frequency width was adjusted by locating the sample approximately 5 cm radially from the center of the iron pole caps. The spectrometer frequency was always centered in the resulting broad line. The sample was in a 5 mm diameter tube and was restricted to the middle 6 mm of a 12 mm long solenoidal coil. The resulting very good H_1 homogeneity was useful in the tests reported here. In the envisioned applications, the present results indicate that such high H_1 homogeneity should not be required.

The x and y channels of the transmitter were about 3% different in RF amplitude. The phase shift differed from 90° by about 2°. The 180° phase shift was ideal by comparison, with no detectable amplitude change.

Simulations were performed on a Macintosh IIci computer. The calculations took into account off-resonance effects during the pulses and also included RF inhomogeneity.

RESULTS AND DISCUSSION

All of the pulse sequences considered here have the Carr–Purcell timing (*1*):

$$\pi/2 — \tau — \pi — 2\tau — \pi — 2\tau — \cdots,$$

with echoes forming between the π pulses. The several sequences differ only in the RF phases of the π pulses and are specified in Table 1. Each sequence is performed for both initial magnetization M_x and M_y, from $\pi/2$ pulses of phases $\bar{y}$ and x, respectively.

Figures 1a and 1b show the quadrature detected data from the Carr–Purcell sequence with initial magnetizations M_x and M_y, respectively. Only the echo peaks are shown and all peaks are displayed. As is well known and shown in Fig. 1a, M_x is preserved by this sequence (*2*), but the initial M_y in Fig. 1b rapidly dephases from nonnegligible H_1 inhomogeneity and resonance offsets (note the shorter time scale). The dephasing depends primarily on the number of pulses. Throughout Figs. 1 and 2, the duration of nominal π pulses is 9.5 μs and the inhomogeneous linewidth results in a $1/e$ decay time of the nonexponential FID of 40 μs. The echoes are spaced with a time 2τ of 50 μs; 700 echoes are displayed. These conditions were chosen with the proposed application to the homonuclear dipole measurement in mind.

Now, we turn to a search for a Carr–Purcell-like sequence which preserves all three components of magnetization. The basic set of π pulses must act like the identity operator over a reasonable range of resonance offsets and H_1 inhomogeneity. As suggested by the results in Figs. 1a and 1b, this set must contain pulses with different phases. It is known that a string of π pulses alternated in phase by 180° performs poorly in restoring z magnetization, thereby eliminating it as a candidate for the identity operator (*10*). Another possibility is to use π pulses of both x and y phases. First, consider the sequence XY-4 (see Table 1; four pulses are needed to form the identity since $\pi_x\pi_y$ is the same as π_z, for ideal pulses). The sequence was previously suggested and its performance examined by numerical calculation by Maudsley (*9*). Figures 1c and 1d show the results of XY-4. Clearly, both components of transverse magnetization are treated equally. An immediate improvement over the Carr–Purcell sequence is obtained, but XY-4 falls far short of the ideal results obtained by the Meiboom–Gill modification of Fig. 1a, where only true T_2 decay occurs. In Figs. 1c and 1d, a beat is clearly evident in the echo envelope, showing that the magnetization slowly rotates in the x–y plane. We verified that a deviation from 90° of the transmitter phase shift causes part of this effect.

The above rotation of magnetization can be reversed with the $(yxyx)^n$ sequence. This reversal and computer simulations suggest the sequence XY-8 (see Table 1). The data from XY-8 displayed in Figs. 1e and 1f show a clear improvement in the ability to preserve the magnetization. Once again, both components of magnetization

TABLE I

Phases of Refocusing Pulses

Sequence name	RF phases
Carr–Purcell or CPMG	$(x)^n$
XY-4	$(xyxy)^n$
XY-8	$(xyxy\ yxyx)^n$
XY-16	$(xyxy\ yxyx\ \overline{xyxy}\ \overline{yxyx})^n$
MLEV-4	$(xx\overline{xx})^n$
MLEV-8	$(xx\overline{xx}\ \bar{x}xx\bar{x})^n$
MLEV-16	$(xx\overline{xx}\ \bar{x}xx\bar{x}\ \overline{xx}xx\ x\overline{xx}x)^n$

