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Decoupling of Excitation and Receive coils in Pulsed Magnetic Resonance Using Sinusoidal Magnetic Field Modulation

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Abstract

In pulsed magnetic resonance, the excitation power is many orders of magnitude larger than that induced by the spin system in the receiving coil or resonator. The receiver must be protected during and immediately after the excitation pulse to allow for the energy stored in the resonator to dissipate to a safe level. The time during which the signal is not detected, the instrumental dead-time, can be shortened by using magnetically decoupled excitation and receive coils. Such coils are oriented, with respect to each other, in a way that minimizes the total magnetic flux produced by one coil in the other. We suggest that magnetically decoupled coils can be isolated to a larger degree by tuning them to separate frequencies. Spins are excited at one frequency, and the echo signal is detected at another. Sinusoidal magnetic field modulation that rapidly changes the Larmor frequency of the spins between the excitation and detection events is used to ensure the resonance conditions for both coils. In this study, the relaxation times of trityl-CD3 were measured in a field-modulated pulsed EPR experiment and compared to results obtained using a standard spin echo method. The excitation and receive coils were tuned to 245 and 256.7 MHz, respectively. Using an available rapid-scan, cross-loop EPR resonator, we demonstrated an isolation improvement of approximately 20–30 dB due to frequency decoupling. Theoretical analysis, numerical simulations, and proof-of-concept experiments demonstrated that substantial excitation-detection decoupling can be achieved. A pulsed L-band system, including a small volume bi-modal resonator equipped with modulation coils, was constructed to demonstrate fivefold dead-time reduction in comparison with the standard EPR experiment. This was achieved by detuning of the excitation and receive coils by 26 MHz and using sinusoidal modulation at 480 kHz.

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Graphical abstract

1. Introduction

In pulsed nuclear magnetic resonance (NMR) and electron paramagnetic resonance (EPR), only a small fraction of the excitation energy is transferred to the spin system. The receiver, whose purpose is to amplify very weak magnetic spin responses, must be protected from excessive energy during and immediately after the pulse to allow for the energy stored in the excitation coil (resonator) to dissipate. During this instrumental dead-time period, the detection circuitry is unable to receive signals. When the receiver becomes operational, the signal of interest may still be contaminated by a residual coil ring-down. As a result, the effective dead-time may be longer than the receiver protection time. Phase cycling is often used to attenuate unwanted signals, including coil ring-down [1].

Current methods for dead-time reduction are based on time or/and space decoupling of the excitation from detection. A classic example of time separation is spin echo, which resets the clock of the free induction decay (FID) to a later time, when it can be observed as a part of the echo signal. Positioning the excitation and receive coils orthogonal to each other so that the magnetic field produced by one coil induces little electromotive force in another can be considered as spatial decoupling. If a high degree of isolation is reached, EPR signals can be detected during the excitation pulse without receiver protection [2]. In this study, we introduce a method of frequency separation between the excitation and receive coils that can be combined with time and spatial decoupling. This method is realized by the addition of sinusoidal magnetic field modulation:

$$B(t) = 0.5B_{pp} \sin(\omega_m t), \quad \omega_m = 2\pi f_m. \quad (1)$$

to the standard $\pi/2$ - τ - π - τ' echo' spin echo experiment (Fig.1).

In Eq. (1) and Fig. 1, B_{pp} represents the peak-to-peak amplitude and f_m represents the frequency of the modulation. The abscissa is labeled in frequency-independent modulation phase units. The first $\pi/2$ pulse occurs at $\theta=30^\circ$. After a delay equal to one third of the modulation period ($\theta=120^\circ$), the inversion π pulse is applied at the same magnetic field. As

a result, an echo signal frequency corresponding to this detection field value. Decoupling the excitation and receive coils is achieved due to separation of their resonance frequencies by

