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The use of composite pulses for improving DEER signal at 94 GHz

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ABSTRACT

The sensitivity of pulsed electron paramagnetic resonance (EPR) measurements on broad-line paramagnetic centers is often limited by the available excitation bandwidth. One way to increase excitation bandwidth is through the use of chirp or composite pulses. However, performance can be limited by cavity or detection bandwidth, which in commercial systems is typically 100–200 MHz. Here we demonstrate in a 94 GHz spectrometer, with >800 MHz system bandwidth, an increase in signal and modulation depth in a 4-pulse DEER experiment through use of composite rather than rectangular π pulses. We show that this leads to an increase in sensitivity by a factor of 3, in line with theoretical predictions, although gains are more limited in nitroxide-nitroxide DEER measurements.

1. Introduction

For many pulsed magnetic-resonance experiments a large factor determining sensitivity is the proportion of spins that can be excited. The number of spins and the fidelity of the excitation profile can be improved by using modulated pulses that use phase or amplitude changes rather than simple rectangular pulses. These work to increase excitation bandwidth and/or compensate for errors such as applied field inhomogeneity. Such pulses include composite, adiabatic, chirp or more general optimal control sequences [1–5]. NMR has been using these methods for almost 40 years but their adoption in EPR has been slower due to the increased technical demands of working at higher electromagnetic frequencies. However, EPR will benefit from increased excitation bandwidth and the ever more complex sequences that can be applied with the increased fidelity of excitation offered. Recent advances have been made in the development and integration of arbitrary waveform generators (AWGs). These systems become more difficult to implement directly at higher frequencies as the performance of filters, amplifiers and IQ mixers becomes more critical. Conversely, higher frequencies can offer increased sensitivity: we have previously shown that a non-resonant wide-bandwidth spectrometer operating at W-band (94 GHz) offers 20–30 times improvement over the commercial X-band (9.5 GHz) system [6]. We show here how fixed-amplitude phase-modulated composite pulses can be implemented at 94 GHz to increase excitation bandwidth and to compensate for applied field inhomogeneity.

Composite pulses are composed of several contiguous subpulses of varying phase and length that produce an excitation ($\pi/2$, 90°) or an inversion (π, 180°) of spin packets over a larger bandwidth than an equivalent standard rectangular pulse. Two of the advantages of composite pulses, over more complex sequences, is that they are still relatively short, typically three times the length of a rectangular inversion pulse, and that they can be used in existing spectrometers that have a phase-cycling capability.

Composite pulses have been used in NMR for a number of years to provide improvements in a range of areas. They were first demonstrated in EPR experiments by the Freed group in 1989, where an excitation bandwidth over 200 MHz was demonstrated [7]. Morton et al. have also utilized the narrow bandwidth BB1 composite pulse sequence to improve B_1 inhomogeneity for quantum computing applications [8]. Composite pulses have also been used by Turro et al. to enhance inversion recovery experiments on nitroxides at X-band [9].

One frequently used experiment that can benefit from composite pulses is the double electron-electron resonance (DEER, also known as PELDOR) sequence, Fig. 1, which is a pump-probe tech-

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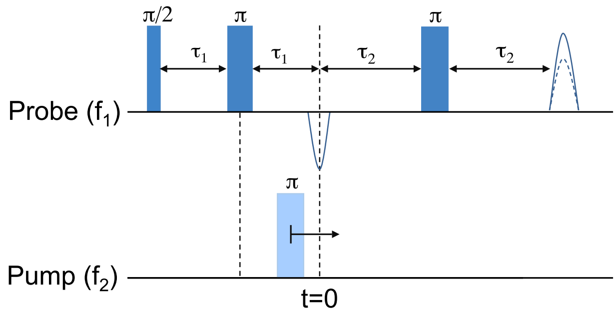

Fig. 1. Standard 4-pulse DEER sequence, consisting of a refocused Hahn echo sequence on the probe or detection (f_1) sequence, and a single inversion pulse on the pump spin (f_2) sequence.

nique [10,11]. In the 4-pulse version the pump pulse inverts spins at one frequency and the probe uses a refocused echo sequence. In this way the dipole–dipole interaction can be measured and this can be related to distances in the 2 to, at least, 10 nm range [12–14].

To a first approximation the sensitivity of the DEER experiment is proportional to the fraction of spins excited by both the pump and probe pulses. This raises a significant challenge for broad-line systems such as metal ions in metalloproteins which would otherwise potentially be very useful markers as intrinsic paramagnetic centers. Thus most applications of DEER in biomolecules have employed nitroxyl spin labeling, though there are notable exceptions [15–17]. Many of the modulated pulse techniques employed so far have focused on replacing the pump pulse where increases in modulation depth by up to a factor of 3 have been demonstrated [3,5,18]. Chirp and other modulated pulses have been utilized coherently to produce enhanced Hahn echoes for use in another dipole spectroscopy experiment, SIFTER (single frequency technique for refocusing dipolar couplings) [19–21].

