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Broadband spin echoes and broadband SIFTER in EPR

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ABSTRACT

Applications of broadband pulses for EPR have been reported for FID, echo detection and inversion pulses recently. Here we present a broadband Hahn, stimulated and refocused echo sequence derived from adiabatic pulses. The formation of echoes is accomplished by using variable chirp rates and pulse lengths. In all three broadband echo experiments the complete spectral shape of a nitroxide (about 70 Gauss at X-band frequency) could be recovered by Fourier transformation of the quadrature detected echo signals. Such broadband echoes provide an exciting opportunity to optimize pulse sequences where a full excitation of the spectrum is mandatory for an optimum performance. We applied our pulses to the SIFTER (single frequency technique for refocusing dipolar couplings) experiment, a solid echo based pulse sequence to measure the dipolar coupling between two unpaired electron spins. By employing our broadband Hahn echo sequence on a nitroxide biradical we could achieve an artifact free dipolar evolution time trace in the SIFTER experiment with 95% modulation depth at X-band frequency and of 10% modulation depth at Q-band frequency.

1. Introduction

Pulsed dipolar spectroscopy (PDS) has been extensively applied in the fields of biology and material science to enable distance determination of 1.4–8 nm between site-directed spin labels or natural occurring paramagnetic spin centers by measuring the interspin dipolar coupling [1,2]. This provides valuable insights in structures, folding, and conformational changes of large biomolecules in frozen solution [3] and polymer materials [4]. Various PDS techniques including PELDOR (also called DEER) [5], DQC [6], SIFTER [7] and '2 + 1' [8] have been developed to measure dipolar electron–electron coupling. All these methods are based on spin echoes. They can be divided into two groups namely double frequency (PELDOR) and single frequency (DQC, SIFTER, '2 + 1') techniques. In the case of single frequency PDS rectangular pulses work as long as the bandwidth of the microwave pulse exceeds the spectral width $\Delta\omega_{sw}$ of the measured spin system. Meaning the B_1-field strength of the excitation pulse given in frequency units by $\omega_1 = \gamma B_1$, (with γ being the gyromagnetic ratio) needs to be larger than $\Delta\omega_{sw}$ [9]. Due to hardware limitations there are many cases where ω_1 is not large enough to fulfil this condition for nitroxide spin labels, which are the most commonly used spin labels [3]. This leads to reduction in sensitivity, small modulation amplitudes and the appearance of artifacts.

By modulating the amplitude and/or phase of microwave pulses the excitation bandwidth can be drastically increased [9–14]. One widespread application of phase and amplitude modulation is the concept of adiabatic pulses [15]. Adiabatic pulses have been used in NMR since 1984 [16] but there are few spin echo applications [17–19]. With the development of fast AWG's (arbitrary waveform generator) adiabatic pulses have also been applied in EPR but mainly for inversion purposes [10,13]. Unlike rectangular pulses adiabatic pulses produce a nonlinear phase dispersion of off resonance spins after the pulse which makes it difficult to refocus off resonance spins and hence create a spin echo. Recently a FT EPR experiment was performed by using chirped pulses for a broadband Hahn echo [14]. To overcome the phase problem the Böhlen–Bodenhausen scheme [20,21] was used. With this scheme the nonlinear phase dispersion produced by the broadband $\pi/2$ pulse can be compensated by a consecutive broadband π pulse. With the broadband Hahn echo sequence we were able to excite and refocus the complete X-band frequency nitroxide powder spectrum. The same concept allowed us to also achieve broadband stimulated and refocused echoes. Optimal control theory (OCT) pulses can also be used to create a broadband spin echo [9]. However, the technique used here has a significant advantage over the existing OCT methods which worked only with a fixed pulse separation time, whereas the pulse separations in broadband spin echo sequences with broadband pulses are fully variable.

SIFTER (single-frequency technique for refocusing dipolar couplings) was first introduced into EPR by Jeschke et al. [7]. It is

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based on the solid echo and the Jeener–Broekaert sequence [22]. Due to the single frequency only moderate requirements of the spectrometer are necessary. SIFTER enables the measurement of distances between nitroxide biradicals [7]. However a large limitation of SIFTER using rectangular pulses is the inclusion of artifacts resulting from inefficient inversion by the pulses. Using the broadband Hahn echo sequence as a basis for a broadband SIFTER experiment for distance measurements on a nitroxide biradical we were able to suppress these artifacts, enabling an improved distance determination at X- and Q-band frequencies. Furthermore, an improved modulation depth of 95% was achieved if the resonator bandwidth was sufficient to fully support the broadband pulses.

2. Theory

2.1. Adiabatic pulses

Adiabatic pulses are known for their robust broadband inversion of the spin magnetization. The phase and amplitude of adiabatic pulses are modulated in such a way that the spin follows the effective field (which in this paper is always expressed as the nutation frequency $\boldsymbol{\omega}_{eff} = \omega_1\boldsymbol{x} + \Delta\omega\boldsymbol{z}$) along the effective field direction in the rotating frame. Here $\boldsymbol{x}$, $\boldsymbol{y}$, $\boldsymbol{z}$ are the unit vectors of the rotating frame, ω_1 is the magnitude of the microwave field in rad/s and $\Delta\omega$ is the instantaneous frequency offset. In order to accomplish a broadband inversion the spin rotation needs to be sufficiently slow, such that the adiabatic condition is fulfilled [15]:

$$Q = \frac{\omega_{eff}}{|d\theta/dt|} \gg 1 \tag{1}$$

with Q being the adiabatic factor and $d\theta/dt$ the instantaneous angular velocity of $\boldsymbol{\omega}_{eff}$. A more complete introduction about adiabatic inversion pulses for EPR can be found in [13]. To accomplish a good inversion performance we combined the sech/tanh pulse [23] with the WURST (wideband, uniform rate, smooth truncation) pulse [24]. The time dependent amplitude $\omega_{s/t}(t)$ and frequency/phase modulation functions $\Delta\varphi(t)$ of the sech/tanh pulse are given by:

$$\begin{aligned} &\omega_{s/t}(t) = \omega_{1max}\mathrm{sech}(\beta t) \quad \Delta\omega(t) = BW \cdot \tanh(\beta t) \\ &\Delta\varphi(t) = \int \Delta\omega(t)dt = \frac{BW \cdot \log(cosh(\beta t))}{\beta} \end{aligned} \tag{2}$$

with ω_{1max} being the maximum ω_1 field, β a tuning parameter concerning the sweep rate, $t \in [-t_{\mathrm{pulse}}/2, t_{\mathrm{pulse}}/2]$, t_{pulse} the length of the pulse and BW the bandwidth parameter. The WURST amplitude function is given by:

$$\omega_{1WURST}(t) = \omega_{1max}(1 - |sin(\beta_{wurst}t)|^n) \tag{3}$$

The index n defines the steepness of the amplitude function. In the ideal case the bandwidth BW corresponds to the rectangular excitation bandwidth of the adiabatic pulse. The instantaneous complex microwave field of an adiabatic pulse can be described as:

$$\omega_{adia\ pulse}(t) = \frac{\omega_{1WURST}(t)}{\omega_{1max}}\omega_{s/t}(t) \cdot (cos(\Delta\varphi(t)) + isin(\Delta\varphi(t))) \tag{4}$$

The combination of the WURST amplitude function with the hyperbolic sech/tanh-pulse led to a smoother rectangular profile concerning the inverted longitudinal magnetization (see Fig. S3). By reducing ω_{1max} a $\pi/2$ pulse can be achieved, the excitation bandwidth of such a $\pi/2$ pulse is comparable to a π pulse (see Fig. 1). The time trace of the microwave field during such a $\pi/2$ pulse can be seen in Fig. S1. This $\pi/2$ pulse is not an adiabatic pulse because the adiabatic condition is not fulfilled.

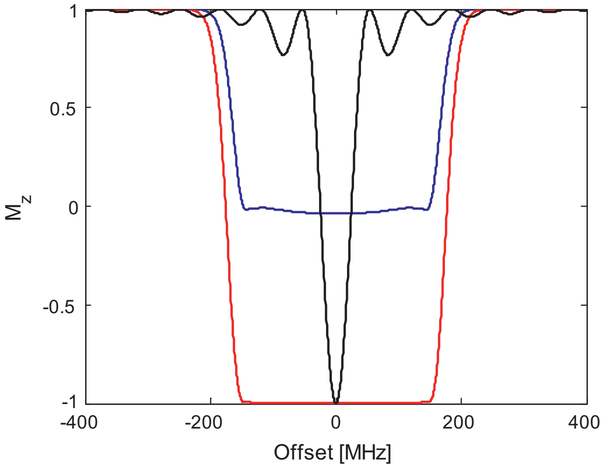

Fig. 1. Simulated M_z profile of an adiabatic inversion (red), broadband $\pi/2$ (blue) and rectangular π (black) pulse. The simulation was done by solving the Bloch equation numerically without implementing any resonator profile. The pulse length of the rectangular pulse is 16 ns and $\omega_1 = 31.25$ MHz. For broadband pulse parameter see Table S1. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

2.2. Phase correction

It is possible to transfer the equilibrium spin magnetization to the x–y plane by broadband pulses, as shown in Fig. 1. However, unlike using rectangular $\pi/2$ pulses the macroscopic transverse magnetization after such a pulse is zero. The times at which spins are flipped to the transverse plane varies with their Larmor/offset frequencies (see Fig. S2). This causes a phase dispersion resulting in zero total transverse magnetization at the end of the pulse. It is possible to compensate this phase distortion with a second pulse of adapted sweep rate and duration. In order to accomplish a uniform phase at 2τ the duration of the π pulse needs to be half as long as the duration of the $\pi/2$ pulse and vice versa the frequency sweep rate β roughly twice as big [14,21]. This concept is illustrated by the pulse sequence diagram shown in Fig. 2.

In a case without anisotropic couplings (as hyperfine and dipolar) the accumulated phase (φ, φ', φ'') at specific times within the pulse sequence (see Fig. 2) can be calculated as follows:

$$\begin{aligned} \varphi &= \omega_L(t_1 - x + x/2) \\ \varphi' &= -\omega_L(t_1 - x + x/2) \\ \varphi'' &= -\omega_L(t_1 - x + x/2) + \omega_L(t_2 - x/2) \\ &= \omega_L(t_2 - t_1) \end{aligned} \tag{5}$$

with φ being the phase of a spin with the Larmor frequency ω_L and x being the time at which the spin is flipped (see Fig. S2). In case of $t_1 = t_2$, all spins independent of ω_L possess the same phase. Hence the condition to generate a spin echo is fulfilled. Based on the same rules it is also possible to create a refocused and stimulated echo sequence. As shown in Fig. 3 the first and second pulses in the refocused sequence have twice the length of the third pulse and therefore half the sweep rate. In the broadband refocused echo sequence the primary echo is phase dispersed because the phase compensation is only done by the third pulse. The situation is slightly different for a stimulated echo, here the first pulse has twice the length of the second and third and hence half the sweep rate. The exact phase dependency without anisotropic couplings can be found in the supporting information (Eqs. (S1) and (S2)). Numerical simulations showed that all three broadband sequences also work in the same way with hyperfine and weak dipolar couplings (see middle column Fig. 7).