$$\Delta f = \frac{3}{8\pi} \gamma B_{pp}. \quad (2)$$

Magnetic field modulation brings the Larmor frequency of the spins to that of the receive coil at the event of echo formation. In Eq. (2), γ represents the gyromagnetic value of an electron or nucleus. Fig. 1 demonstrates just one of many possible designs to implement field-modulated pulsed (FMP) magnetic resonance. Various pulse sequences and modulation waveforms can be used, some of which are described below. Sinusoidal modulation has the advantage of producing high frequency and amplitude magnetic field scans and is achieved by resonating the modulation coils at a specific frequency [3-5]. The consequence of sinusoidal modulation is magnetic field variation during echo detection. As a result, the echo signal becomes frequency modulated. The spin precession frequency, which is proportional to $B(t)$, increases when $\theta < 270^\circ$ and decreases after it passes the peak value at $\theta = 270^\circ$. As a result, the echo signal demonstrates accelerating oscillations (Fig.1). The same phenomenon is observed in a rapid-scan EPR experiment [6, 7], where a rapidly changing magnetic field drives acceleration or deceleration of the magnetization vector precession, depending on the scan direction. As in rapid-scan data processing, numerical transformation into the frame associated with the changing Larmor frequency can be utilized to convert the field-modulated echo in Fig.1 back into its 'conventional' shape, which would have been observed in a constant magnetic field. In the new frame associated with the changing Larmor frequency, the excitation frequency within the pulse becomes time-dependent because the frame change is equivalent to changing from the magnetic field modulated pulsed experiment (see Fig.1) to one with a constant field but changing frequency [1, 7-9]. As a result, different spin packets within an inhomogeneously broadened line would be refocused at the echo time with slightly different instances. If the frequency change during the pulse is relatively small compared to the excitation bandwidth, the resulting echo distortion is negligible. This effect is discussed in more detail in section 2.1.

The concept of using synchronous sinusoidal field modulation in a pulsed experiment is not novel and was first implemented in EPR by Eichel and Schweiger in a single mode resonator [4]. Pulses were applied at the modulation zero-crossing points ($\theta = 0^\circ$ and 180° in Fig.1), with a goal to measure Zeeman-resolved EPR spectra. This study demonstrates that excitation/detection decoupling can be achieved by detuning transmit and receive coils. Magnetic field modulation permits observation of frequency-modulated spin echoes that can be post-processed by signal transformation into the accelerating reference frame associated with the modulation-driven Larmor frequency.

The FMP method described in this study can be equally applied to both electron and nuclear spins. Because detection of many paramagnetic centers is problematic, due to the short relaxation times, this method is expected to be more practical for use in EPR. Both theoretical analysis and experimental results provided below are for the electron spin.

2. Theory and Numerical Simulations

2.1 Reference frame transformation and chirping effect

The Larmor frequency, ω_L , of the spins becomes time-dependent in the presence of modulation:

$$\omega_L(t) = \gamma(B_0 + B_{loc} + B(t)) = \omega_0 + \gamma B_{loc} + \gamma B(t) \quad (3)$$

In Eq. (3), B_0 is the external magnetic field, B_{loc} is a local field produced by the magnetic environment, and γ presents the electron gyromagnetic ratio. In most modern EPR spectrometers, signals are down-converted to the baseband, either in hardware or software. The latter is done by multiplication of the signal by the exponent:

$$f_{tr}(t) = \exp[-j\varphi_0(t)], \quad \varphi_0(t) = \omega_0 t, \quad (4)$$

followed by low-pass filtering [2]. In Eq. (4), $\varphi_0(t)$ is the reference phase, the local oscillator phase in the case of hardware down-conversion. Data processing results in signal transformation into a frame that rotates with ω_0 . In this frame, the magnetization phase can be calculated by time-integration of the last two terms in Eq. (3):

$$\varphi_L(t) = \gamma B_{loc} t + \gamma \int_0^t B(\tau) d\tau. \quad (5)$$

Substitution of Eq. (1) in Eq. (5) gives the analytical expression for $\varphi_L(t)$:

$$\varphi_L(t) = \gamma B_{loc} t + \varphi_{mod}(t), \quad \varphi_{mod}(t) = [1 - \cos\theta(t)] \frac{\gamma B_{pp}}{2\omega_m}, \quad \theta(t) = \omega_m t. \quad (6)$$

