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Use of the Frank sequence in pulsed EPR

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ABSTRACT

The Frank polyphase sequence has been applied to pulsed EPR of triarylmethyl radicals at 256 MHz (9.1 mT magnetic field), using 256 phase pulses. In EPR, as in NMR, use of a Frank sequence of phase steps permits pulsed FID signal acquisition with very low power microwave/RF pulses (ca. 1.5 mW in the application reported here) relative to standard pulsed EPR. A 0.2 mM aqueous solution of a triarylmethyl radical was studied using a 16 mm diameter cross-loop resonator to isolate the EPR signal detection system from the incident pulses.

1. Introduction

Coded pulse sequences have long been used in communications, radar, and other fields to distinguish signals from noise and other interfering signals, and there is a very extensive literature in this field. The use of phase-incremented pulses in NMR was reviewed by Zhang [1]. The sequences proposed by Heimiller [2], Frank [3], and Chu [4] have been judged to have good correlation properties, and Blümich et al. [5] demonstrated that the use of the Frank sequence facilitated NMR FID detection with very low power excitation pulses. The final step in the data analysis involves the well-known Fourier transformation of an FID to obtain the absorption and dispersion spectra (see, e.g. [6]). The Frank sequence appears to encode magnetic resonance signals more effectively than other methods, such as the Hadamard transform [7]. The Blümich et al. paper [5] stimulated our labs to examine the extent to which the Frank phase sequence could be applied to pulsed EPR. Initial consideration of the fact that electron spin relaxation times are shorter than nuclear spin relaxation times by about a factor of 10^3 or more, and that consequently the spectrometer dead time following a pulse is a much larger fraction of available observation time in EPR than in NMR, suggested that success was unlikely. However, this paper reports successful application of a Frank sequence of pulse phases to EPR FID detection of a triaryl methyl radical. This was accomplished by recording the signal continuously, including during the pulses, and subtracting an off-resonance signal to reduce the background.

2. Experimental

The sample used was a 0.2 mM aqueous solution of deuterated symmetric trityl (sometimes called Finland trityl) (methyl tris(8-carboxy-2,2,6,6-tetramethyl(d_3)-benzo[1,2-d:4,5-d′]bis(1,3)dithiol-4-yl)-tripotassium salt) in a 10 mm o.d. tube, purged with N_2 and flame-sealed. This sample has T_2 about 11 μs [8], and was chosen because it has sufficiently long T_2 to facilitate demonstration of the Frank sequence for EPR.

Experiments were performed at 256 MHz RF frequency (ca. 9.1 mT magnetic field) using components of the VHF spectrometer and air-core magnet previously described [9,10]. Isolation (ca. 40 db) of the detected signal from the RF pulses in a wire cross-loop resonator (CLR) [11] contributed to the success of this experiment. The sample resonator is 16 mm in diameter and 15 mm long and the orthogonal excitation resonator consists of two coils 32 mm in diameter and spaced 20 mm apart. The resonator Q was reduced to about 50 by inserting the 10 mm diameter sample into a 16 mm tube with the annular space filled with water.

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2.1. Phase-stepped pulses

The phase-stepped RF pulses were generated with a Tektronix arbitrary waveform generator, AWG2041, at 1023.12 MHz clock frequency, which is near the instrument's maximum. To facilitate creation of the waveforms, a Matlab program was written to produce AWG compatible files. The 8-bit signal channel was used to form the pulse sequence. The r.f. frequency carrier was one fourth of the AWG clock frequency, so there were only four points per sinusoidal cycle. The lack of resolution could have produced higher harmonics of the fundamental frequency if it were not for the resonator, which when tuned to the carrier frequency acted as a pass-band filter. Consequently, all of frequencies higher or lower than the resonator bandwidth were strongly suppressed. One marker output from the AWG was used to produce a constant 255.78 MHz signal for the LO side of the double-balanced mixer (DBM) that was used to detect the EPR signal. The output of the DBM has signals at baseband and 511.56 MHz, but the bandwidth of the amplifier (~10 MHz) passes only the baseband signal. The second marker output was used to trigger the digitizer. Synchronization of the signal channel and the two markers by the same AWG clock made possible successive data averaging by a Bruker SpecJet II digitizer that was run at the 250 MS/s sampling rate.

