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Composite Pulses in Time-Domain ESR*

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Recently, new and important Fourier transform (*1–4*) and two-dimensional Fourier transform ESR (*1, 3, 5*) techniques have been developed which have the promise of revolutionizing ESR as they have NMR. The techniques have been described in detail and have been successfully applied to the class of nitroxide ESR spectra (*1, 3, 6*). A fundamental problem is the competing requirements of (1) delivering a large enough rotating microwave B_1 field at the sample to irradiate the whole spectrum (i.e., $2\gamma_e B_1 \geqslant \Delta\omega_s$, where $\Delta\omega_s$ is the spectral extent) and at the same time (2) having a resonator with a low enough Q_L (loaded Q) that the short pulse of width t_p required for a $\pi/2$ (or π) rotation of the spins (i.e., $\gamma_e B_1 t_p = \pi/2$) is not significantly distorted. That is, we require that the half-power full bandwidth of the resonator, $\Delta\omega = \omega/Q_L$, obey $\Delta\omega \geqslant \Delta\omega_s$. The problem, of course, is that for a given power, P_0 incident on the resonator, B_1 and Q_L are intimately related (*7*) by $P_0 = \mu_0 V_c B_1^2 \nu / 2Q_L$, where ν is the resonator frequency and V_c is the effective volume.

From the above comments we can then state that the power required to irradiate the spectrum obeys $P_0 \propto \Delta\omega_s^3$ (*3*). Gorcester and Freed (GF) (*3*) found for their 2D FT ESR spectrometer with a cavity resonator and TWT output of 1 kW that the optimum bandwidth was achieved with a B_1 of 6 G (t_p = 14 ns for a $\pi/2$ pulse) and a $Q_L \approx 100$ for which $\Delta\omega/2\pi$ = 95 MHz, corresponding to uniform spectral rotation over a bandwidth of about 34 MHz ($=\gamma_e B_1/\pi$). Nevertheless, they succeeded in obtaining wideband excitation for a motionally narrowed nitroxide with spectral extent, $\Delta\omega_s$ = 90 MHz. However, the single-pulse FID leads to an FT spectrum with outer hyperfine lines of reduced intensity (i.e., 50–60% of the central line). In a three-pulse 2D FT spectrum (i.e., 2D ELDOR), this attenuation of the outer peaks goes approximately as the cube of the attenuation of the simple FT spectral line. While appropriate corrections may be made for this effect in the analysis of the experiment, it does lead to reduced sensitivity.

An even more serious problem arises in attempting to perform FT experiments on slow-motional nitroxide spectra. These have a spectral extent of $\Delta\omega_s/2\pi \approx 220$ MHz

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which would require at least a 14 G B_1 field (for $t_p = 6$ ns) and a $Q_L \approx 40$ for spectral coverage comparable to what was achieved in the case of a motionally narrowed nitroxide. This is impossible to achieve in the spectrometer described by GF; an order of magnitude increase in P_0 would be necessary.

GF point out two ways to circumvent these problems and achieve wider band coverage. First of all, the implementation of a loop-gap resonator (*8*) should enable the generation of larger B_1 fields because of its high conversion efficiency. However, such loop-gap resonators must be stabilized against electrical breakdown because of the large microwave powers used. Second, it is possible to shape pulses which produce more uniform coverage across the spectrum than the simple rectangular pulses referred to above. Pulse shaping, particularly by use of composite pulses, is well known in NMR (*9*), but has until now not been employed in pulsed ESR. While this is due, in part, to the relative youth of FT ESR, it is also true that composite-pulse technology is much more challenging for ESR, where one must use microwave (rather than RF) technology, and the elementary pulses in a composite pulse, which must be very accurate, are on the nanosecond time scale. Furthermore, short FID T_2^* values (and T_2 values) limit the length of time available for a composite pulse made up of many elementary pulses.

In the present Communication we report our results on the successful implementation of composite ESR pulses optimized for ESR conditions in conjunction with the use of a particular type of loop-gap resonator which satisfies the criteria noted above.

In order to select pulse shapes that would meet the constraints of pulsed-ESR technology, we first considered the problem theoretically. We initially solved the standard Bloch equations in the presence of an irradiating field and with T_1 and T_2 relaxation present. The rotating field $\mathbf{B}_1(t)$ was allowed to have an arbitrary time dependence both in amplitude $|\mathbf{B}_1(t)|$ and in phase. We took account of the filtering effect of the finite Q_L of the resonator by convoluting $\mathbf{B}_1(t)$ with the function $\exp[-\omega t/2Q_L]$. The resulting Bloch equations with time varying irradiation were integrated numerically at each frequency offset. An efficient algorithm (*10*) allowed us to introduce a nonlinear constrained optimization scheme (*11*) in order to optimize the pulse shape. The principal constraint is in the maximum amplitude ($B_{1\max}$) of the available magnetic field, $|B_1(t)|$.