The first term in Eq. (6) defines the spectral line position. The second modulation term introduces an additional phase that is responsible for the accelerating oscillations in EPR signals that are observed experimentally and in simulations. The phase of the magnetization vector $\varphi_L(t)$ changes with respect to the reference $\varphi_0(t)$ at the time of signal measurement. Detection of such transient signals has been observed and discussed in NMR [10-12]. This also occurs in continuous-wave rapid scan (RS) EPR experiments [7, 13, 14]. Similar to FMP EPR, RS signals are detected in the presence of a changing magnetic field. In RS EPR, the oscillations appear only on the trailing edge of the signal. In both RS and FMP EPR, the second transformation to a frame associated with $\varphi_{mod}(t)$ is required for data post-processing. Similar to the transformation with Eq. (4), this is done by signal multiplication by the exponent:

$$d(t) = \exp[-j\varphi_{mod}(t)], \quad (7)$$

which is called the driving function [7]. In the new frame, the precession frequency is modulation-independent. At the same time, the frequency of the excitation field, B_1 , becomes time-dependent and equal to

$$B_1^{mod}(t) = B_1 \exp[-j\varphi_{mod}(t)] \quad (8)$$

for an observer in the accelerating system of coordinates associated with $\varphi_{mod}(t)$. This change of reference is equivalent to modification of the experiment in Fig. (1) to one with no magnetic field modulation but with frequency-modulated pulses. Such pulses are called chirp pulses in magnetic resonance [1, 8] and are used, for example, to extend the excitation bandwidth [15, 16]. Due to the chirping effect, different spin packets refocus in the spin echo at different times and with different phases, which may distort the observed echo shape. In the experiment described in Fig.1, the effect of the modulation on echo formation needs to be taken into account. Simulations with different spectral models and modulation parameters have been done. Results of a representative simulation are shown in Fig. 2. The model of an $S=1/2$ system coupled to a nuclei spin $I=1$ with a hyperfine constant of 2.5 G was used. Relaxation times were $T_1=1000$ ns and $T_2=700$ ns. Gaussian inhomogeneous broadening of 0.8 G for three equal intensity lines was introduced into the model. The modulation frequency was $f_m=500$ kHz, and the field modulation amplitudes, B_{pp} , were 0, 8, and 24 G. Both 90° and 180° pulses were 50 ns long. To simulate the effect of the coil quality factor on the echoes, $Q = 10$ at the excitation frequency of 250 MHz was used. The selected experimental parameters are analogous to those in 250 MHz *in vivo* EPR imaging settings [17].

Simulated echo signals in Fig. 2a and Fig. 2b correspond to $B_{pp}=8$ G and 24 G, respectively. Fig. 2b demonstrates increasing oscillation frequency at the edges of the echo signal due to the faster rate of magnetic field change. The signals in Fig. 2a and Fig. 2b were transformed into EPR spectra by the frame change (see Eq. (8)), followed by Fourier transformation. The red lines in Fig. 2c and Fig. 2d correspond to the signals in Fig. 2a and Fig. 2b, respectively. For the purpose of comparison, EPR spectra (blue lines) calculated with no modulation were added to Fig. 2c and Fig. 2d. Attenuation of the outer EPR lines observed by comparison with the model EPR spectrum (black line) is the result of the finite bandwidth of the excitation pulses and the coil Q . A faster rate of change for the magnetic field (stronger chirping effect) explains the larger EPR spectra discrepancies in Fig. 2d compared to Fig. 2c. The chirping effect can be evaluated quantitatively by computation of the magnetic field change during the pulse by multiplication of $B(t)$ time derivative at $\theta=30^\circ$ by the effective pulse length t_{eff} :

$$|\Delta B| = 0.5 \pi f_m B_{pp} \Delta t_{eff}. \quad (9)$$

The pulse duration is prolonged because of the coil Q factor. Echo distortion is negligible if the B is much smaller than the excitation bandwidth, BW, expressed in the units of magnetic field:

$$R = \frac{\Delta B}{BW} \ll 1. \quad (10)$$

BW can be estimated as follows [1]:

$$BW = \frac{2\pi}{\gamma} \frac{1.2}{\Delta t_{eff}} \quad (11)$$

Substitution of Eq. (11) into Eq.(10) gives:

$$R \cong 0.2 f_m B_{pp} \Delta t_{eff}^2 \ll 1. \quad (12)$$

For computational results in Fig. 2c and Fig. 2d, the t_{eff} was estimated to be 78 ns, resulting in $R=0.1$ and $R=0.3$, respectively. Eq. (12) was derived with the assumption that the excitation bandwidth is approximately equal to the spectral width. The outer most lines in the EPR spectrum should be distorted the most, with less distortion toward the central magnetic field (Fig. 2).

The negative impacts of chirping may be reduced by lowering the modulation amplitude or frequency. The former affects isolation between transmit and receive coils (larger B_{pp} gives better isolation), and the latter defines the inter-pulse delay in the spin echo sequence. The quadratic dependence of R on the pulse length favors high power short pulses. Strategies for the selection of modulation parameters, as well as for chirping effect mitigation, are provided in the Discussion section.

2.2 Isolation due to frequency detuning

Numerical simulations to evaluate isolation as a function of the frequency separation (see Eq. (2)) have been conducted (Fig. 3). The excitation 3 dB bandwidth, BW, of a square pulse was selected to be equal to that of both the excitation and receive coils. The abscissas in both the main figure and insert represent frequency in the units of BW. The isolation was measured as the ratio of the integrated excitation frequency response within the detection BW (red area in the insert) to the integral excitation area under the black curve. The oscillations occur because the Fourier transformation of a square pulse is a sinc function. Shaping the pulse to sharpen the frequency response would have improved the isolation.

2.3 Field modulated spin echo for relaxation time measurement

Fig 4 describes a field-modulated pulsed experiment to measure relaxation times.

For transverse relaxation T_2 measurements (Fig. 4a, b), the pulses must be placed at the intervals:

$$\tau = [1, 2, 4, 5, \dots, 3k + 1, 3k + 2, \dots] \times 120^0, \quad k \geq 0. \quad (13)$$

In Eq. (13), τ is in the unit of modulation phase as described above. Conversion to time units can be done by multiplication on $(f_m * 360^\circ)^{-1}$. Inter-pulse delays equal to the integer multipliers of the modulation period ($k*360^\circ$) are omitted because they do not provide frequency separation between excitation and detection.

Inversion recovery experiments to measure the longitudinal relaxation time T_1 (Fig. 4c, d) can be realized by addition of a π pulse to the T_2 experiment. The allowed intervals are:

$$\tau = [2, 3, 5, 6, \dots, 3k - 1, 3k, \dots] \times 120^0, \quad k \geq 1. \quad (14)$$

As in the case of the T_2 experiment, $(3k - 2) \times 120^\circ$ intervals are omitted in the experiment described. However, if the receive coil can be used as a transmit coil as well, spin echoes for these intervals can be measured by placing the first π pulse at

$$\theta = -90^0 - (k * 360^0), \quad k \geq 0 \quad (15)$$

This case still provides an improved isolation because the time separation between the pulse and echo in the same coil is increased by a factor of three compared to the standard spin echo experiment.

3. Proof-of-Concept Experiments

3.1 250 MHz Spectrometer

A pulsed EPR spectrometer used for field-modulated spin echo measurements operating at 250 MHz was assembled in the Center for EPR Imaging in Vivo Physiology at the University of Chicago. Direct detection at the carrier frequency permitted a simple and versatile design [2]. Fig. 5 shows the block diagram of the spectrometer.