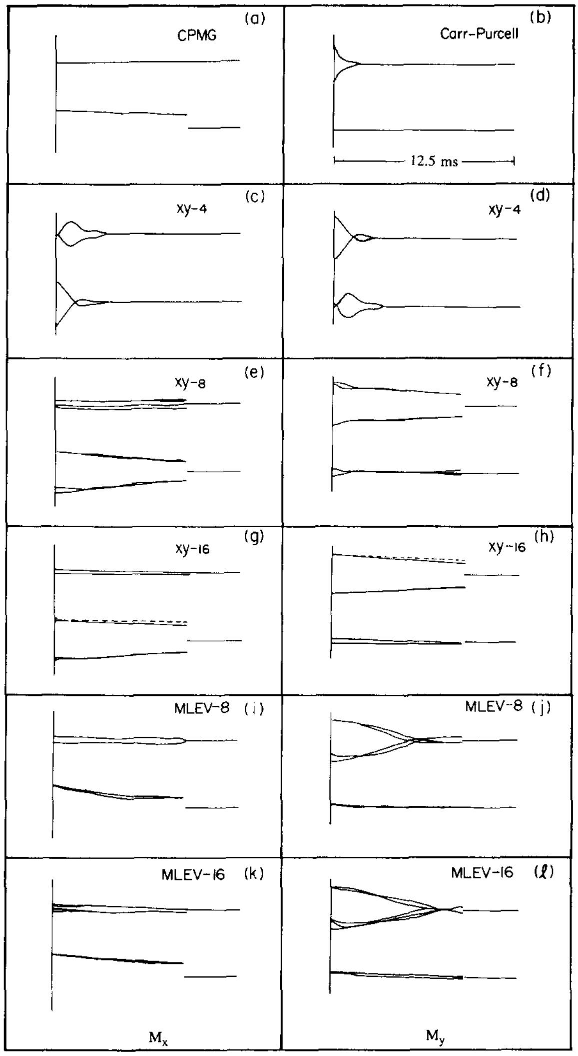

FIG. 1. Performance comparison of several Carr–Purcell-type pulse sequences. In each case the quadrature-detected signals are from an inhomogeneously broadened water sample. Only the echo peaks are shown. The left-hand traces are for an initial $(\pi/2)_{\bar{y}}$ pulse; the right-hand traces use $(\pi/2)_x$. The traces are all 50 ms long with $2\tau = 50$ μs (700 echoes are shown). The RF phases of the π pulses are specified in Table 1. The time axis of (b) has been expanded because of the rapid decay. The envelope of (a) (CPMG) is superimposed onto (g) and (h) for comparison.

are treated equally and the sequence begins to approach the stability of the echo train provided by CPMG. We note that, for ideal π pulses, $\pi_x\pi_y = \pi_z$ and $\pi_y\pi_x = \pi_{\bar{z}}$ [see for example Ref. (*11*)]. Then, the sequence XY-8 is just $(zz\bar{z}\bar{z})^n$ and resembles (*12*) MLEV-4. For slightly nonideal pulses, the argument is still correct.

Further simulations suggested even better compensation from the XY-16 sequence (see Table 1). The data for XY-16 are shown in Figs. 1g and 1h. The performance of XY-16 is comparable to that of CPMG, as shown in Figs. 1g and 1h by the dashed curves. Unlike CPMG, however, XY-16 treats both transverse components of magnetization the same. In this regard XY-16 is vastly superior to CPMG for the applications discussed above.

Not surprisingly, the XY-8 and XY-16 sequences are predetermined by the selection of the XY-4 sequence. The expansion of the pulse sequence (from 4 pulses to 8 to 16) to obtain higher-order corrections of the pulse train follows the same rules used to determine good decoupling sequences for high-resolution NMR (*10, 12–14*). The most familiar sequences are the MLEV (*12*) and WALTZ (*10*) collections. The theory of the expansion procedure is well developed. In principle, XY-32 and higher are easily determined. Since our desire is to keep the sequence as short as possible and since the performance of XY-16 approaches CPMG, experiments on XY-32 have not been performed.