In order to consider general pulse shapes, we first expanded $B_{1x}(t)$ and $B_{1y}(t)$ each in terms of up to 10 Hermite functions (*12*) (and utilized an arbitrary finite segment of these functions). The optimization of so many parameters necessitated the use of the Cornell National Supercomputer Facility (CNSF). The best results we achieved (both for composite π and $\pi/2$ pulses) led to fairly uniform pulse amplitudes with phases that jump between about 0° and 180°. Given that we maintained $B_{1\max}/\Delta\omega_s < 1$, it is not surprising that the optimization seeks to maintain $|\mathbf{B}_1(t)| = B_{1\max}$ in order to provide the best spectral coverage. That the optimized phases are close to 0° or 180° was somewhat surprising.

Given these results, as well as experimental considerations, we chose to consider composite pulses produced from a sequence of elementary square pulses (with correction for finite Q_L) of the same amplitude, $B_{1\max}$. Each elementary pulse varies only in its phase, either 0° or 180°, and in its duration. In fact, simple composite pulses of

TABLE 1

Some Illustrative Composite Pulses

Pulse type	Duration (in ns) and phase of components[a]	Bandwidth in units of B_1	Mean deviation[b]	Maximum deviation[c]
$z \rightarrow xy$	11.9, $\overline{5.8}$, 3.0	5.0	0.005	0.043
$z \rightarrow y$	14.8, $\overline{19.4}$, 5.0, $\overline{15.4}$, 10.6	4.0	0.10	0.31
$z \rightarrow y$	41.0, $\overline{14.8}$, 34.6	2.9	0.034	0.10
$z \rightarrow -z$	30.7, $\overline{10.3}$, 7.4, $\overline{20.4}$, 14.3	4.7	0.13	0.32
$y \rightarrow -z$	8.6, $\overline{6.5}$, 24.6, $\overline{21.1}$	3.9	0.12	0.21

[a] The overbars imply phase shifting by 180°.

[b] This measures the average deviation from perfect coverage across the bandwidth for the relevant normalized magnetization (i.e., range of 0 to 1); e.g., for $z \rightarrow xy$ the deviation is of the normalized transverse magnetization.

[c] This gives the maximum deviation at any point in the bandwidth (typically found at the wings). Units as in footnote *b*.

this type can be realized experimentally with current ESR technology (see below). To further simplify the analysis, we used the well-known solution to the equation of motion of the magnetization under a simple RF field (*13*), thus ignoring spin relaxation. A simple FT of the composite pulses is, of course, inappropriate because of the nonlinear nature of the response of the spins (*9*). This leads to a much faster algorithm and thereby permitted more extensive computer searches, which proved to be necessary, since this model of composite pulses yielded many local optima. Thus, the nonlinear optimization had to be repeated many times with different seed values (chosen randomly) in order to seek the best composite pulse. We considered a maximum of $n = 5$ elementary pulses, since that corresponded to our present experimental limit. Such a procedure did uncover composite pulses with significantly extended coverage. For example, we give in Table 1 an $n = 5$ composite π pulse which provides rather uniform coverage over a spectral band for which $\Delta\omega_s/\gamma_e B_1 = 4$. This result has about twice the coverage of a previously reported five-component pulse with unconstrained phases (*14*) and compares very well with results predicted for very complicated pulse sequences (based upon more elegant analysis) for NMR (*14*) which would be impossible to execute for ESR.

Our experiments were performed on our 2D FT ESR spectrometer (*3*), modified to permit composite pulsing. This required the installation of a microwave circuit enabling rapid phase shifting by 180° within a single overall pulse. The composite-pulse generation hardware, shown in Fig. 1a, was installed between the microwave klystron and the phase shifter (used to set the phases of the pulses in a multipulse experiment). The klystron signal is first routed, by means of a three-port circulator, to a fast ECL driven switch. This switch either passes the cw signal to a continuously adjustable phase shifter followed by the 0° port of a combiner or reflects it back through the circulator to a second path through a variable attenuator to the 90° port of the combiner. With proper adjustment of the attenuator and phase shifter, the signals from the two paths differ by only a 180° phase shift after recombination.