A 12-bit DAx14000 arbitrary waveform generator (AWG, Chase Scientific Company, Langley, WA) was used to directly form pulses at an excitation frequency of 245 MHz. The AWG was phase-locked to a DS360 (Stanford Research Systems, Sunnyvale, CA) ultra-low distortion function generator and 12-bit U5303A digitizer/averager (Keysight Technologies, Santa Rosa, CA). The sinusoidal output of the function generator was amplified by a Model 7500 (Krohn-Hite, Brockton, MA) power amplifier (LF PA in Fig.5) and supplied to the modulation coils of the cross-loop resonator [18]. The resonator was designed and manufactured in the laboratory of professors G. R. Eaton and S. S. Eaton at Denver University to conduct *in vivo* rapid scan EPR experiments. An 80 dB isolation between the transmit and receive coils was achieved at a detection frequency of 265.7 MHz, as measured

by a network analyzer. The scan coils were resonated at 96 kHz using a 470 pF capacitor rated to 2000V (Vishay Americas, CT). At higher frequencies, the coils showed self-resonance. A 2kW Tomco VHF power amplifier (VHF PA in Fig.5) was used to produce the excitation pulses. The Q factors for the transmit and receive coils were 60 and 25, respectively. Echoes were detected directly after amplification at the carrier frequency. A constant magnetic field gradient of 1 G/cm was used to shorten the FID signal for echo detection. The entire experiment was controlled by SpecMan4EPR v. 2.1 (Femi Instruments, Chicago, IL) software. Digitized signals were down-converted and post-processed using Matlab code.

3.2 L-band spectrometer

Because the rapid scan coils in 250 MHz spectrometer self-resonate above 100 kHz, it was not possible to evaluate the dead time reduction effect due to frequency detuning. The inter-pulse delay, τ , was longer compared to the ring-down time. To evaluate the dead-time reduction in the experiment shown in Fig. 1, an FMP L-band spectrometer with small volume resonator was constructed. The overall design was very similar to the 250 MHz spectrometer described above (see Fig.5). Multichannel Keysight 33622A waveform generator was programmed to synchronously produce RF pulses and 480 kHz modulation. Power amplifier LZY-22+ (Minicircuits) was used to drive the modulation coils that were tuned to 480 kHz and matched to 50 Ohms with high-voltage capacitors. The specified AWG bandwidth is 120 MHz, but it was possible to generate pulses up to 250 MHz with some attenuation. The 240 MHz pulses were amplified and frequency-multiplied by a factor of four to produce L-band MW pulses at 960 MHz. 20 W broadband power amplifier ZHL-20W-13+ (Minicircuits) was used to produce pulses of sufficient for the experiment power. A cross-loop resonator equipped with modulation coils was manufactured. The excitation loop had medium diameter 5 mm and the detection loop had medium diameter of 11 mm. The copper wires used to make resonator loops had 0.8 mm and 0.6 mm diameters, respectively. The excitation loop was positioned orthogonal to the excitation loop. Both loops were orthogonal to the direction of the external magnetic field that was produced by an electromagnet. Loaded with the trityl sample, described below, the quality factors were about $Q=40$ and $Q=100$ for the excitation and receive coils, respectively. Detuning resonators improved isolation from 20 to 30 dB. The power amplifier output was connected to the excitation coil through an isolator for its protection. Single 100 ns pulse were used to excite spins and observe free induction decays, FID, which were digitized and averaged using Keysight U1084A high-speed digitizer. The digitizer was phase-locked to the AWG using the 10 MHz external reference. The sampling rate was 4GS/s, sufficient for direct measuring signal at 986 MHz carrier frequency.

3.3 Samples

A degassed 2 mM solution of trityl-CD₃ (methyl tris(8-carboxy-2,2,6,6-tetramethyl (d₃)-benzo[1,2-d:4,5-d₀]bis(1,3)dithiol-4-yl)-tri sodium salt) in water in a 5 mm O.D. tube was used for the experiments at 250 MHz. Relaxation time measurements using the standard pulse EPR at the same RF frequency were as follows: $T_1=7.8 \mu\text{s}$ and $T_2=5.1 \mu\text{s}$. A similar 1 mM sample in a flame-sealed Bruker quartz I.D.=3mm tube was used for measurements with the L-band spectrometer.