Shaka *et al.* previously reported the use of MLEV Carr–Purcell pulse sequences (*3*). We show the results of MLEV-8 and MLEV-16 in Figs. 1i, 1j and 1k, 1l, respectively. The results of the MLEV-4 sequence are not shown, because of its poorer performance. Shaka *et al.* showed the MLEV-16 sequence to treat both transverse components of magnetization equally (they followed approximately 64 echoes). However, with *our experimental conditions,* none of the MLEV sequences treats M_x and M_y identically (as does XY-16). For the first part of the echo train, the MLEV sequences behave well, treating M_x and M_y identically, in agreement with previous results. For longer times, the MLEV-16 sequence continues to compensate M_x but fails to compensate M_y. We emphasize that we have restricted ourselves to conditions similar to the intended solid-state conditions. Experimentally we find that the compensation provided by MLEV-16 improves with weaker H_1 (i.e., longer pulses), but is independent of the presence of large resonance offsets. In fact, our computer simulations showed the behaviors of MLEV-16 and XY-16 to be nearly identical over a wide range of offsets and H_1 inhomogeneity. We attribute the experimental decay with MLEV-16 to pulse imperfections not included in our simulations (such as phase glitch) which are apparently compensated by XY-16.

The tolerance to nutation angle errors of XY-16 becomes smaller with increasing number of pulses, naturally. Presented in Fig. 2 is the time evolution of the magnetization as the pulse length is varied from a nominal π pulse of 9.5 μs. This sequence works best with nutation angles about 10% greater than π (π as determined by the original CP sequence of Fig. 1b). The extent of "line narrowing" evident in Fig. 2 is large: the FID decays in 40 μs and the echo train extends much longer than the 35 ms shown (700 echoes). The T_2 decay of the sample can be seen in Fig. 1a and is superimposed on Figs. 1g and 1h for comparison.

For completeness, we note that the CPMG sequence of Fig. 1a is still the best choice for T_2 measurements. This sequence can be regarded as a pulsatile spin lock and results in a truly static fraction of the initial M_x. The fractional amplitude depends on offset, pulse spacing, and pulse length. The existence of a static M_x (aside from true T_2 decay) even with very small refocusing pulses demonstrates that CPMG preserves M_x in a very different fashion than the MLEV and XY sequences studied here.

CONCLUSIONS

The Carr–Purcell-type sequences XY-4, XY-8, and XY-16 have similar behavior for initial x and y spin magnetizations. The best sequence reported here is 16 pulses

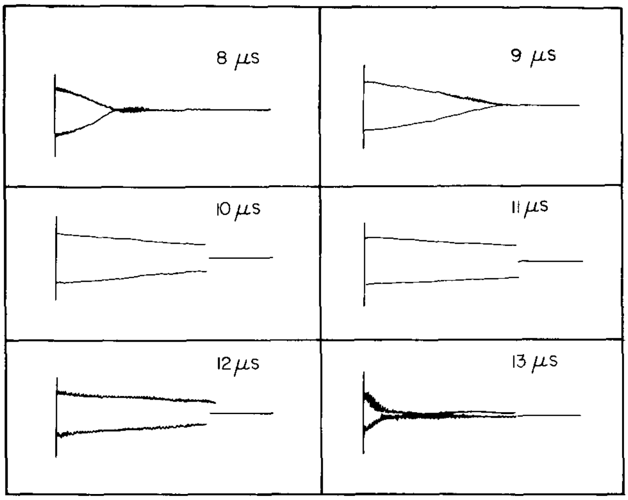

FIG. 2. Data from the XY-16 pulse sequence (as in Figs. 1g and 1h). The duration of the refocusing pulses is marked in each box; H_1 is constant. From the Carr–Purcell sequence of Fig. 1b, the duration for exact π pulses is 9.5 μs. Each trace is 50 ms long and only the in-phase detected signal is shown.

long and compensates M_x and M_y better than previously reported schemes. The new pulse sequences, which appear to be in the same class of sequences as the MLEV and WALTZ, should find application in the measurement of homonuclear interactions when chemical shifts are present. A second application is the determination of heteronuclear dipole couplings in magic-angle spinning solids.

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