Recently we reported that our 1 kW wideband (>800 MHz) W-band spectrometer, HiPER, can be used to measure the dipolar interaction, and therefore distance, between nitroxyl spin labels and a spin-half ferric (Fe(III)) heme in proteins [6]. We reported substantial increases in the signal-to-noise of the DEER measurement partly from improvements in both the pump and probe excitation bandwidth. This is despite the large *g*-anisotropy of the ferric-heme, which resulted in an absorption profile on the order of 1.5 T at W-band.

In this paper, we discuss the choice of composite pulse sequence to replace the π pulses in the DEER experiment (Fig. 1). We show the implementation on HiPER using a 4 channel 16-state vector modulator to provide phase control with 4 ns sub-pulse resolution. Finally, we demonstrate the gains of using composite pulses for echo and DEER sequences on extremely broad-line systems such as iron-heme and compare them to nitroxyl-nitroxyl systems.

2. Composite pulses

2.1. Background

Composite pulses were first reported by Levitt et al. [1] demonstrating a simple sequence of 3 contiguous pulses that performed the same action as a 180° pulse, but compensated for B_1 inhomogeneity across the sample and increased excitation bandwidth. Composite pulses are commonly described using the following notation [22]: $(\beta_1^0)_{\phi 1}(\beta_1^0)_{\phi 1}\cdots(\beta_n^0)_{\phi n}$ where $\left(\beta_p^0\right)$ describes the nominal flip angle (usually 90° or 180°) of the sub-pulse *p*, and ϕp describes its phase, or axis of rotation. Levitt's original 180° equivalent composite pulse, $90_{90}180_{0}90_{90}$ (when applied to a set of spins at equilibrium, M_z) thus equates to a 90° rotation around the *y*-axis (ϕ=90°), rotating the spins into the transverse plane along *x*, followed by a 180° rotation around this axis (=0°), finishing with another 90° rotation around the y-axis. The sequence can compensate for B_1 inhomogeneity by helping or hindering spins that under and over-rotate due to spatial applied field inhomo-

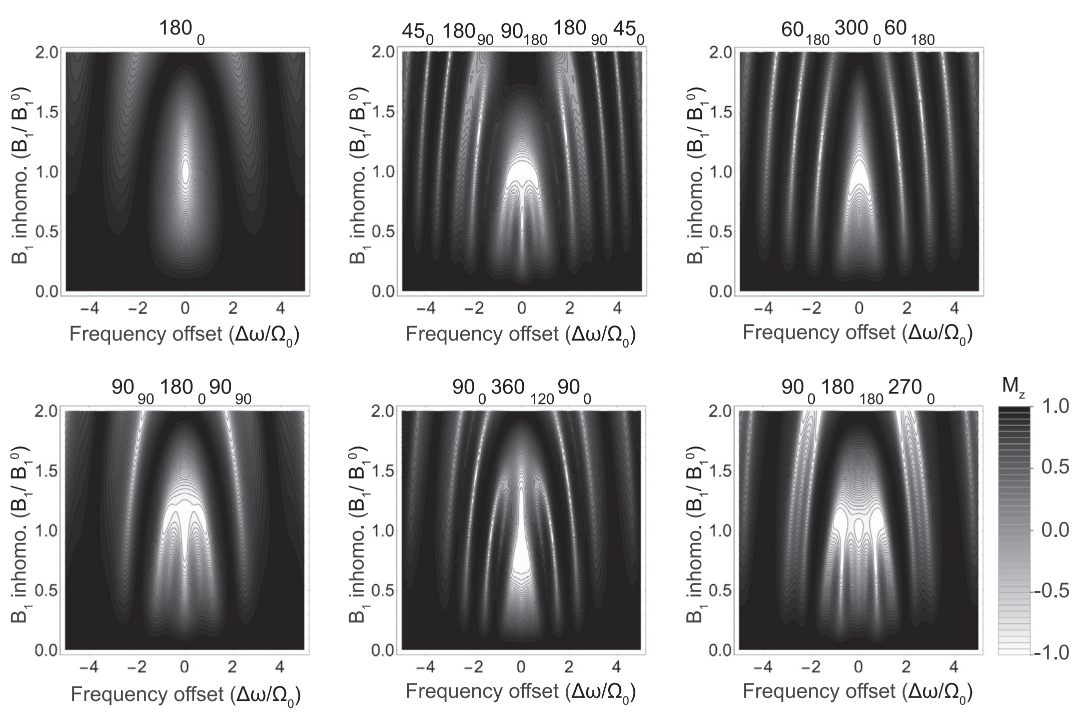

Fig. 2. Contour plots showing the inversion performance of a range of composite pulses in terms of their ability to invert across frequency offset (*x*-axis) and in the presence of B_1 inhomogeneity (*y*-axis), where Ω_0 is the resonant frequency and B_1^0 is the nominal amplitude of the applied pulse. The plot scales between white = 95–100% inversion (M_z = −1) to black = 0% inversion (M_z = +1).