3.4 Modulation field calibration

Accurate timing of the pulses with respect to the modulation phase is important for the success of the field-modulated pulsed experiment (see Fig.1). The modulation amplitude needs to be precisely known for data post-processing. The modulation phase and amplitude were measured in the experiment shown in Fig. 6a. FID signals after an RF pulse were detected and post-processed to extract the required modulation parameters. Fig.6b shows the real and imaginary components of an FID from the trityl sample. The signal does not look like a standard free induction decay due to the modulation, which changes the Larmor frequency of the spins with respect to the receive coil resonant frequency. The signal amplitude is maximum when the precession frequency approaches the resonant value at 257.6 MHz and is attenuated off-resonance. The instantaneous FID frequency is proportional to the magnetic field. The short-time Fourier transform (FT), FT within a small time window, reveals the Larmor frequency and magnetic field strength as a function of time (Fig. 6c). Fitting of the $B(t)$ curve to a sinusoid permits measurement of the modulation amplitude and phase. Calibration of the modulation parameters is independent of the resonator tuning and coupling. A similar procedure was performed to calibrate 480 kHz modulation for the L-band experiments.

3.5 Relaxation times measurements at 250 MHz

Relaxations times of the trityl sample, T_1 and T_2 , were measured as described above. Echo signals, digitized at the carrier frequency with the sampling 3.2 GS/s, were post-processed in two steps. First, the signals were numerically transformed in to a reference frame rotating with the Larmor frequency of the spins at the highest point of the modulation waveform, $\theta=270^\circ$ in Fig.4. Real and imaginary parts of the echo signals in T_1 experiment are shown in Fig.7a, b. Two values of $\tau=7$ and 28 μs were chosen for comparison. Because of the magnetic field modulation, the signals demonstrate oscillations. A second transformation into the variable Larmor frequency accelerating frame associated with modulated magnetic field was accomplished by signal multiplication on the driving function described in Eq. (7). Transformation signals in Fig. 7a, b produced echoes shown in Fig.7c.

Fig. 8 shows the T_1 and T_2 experimental results in comparison with the values measured in the standard inversion recovery and spin echo experiments with a 250 MHz pulsed spectrometer [19]. Because of the limitation on the modulation frequency f_m , only two experimental points were measured for the exponent decaying with the T_2 . In the case of T_1 , five measurements were done. Exponential fitting of T_1 data resulted in a value 6.9 μs , 13% smaller than the 7.8 μs value measured using the standard method.

3.6 Dead-time reduction in FM FID experiment at L-band

Dead-time reduction in the experiment described in Fig. 1 was evaluated by comparison of the FID signals measured with and without field modulation. In the latter case, the resonators were tuned to the same 986 MHz frequency (see Fig. 5). Figures 9a, b demonstrate the signal observed after 100 ns pulse that was placed at the modulation phase $\theta=150^\circ$ (see Fig.1). Because the receive coil was detuned by 26 MHz from the excitation frequency, FID signal is only seen when the Larmor frequency is within the bandwidth of the resonator. This happens at $\theta=270^\circ + k \cdot 360^\circ$, where k is an integer number. Fig.9a shows

the beginning of the measured signal from a pulse placed at $\theta=150^\circ$. In Fig.9b the y-axis is zoomed in to the EPR signal that is much weaker compared to the resonator ring-down component. Fig.9c, d demonstrate analogous experiment but with pulse placed at $\theta=30^\circ$. Fig.9e, f shows the signals obtained in conventional way without field modulation. The excitation and receive coils were tuned to the same frequency. For this reason, the entire FID signals is present in the data. It can be seen that the ring-down components dominates EPR at times below about 3 us.