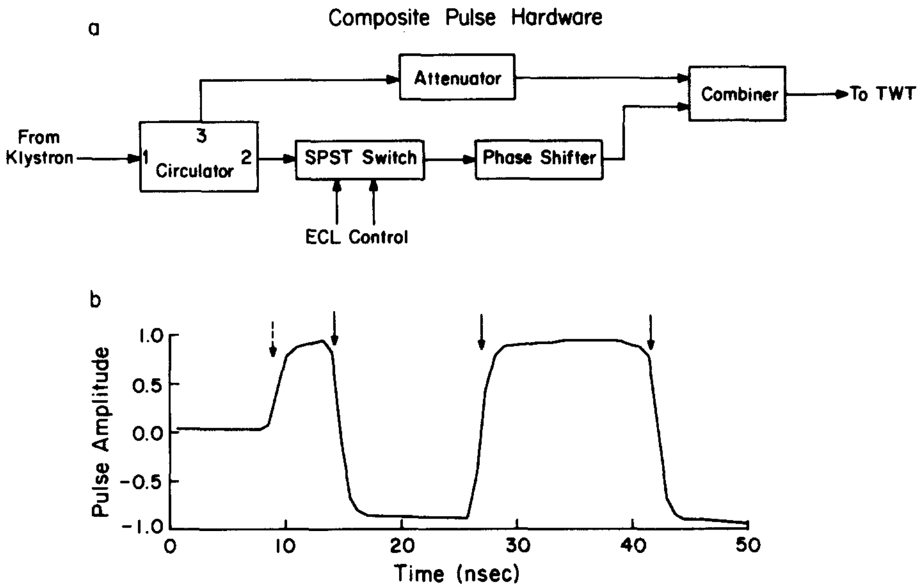

FIG. 1. (a) Layout of the hardware used to produce the composite pulses in this study. The reflective microwave switch was from New England Microwave, and the required complementary ECL logic inputs were obtained from a Precision Instruments, Inc., four-channel digital delay generator. (b) Phase-sensitive detection of a typical composite pulse supplied to the input to the TWT. The vertical solid arrows indicate 180° phase shifts; the vertical dashed arrow represents the turning on of the microwave power.

The ECL control for the switch was provided by combining the pulse outputs from a four-channel digital delay generator. The leading edges of each of the four pulse outputs can signal a 180° phase shift, and the existing logic and switching capability of the spectrometer provide for the rising and falling edges of the composite pulse. Thus, this combination could provide a pulse of $n \leq 5$. The switch transition time is about one to two nanoseconds, and the delay adjustment could be made in 10 ps steps. It was possible to carefully examine the detailed shape of the composite pulses to better than 100 ps time resolution utilizing the HP54100A sampling oscilloscope, which receives the signal from the quadrature mixer of the spectrometer (*3*), by sending the composite pulse directly to the mixer. A typical observation is shown in Fig. 1b for the in-phase arm, with the reference phase of the quadrature mixer appropriately adjusted to optimize this arm. The clean transitions (seen in Fig. 1b) when the microwave signal is turned on and when the phased is shifted by 180° are consistent with the specifications of the components, and we observe very little phase noise or ringing in either the input to or the output from the high-power TWT.

We have found that the bridged loop-gap resonator (BLGR) design by Pfenninger *et al.* (*15*) is appropriate for present purposes. We modified the construction to provide the lower Q values and to permit easy adjustment of its resonant frequency and Q. Our BLGR was constructed from standard 5 mm NMR glass tubing (o.d. = 5 mm, i.d. = 3.5 mm). It had two gaps (and bridges). Conducting silver paint was used to paint the inner conducting surface, and two gaps were carefully scratched about

0.5 mm wide on the inner surface. The bridges were then painted on the outer surface covering these gaps and shaped with a razor blade. The BLGR was mounted on the end of a clear NMR tube through which the sample could be admitted. This structure was contained in a brass box with a cylindrical metal insert to prevent radiation of the microwave energy. Coupling was accomplished with a SMA feedthrough to a ring of wire about the same diameter as the BLGR and situated below it. The resonant frequency could be adjusted by varying the width of the bridge, and a value of Q in the range 20–100 could be obtained by controlling the thickness of the paint layer. This structure can readily handle high incident power without sparking. The BLGR utilized in this study had a matched $Q_L \approx 45$, and we obtained a $B_{1\max}$ of 14 G which was uniform to within 20% over the length of the BLGR. Using this resonator, it was possible to obtain nearly uniform coverage over a motionally narrowed (90 MHz) nitroxide spectrum (see Ref. (*16*)) with just a simple $\pi/2$ pulse.

Our procedure was first to compute an optimum composite $\pi/2$ pulse and then to set up the corresponding pulse experimentally. We used a sample of PD-Tempone in toluene at room temperature (*1, 3*) to study the magnitude of the magnetization in the x–y plane, which could be obtained from the quadrature detector. We "fine-tuned" the actual B_1 and the pulse component widths. In general, the best results were obtained with experimental pulse lengths that were a little shorter (longer) than those in the simulation for the higher (lower) power cases, undoubtedly due to experimental factors (see below) not included in the simulations. We show in Fig. 2 results for three different composite pulses of $n = 4$, each with different B_1 and optimized to maximize the rotation of spins into the x–y plane across a $\pm 2.8\,B_1$ spectrum.

