# Multipulse sequences in electron-spin echoes

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(Received 28 March 1983; accepted for publication 5 June 1983)

A method is described whereby Carr–Purcell (CP) multipulse sequences may be generated at a rate rapid enough for electron-spin echoes ESE and in a manner consistent with constraints of typical ESE spectrometers. Both Carr–Purcell–Meiboom–Gill and alternating phase-CP sequences may be produced. It is shown how such sequences may be utilized (1) to increase the rate of data collection, which is especially important in laser photo-induced experiments, and (2) to study slow motions. They are respectively illustrated with results on transient spin-polarized photoelectrons and electrons trapped in irradiated quartz.

PACS numbers: 07.58. + g, 61.16.Hn, 76.30. − v, 43.35.Rw

In recent years there has been a growing interest in applying electron-spin echo (ESE) techniques to studies of transient species[1,2] and more recently to slow-motional studies.[3] These previous studies have employed the usual two pulse: 90°-$\tau$–180°-$\tau$ echo sequence,[4,5] in order to obtain the phase memory time $T_M$ by stepping $\tau$.

In the study of transient species such as these generated with a pulsed laser, a major inhibiting factor in rate of data collection is the low repetition rate of the laser (30–100 pps) but with about the same average power over this range) combined with a *single* two-pulse echo sequence after each laser pulse. This makes the experiment a very time consuming one. In order to overcome this problem, one must maximize the data collected after *each* laser pulse. This may be done by resorting to multipulse sequences such as modified Carr–Purcell sequences, which are commonly used in NMR spectroscopy,[4,5] but have not previously been used in modern high-power ESE spectroscopy.[6] These are 90°-$\tau$–180°-2$\tau$–

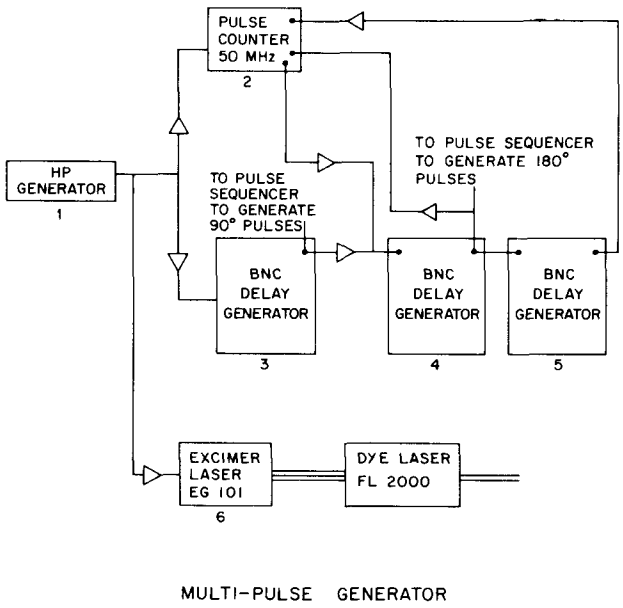


FIG. 1. Diagram of a multipulse sequencer. A HP generator synchronized the pulse counter, the delay generators, and the dye laser pumped by the excimer laser. After being triggered, the BNC delay generator No. 3 causes sequential triggering of the BNC delay generators No. 4 and No. 5. The pulse from No. 5 is fed back to the pulse counter which generates a pulse that triggers No. 4. This cycle continues until the desired number of times of triggering BNC (No. 4) is achieved. This delay generator (No. 4) is the one that triggers the 180° pulse generator. The required delay between the laser and the first 90° is controlled by BNC No. 3.