4. Results and Discussion

Numerical simulations and experimental results demonstrate the validity of the FMP EPR method. 250 MHz pulsed EPR system was used to perform a proof-of-concept spin-echo experiment and measure relaxation times. Frequency detuning by $\Delta f=12.6$ MHz between the transmit and receive coils provided 80 dB isolation. A higher degree of isolation could be achieved by increasing the modulation amplitude (see. Eq. (2) and Fig. (3)). If the goal of the experiment is to acquire undistorted EPR spectra, there is a limit over which the chirping effect needs to be taken into account (see Eq. (12)). Distorted EPR spectra can be corrected in post-processing if the frequency responses of the excitation and receive coils are measured. Attenuation and phase shifts for each spin packet can be calculated and included into spectral fitting. An alternative approach to reduce the chirping effect is to modify the experiment described in Fig. 1 and place the pulses on modulation curves, where $B(t)$ rate change is the slowest (see Eq. (15)). In this experiment, the inter-pulse delays would be 1.5 times longer and the receive coil must work in transmit/receive mode, but the frequency separation would increase by 25 %. In comparison with the standard spin echo, where τ values can be changed in small increments, in FMP EPR, the increment values are limited, as described by Eqs. (13-15). Increasing the modulation frequency decreases the step size and increases the number of measurements. If FID is known to be a single exponent, as in oxymetric imaging, a relatively small number of data points is sufficient. Otherwise, the data size can be increased by varying the modulation frequency. FMP EPR can also be complementary to the standard spin-echo method to provide measurements at small τ values. The 250 MHz proof-of-concept experiment did not fully explore the advantages of FMP EPR due to hardware limitations. The coils mounted on the rapid-scan resonator self-resonated above 100 kHz. For demonstration of the dead-time reduction a proof-of-concept L-band system was constructed. Available 20 W amplifier was able to produce 100 ns pulses that corresponded to approximately 20 degree turning angle. Comparison of the FID and resonator ring-down components demonstrated five times ring-down reduction. The dead time reduction is the result of two different but related mechanisms: (i) improved excitation/detection isolation, (ii) separation of the resonator ring-down and FID signal in the frequency domain. Isolation reduces the detector protection time, during which no EPR signal can be detected. The second mechanism solves the problem of a strong ring-down signal that overwhelms the EPR component. Because the ring-down is centered around the excitation frequency, which is shifted from the detection frequency, band-pass filtering can be used to eliminate the resonator ringing contamination. The latter is the major dead-time factor in the L-band experiment, in which the receive coil was critically coupled. This suggests that in FMP EPR there is no need to over-couple resonator to reduce ring-down

time beyond what is necessary to capture the required bandwidth. This would be the case of narrow spin probes spectroscopy.

To take full advantage of the suggested methodology, a dedicated system is being designed to operate at $f_m = 1$ MHz. In this case, the minimum inter-pulse delay time will become a few hundred nanoseconds, which will allow for an increased number of data points in the T_2 and T_1 experiment. The promising application of this method is oximetric EPR imaging, especially that using fast relaxing spin probes, such as nitroxides.

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Highlights

Receiver and transmit coils can be tuned to separate frequencies

Detuning improves excitation/detection isolation and reduces dead-time

Sinusoidal magnetic field modulation enables spin echo detection

Fig. 1.

Schematic description of a field-modulated spin echo experiment with separation of the detection and excitation frequencies. The first excitation $\pi/2$ pulse is applied when modulation phase θ is equal to 30° . It is followed by the second inversion π pulse at $\theta = 150^\circ$. Both pulses are applied at the same magnetic field. The external magnetic field and modulation amplitude are selected to match the Larmor frequency at this field value to the resonance frequency of the transmit coils. The inter-pulse delay τ is equal to $1/3$ of the modulation period ($\theta = 120^\circ$). The transverse magnetization refocuses to form an echo signal at $\theta = 270^\circ$. The receive coil is tuned to a higher frequency, defined by Eq. (2). Accelerating oscillations observed in the echo signal are the result of the magnetic field change during signal detection. Frequency separation (see Eq. (2)) translates into an improved isolation between the excitation and detection.

Fig. 2.