The AWG waveform for the Frank sequence of 256 pulses was computed using a Matlab program. Each pulse was formed by 112 points. It was followed by 112 zeros. The total number of points in the waveform was $224 \times 256 = 57{,}344$, which for the 1024 MHz clock frequency is 56 μs. This sequence length was about $5T_2$ for the trityl radical. The phase of each individual pulse was calculated based on the Frank sequence of $16^2 = 256$ elements [3]. There were 16 different RF phases distributed among the 256 pulses, and the phase increments are multiples of $360°/16 = 22.5°$ (Fig. 1). The length of each pulse was about 109 ns, which produces a 3 dB excitation bandwidth of about 8 MHz. For the resonator Q about 50 at 250 MHz resonance frequency, the 3 dB bandwidth is 5 MHz. Thus the bandwidth of each pulse is larger than the bandwidth of the resonator. The power incident on the excitation resonator was about 1.5 mW. This power was demonstrated to be within a few dB of that required to achieve the desired 90°/256 (0.35°) turning angle for the electron spins for the pulse length and resonator Q. With an isolation of about 40 dB between the excitation and detection CLR resonators, the 'leakage' power at the detector was on the order of 150 nW. Such a low power is many orders of magnitude smaller than would occur for a single high-power pulse. A power of 150 nW would not damage the detection system, so there was no need for detector protections. Consequently, the signal could be measured even during the pulse. In spite of the isolation, a background signal produced by transition effects in the CLR was much larger than the EPR signal. In order to reduce the background, data collected off-resonance were subtracted from the on-resonance signal. The resultant complex signal was cross-correlated with the Frank sequence to produce an FID, the Fourier transform of which yielded the absorption and dispersion components of the EPR spectrum (Fig. 2).

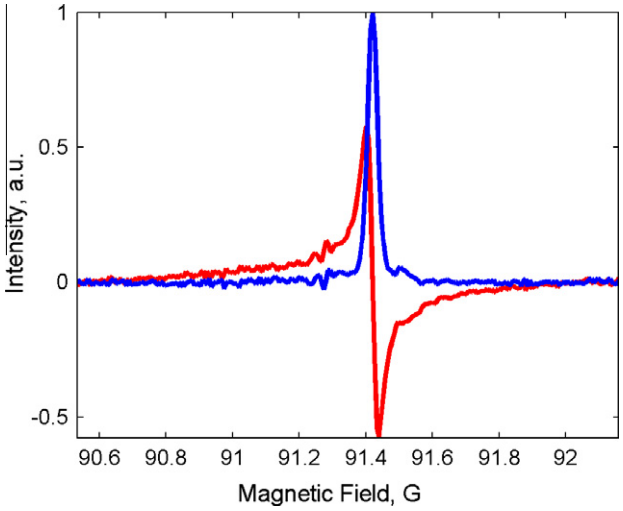

Fig. 2. EPR spectrum of the trityl radical obtained by means of Frank sequence EPR. The blue line is the absorption component and the red line is the dispersion component. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

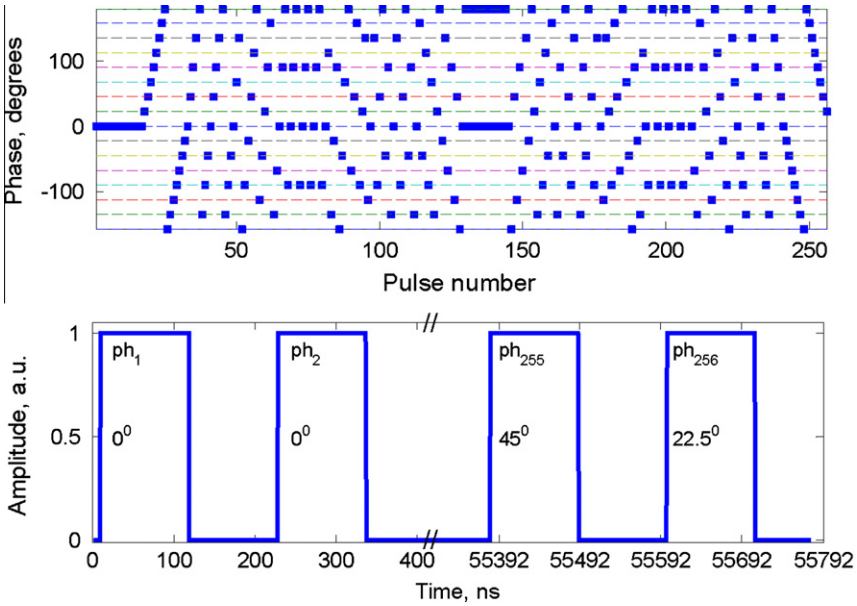

Fig. 1. The pulse sequence that was used to produce the spectra in Fig. 2 consisted of 256 pulses of 109 ns with the 16 different phases selected as shown in part a. The time required for the complete sequence was about 56 μs. The detailed timing of the first 2 and last 2 pulses is shown in part b. Data were acquired continuously at 4 ns intervals during the entire pulse sequence, but only the signal corresponding to times between the pulses was analyzed.