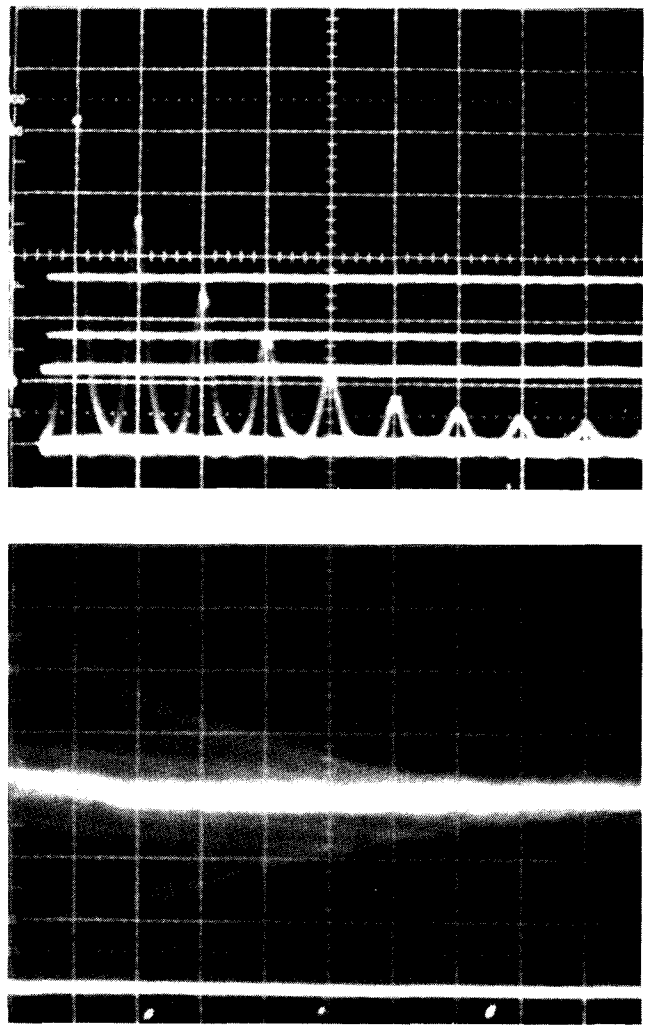

FIG. 2. Both photos are ESE for an irradiated quartz sample; they show the effect of the Carr–Purcell sequence on the measured $T_M$. Upper photo: Normal 90°–180° echoes. The time $\tau$ is stepped and a sequence of echoes is obtained which are superimposed on the photo. Each division of $x$ axis equals 1.5 $\mu$s and $T_M = 7.5\,\mu$s. Lower photo: Carr–Purcell sequence with alternating phase. Each division of $x$ axis equals 20 $\mu$s and $2\tau = 1\,\mu$s with $T_M^{CP} = 25$ $\mu$s.

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180°-2$\tau$—sequences in which either (a) the phase of the 180° pulses are alternately shifted by 180° or (b) the first 90° pulse is phase shifted by 90° (Carr–Purcell–Meiboom–Gill or CPMG). In this work we introduce a method that allows us to produce such sequences, employing pulses as narrow as 10–15 ns and peak power of 1 kW. We demonstrate some applications as well. These include the study of photo-induced transient radicals and also the study of slow motions.

In order to produce multipulse sequences it was necessary to modify the pulsing system of our ESE spectrometer.[7,8] The block diagram in Fig. 1 shows how three BNC delay generators[9] combined with a pulse counter can be used to generate such sequences. The three BNC generators are used as follows. BNC-3 provides the first 90° pulse with a programmable delay with respect to the initial laser pulse. It also triggers BNC-4, which plays a triple role: (1) it triggers the pulse sequencer to generate a 180° pulse with a programmable delay; (2) its output pulses are counted by the pulse counter (2); and (3) it triggers BNC-5. The function of BNC-5 is to generate a pulse that can activate an "AND" gate in the pulse counter to generate a new pulse that will reactivate BNC-4. This process continues until the predetermined number of pulses from BNC-4 (generating the 180° pulses) has been counted.

The master clock (HP generator) typically produces a 10–20-$\mu$s pulse, with the leading edge acting as the initial trigger for the multipulse sequence. However, we select its pulse width so it also acts as a protect pulse sent to the pulse counter. This is done to keep the duty cycle from exceeding 0.2% in order to satisfy the requirements of the 1-kW pulsed traveling wavetube (TWT) microwave amplifier. Thus, if a chosen pulse sequence exceeds the total width of the protect pulse, it will automatically be terminated at the end of the protect pulse. The BNC delay generators allow for programmable delays of 10 ns–10 ms. The 25 MHz counting rate of the pulse counter permits trigger pulses as often as 40 ns driving the 180° pulses, while the maximum number of such pulses is 999°.

In order to compensate for deviations of the pulses from their nominal 90° and 180° values we used a microwave phase shifter permitting us to either phase shift the 90° (CPMG sequence), or to phase shift alternate 180° pulses (alternating CP sequence).