Results of numerical simulations for FMP EPR spin echo with the following parameters: $T_1=1000$ ns, $T_2=700$ ns, $f_m=500$ kHz, $f_0=250$ MHz, $Q=10$, pulse=50 ns. The EPR spectrum consisted of three equidistant equal intensity Gaussian lines with 2.5 G splitting and 0.8 G Gaussian broadening. **(a, b)** Field-modulated spin echo signals with **(a)** $B_{pp}=8$ G and **(b)** $B_{pp}=24$ G. The abscissa is given in the modulation field phase units (see Fig. 1). **(c, d)** EPR spectra (red lines) obtained from **(a, b)**, respectively, are compared with the nomodulation spectrum (blue lines). The model EPR spectrum unaffected by the bandwidth limitation of RF pulses and Q is shown by black lines

Fig. 3. Numerically calculated isolation between the excitation and receive coils as a function of the frequency offset normalized to the coils BW. Insert: Integrated contribution (red area) within the detection BW was calculated.

Fig. 4. Schematic description of the experiment to measure relaxation times T_2 (**a, b**) and T_1 (**c, d**). The inter-pulse intervals τ are incremented as described in Eq. (13) and Eq. (14). In (**a**) $\tau = 120^\circ$ and in (**b**) $\tau = 240^\circ$. To measure T_1 , a preceding π pulse is added to implement the inversion-recovery experiment and interval for the spin echo sequence is fixed. In (**c**) the delay after the inversion pulse is $\tau = 240^\circ$ and in (**d**) it is $\tau = 360^\circ$.

Fig. 5. Simplified block diagram of the EPR experimental setup for both 250MHz and L-band spectrometers. RF excitation, detection and modulation frequencies for the low frequency spectrometer were 245MHz, 256.7 MHz and 96 kHz, respectively. The values for the L-band design, shown in brackets, were 960 MHz, 986 MHz, and 480 kHz, respectively. Excitation pulses were generated by the AWGs, which were time-locked to the digitizers, ADC. The pulses were amplified and applied to the transmit coil, TC. The EPR signals were detected by the orthogonal receive coil, RC, amplified and digitized. B(t) was produced by the modulation coils, MC, resonated at 96 kHz and 480 kHz, respectively.

Fig. 6. Measurement of the modulation amplitude and phase inside the resonator. **(a)** A single 90° pulse is used to generate FID signal produced by the unpaired electrons in trityl radical. **(b)** The Larmor frequency of the spins precession varies in time. It is driven by the changing magnetic field $B(t)$. When the precession frequency matches that of the receive coil, the observed signal is the strongest. Otherwise, it is attenuated. **(c)** Short-term Fourier transform within a small moving time window produces the modulation waveform.

Fig. 7.

Results of the transformation into a constant frequency reference frame. (a, b) Real and imaginary parts of the echo signals detected in the T_1 experiment at $\tau = 7$ us and 28 us, respectively. Signal at $\tau = 7$ us was multiplied by factor of 2.7 to facilitate echo shape comparison. (c) Real parts of the echo signals after the second transformation into the accelerating frame.

Fig. 8. Validation of the field-modulated pulsed methodology by comparison with the independent T_2 (a) and T_1 (b) measurements. Echo amplitudes are presented.

Fig. 9.

Evaluation of dead-time reduction in the FMP EPR experiment with 26 MHz excitation/detection detuning. Spectrometer traces during and after 100 ns pulse are presented. Left column presents traces scaled to the maximum signal. Right column shows traces scaled to the EPR signals, which are much smaller compared to the ring-down amplitude. (a, b) FMP EPR with the pulse applied at $\theta=150^\circ$. Clear FID signal was observed at about 600 ns, indicated by an arrow. (c, d) FMP EPR with the pulse was applied at $\theta=30^\circ$. An arrow indicates the first observed signal. (e, f) Conventional EPR experiment. The resonator ring-down related signal component is significant even at 3 us after the pulse. The dead-time reduction is about a factor of five. Field modulation with $f_m=480$ kHz and $B_{pp}=12.4$ G was used in FMP experiments.