The computed composite pulse, in each case, showed significantly improved spectral coverage as compared to a single experimental $\pi/2$ pulse. Also, in each case, the experimental result from the $n = 4$ composite pulse shows a clear improvement over the single-pulse result. In general, however, the relative effectiveness of the composite pulse is less, the greater the value of B_1. We have found from calculations that this is largely due to the Q of our BLGR with its half-power half-width of 100 MHz. The theoretical computations do not include the effect of the finite Q on the signal *from* the resonator (just the effect on the pulse shape into the resonator), and hence will show what appears to be greater coverage. The finite (1 ns) switching times of the ECL driven switch may also contribute as well as the (small) $B_{1\max}$ variation in the BLGR.

Several other very effective composite pulses (based on undistorted component square pulses) obtained from our computer analysis are summarized in Table 1. We plan to investigate them in future experiments.

We also note that it would be difficult to produce high-power pulses of varying amplitude. It is not difficult to vary the amplitude of the microwave signal to the TWT pulse amplifier, but this amplifier is usually operated at saturation (to minimize amplitude noise) and is thus rather insensitive to amplitude variations in the input microwave signal.

In conclusion, we have demonstrated that composite pulses can be successfully employed in time-domain ESR to enhance spectral coverage. Also, we have shown that this approach, in conjunction with a specially designed BLGR, can now provide

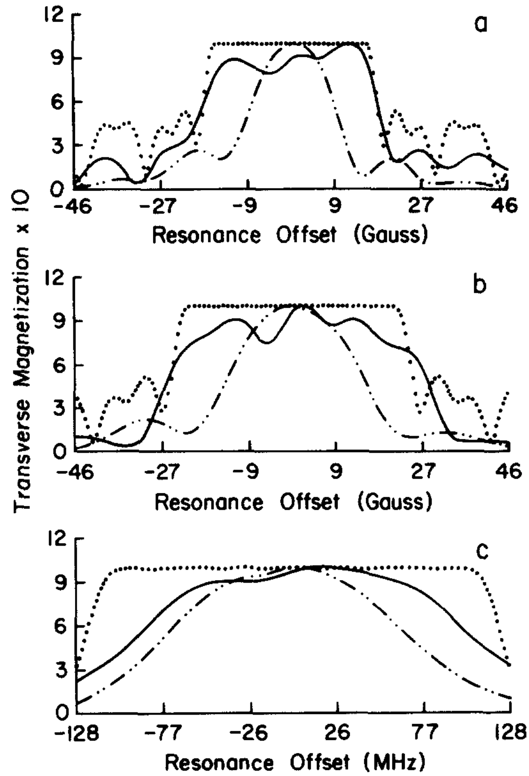

FIG. 2. A comparison of the extent of magnetization rotated into the x–y plane (i.e., $M_{xy} \equiv |M_x^2 + M_y^2|^{1/2}$) by a simulated composite $\pi/2$ pulse (· · ·), an experimentally generated composite pulse (—), and an experimental single-component pulse (-· -·-· ·) at different B_1 levels. (a) B_1 of 4.23 G: experimental composite pulse (30 ns $\overline{15}$ ns 12 ns $\overline{6}$ ns), simulated composite pulse (29.3 ns $\overline{15.2}$ ns 12.5 ns $\overline{7.8}$ ns), single-component $\pi/2$ pulse (27 ns). (b) B_1 of 6.0 G: experimental (19 ns $\overline{9}$ ns 8 ns $\overline{4}$ ns), simulated (21.0 ns $\overline{11.0}$ ns 9.2 ns $\overline{6.2}$ ns), single-component (19 ns). (c) B_1 of 11.0 G: experimental (9 ns $\overline{5}$ ns 4 ns $\overline{3}$ ns), simulated (11.8 ns $\overline{6.2}$ ns 5.4 ns $\overline{4.4}$ ns), single-component (9.4 ns). The component widths are given in the order in which they are applied to the BLGR. The B_1 values are estimated from the pulse durations required to rotate the spins on resonance by $\pi/2$. Note that the experimental results (but not the simulated ones) show the effects of the finite Q on the signal *from* the BLGR. The abscissa is scaled equally for all three plots and labeled in gauss or megahertz for comparison.

effective (although nonuniform) coverage over at least a 200 MHz spectrum. Considerable further improvement in coverage can be expected from these simple phase-alternating composite pulses based upon the theoretical predictions with careful choice of resonator Q and (perhaps) improved switching times.

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