We discuss results using these sequences for two systems. In Fig. 2 we first show results with a standard sample of irradiated quartz (yielding trapped electrons) with long $T_M = 7.5\,\mu$s. We compare the results of a series of two-pulse 90°–180° echoes in Fig. 2(a) with that of a single alternating CP sequence. This clearly demonstrates the advantage of a CP sequence in rapid data collection. In Fig. 3 we show results on a photo-induced transient signal from photoelectrons of short lifetime that have been ejected from alkali anions. The particular system studied is that of Rb atoms dissolved in THF. The Rb atoms exist as $Rb^+$–$Rb^-$ ion pairs. The photoelectrons were generated with a Lambda–Physik pulsed dye laser over the wavelength range $693 \leqslant \lambda \leqslant 932$ nm.[10] Each laser pulse is followed by the microwave pulse sequence; the $T_M = 1.0\,\mu$s. We see in Fig. 3 a series of three echoes obtained with an alternating CP sequence. We

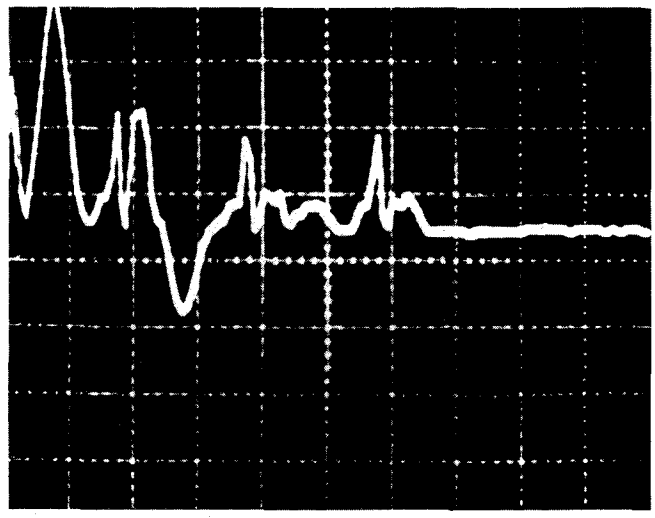

FIG. 3. Carr–Purcell sequence with alternating phase for the polarized photoelectron at $-87$ °C, and $[Rb^-] = 5\times10^{-5}$ M. Each division of $x$ axis equals 0.5 $\mu$s and $2\tau = 0.9\,\mu$s. The measured $T_M$ is consistent with 1.0 $\mu$s measured by 90°–180° sequences.

observe that while CP and standard 90°–180° sequences yield the same $T_M$ for the photoelectrons (cf. Fig. 3), this is not so for the irradiated quartz. Instead, in the latter case (cf. Fig. 2), the $T_M^{CP}$ is significantly longer than $T_M$, implying a slow motional mechanism.[3]

The digital electronics shown in Fig. 1 allows us to perform successive 180° pulses as fast as every 150 ns (i.e., $\tau = 75$ ns). We have found that by somewhat different wiring we can reduce $\tau$ to 20 ns. At present the pulse rate is limited by the spectrometer "ring" or dead time of 100–200 ns following a microwave pulse. Current efforts at reducing this dead time are expected to allow us to utilize our maximum rate of $2\tau = 40$ ns for the successive 180° pulses.

This paper was supported by Grant No. DE-AC02-80ER04991 from the office of Basic Energy Sciences of the DOE and by NSF Grant No. CHE 8024124.

[1]A. D. Trifunac and S. R. Norris, Chem. Phys. Lett. **59**, 140 (1978).
[2]A. D. Trifunac, J. R. Norris, and R. G. Lawler, J. Chem. Phys. **71**, 4380 (1979).
[3]L. J. Schwartz, A. E. Stillman, and J. H. Freed, J. Chem. Phys. **77**, 5410 (1982).
[4]C. P. Slichter, *Principles of Magnetic Resonance* (Springer, New York, 1980).
[5]A. Abragam, *The Principles of Nuclear Magnetism* (Oxford University, London, 1961).
[6]Low Power ESE examples are found in: W. G. Breiland, C. B. Harris, and A. Pines, Phys. Rev. Lett. **30**, 158 (1973); W. G. Breiland, H. C. Brenner, and C. B. Harris, J. Chem. Phys. **62**, 3458 (1978); and an optical detection example is in: C. A. Van't Hof, T. Schmidt, D. H. F. Verbeck, and J. H. Van der Waals, Chem. Phys. Lett. **21**, 437 (1973).
[7]A. E. Stillman, L. J. Schwartz, and J. H. Freed, J. Chem. Phys. **73**, 3502 (1980).
[8]A. E. Stillman and R. N. Schwartz, J. Phys. Chem. **85**, 3031 (1981).
[9]Berkeley Nucleonics Corporation, Berkeley, CA 94710.
[10]U. Eliav and J. H. Freed (to be published).