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Corrections for sinusoidal background and non-orthogonality of signal channels in sinusoidal rapid magnetic field scans

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Abstract

The rapidly-changing magnetic field of sinusoidal rapid scans creates background signals that are dominated by oscillations at the scan frequency. The background oscillations can be removed without acquiring off-resonance data. For data acquired in quadrature, up-field and down-field scan signals can be separated in the frequency domain. For each scan direction, the background oscillation can be calculated by fitting to the half cycle that does not contain the EPR signal. The extrapolated fit function is then subtracted from the half cycle that contains the EPR signal. By zeroing the array for the half cycles that do not contain the EPR signal, the signal-to-noise is improved and the data are corrected for non-orthogonality of the quadrature channels.

1. Introduction

In rapid scan EPR the magnetic field is scanned through resonance in a time that is short relative to electron spin relaxation times. Since the time on resonance is short, higher B_1 can be used without saturating the spin system, which can improve the signal-to-noise (S/N) ratio relative to conventional continuous wave (CW) spectroscopy. This improvement in S/N has been demonstrated for the E' signal in irradiated quartz [1] and for nitroxyl radicals tumbling rapidly in fluid solution [2]. Methods to deconvolve linear [3] and sinusoidal [4] rapid scans and calculate the slow-scan spectra have been demonstrated. Signals are recorded with direct quadrature detection. Use of both the real and imaginary channels improves the S/N by a factor of 2, provided that the two channels are exactly orthogonal [5]. For samples with relaxation times and lineshapes typical of nitroxyl radicals, scan rates of the order of megagauss per second may be desirable. The amplifier power requirements for the electronics to generate scans at these rates are lower for sinusoidal scans with resonated coils [4] than for linear scans.

The rapidly-changing magnetic field of the sinusoidal scans creates background signals that are dominated by oscillations at the scan frequency. The background signal can be decreased by shielding the resonator and by avoiding mechanical resonances, but background correction is still required for weak signals or wide scans. One approach to correction for the background oscillations is to record the off-resonance signal and subtract it. This approach has two disadvantages. First, it doubles the experimental time without adding signal intensity. Even if the background can be filtered to suppress high-frequency noise, the subtraction lowers the S/N . Secondly, changing the external magnetic field may impact the background signal.

This paper reports a novel background removal method for sinusoidal scans that does not require an off-resonance signal. It is assumed that the background is sinusoidal, with unknown amplitude and phase with respect to the scan waveform. This assumption is consistent with experimental observations. It also comes from the expectation that sinusoidal excitation should produce a sinusoidal response.

2. Theory

2.1 Background subtraction

The theory that underlies the subtraction process is described in Eq. (1) – (13). It is illustrated in Fig. 1 for a single Lorentzian line and orthogonal detection channels.

Rapid scan EPR signals are acquired using quadrature detection for the full period ($2\pi/\omega_m$) of sinusoidal excitation with angular frequency ω_m , averaged many times [4]. The data consist of pairs of EPR signals: in one half cycle the magnetic field is increasing and in the other half cycle the magnetic field is decreasing (Fig. 1a). It is assumed that the spin response to excitation has decayed to baseline before the start of the next half cycle. The two channels of the detected signal contain $rs(t)$, and a background signal that is induced by the rapidly changing magnetic field. It is assumed that the background is sinusoidal, with arbitrary amplitude and phase in the two channels, as expressed in Eq. (1) and (2).

$$I(t) = \text{real}(rs(t)e^{j\phi}) + a\cos(\omega_m t + \alpha) \quad (1)$$

$$Q(t) = \text{imag}(rs(t)e^{j\phi}) + b\cos(\omega_m t + \beta) \quad (2)$$

where $j = -1$, and a , b , α , and β are the amplitudes and phases for the background. The signal phase ϕ , is also arbitrary, and is adjusted experimentally or in software to obtain the pure absorption and dispersion spectra, after deconvolution [4]. Using the relationship $\cos(x) = 0.5(e^{jx} + e^{-jx})$, the I and Q signals can be combined into a complex signal $s(t)$:

$$s(t) = I(t) + jQ(t) = rs(t)e^{j\phi} + Ue^{j\omega_m t} + De^{-j\omega_m t}, \quad 0 \leq t < 2\pi/\omega_m \quad (3)$$

where U and D are complex numbers that depend on a , b , α , and β as shown in Eq. (4).

$$Ue^{j\omega_m t} + De^{-j\omega_m t} = a\cos(\omega_m t + \alpha) + j b\cos(\omega_m t + \beta) \quad (4)$$

The Fourier transform of $s(t)$ is $S(\omega)$, Fig. 1b,

$$S(\omega) = RS(\omega)e^{j\phi} + U\delta(\omega - \omega_m) + D\delta(-\omega - \omega_m) \quad (5)$$

where $RS(\omega)$ is the Fourier transform of the rapid scan and δ is the delta function.

$RS(\omega)$ can be separated into $RS^\uparrow(\omega)$ and $RS^\downarrow(\omega)$, which are the Fourier transforms of the upfield and down-field time-domain EPR signals, respectively, as shown in (6). The up- and down scans do not overlap in the frequency domain except at $\omega = 0$.

$$S(\omega) = RS^\uparrow(\omega)e^{j\phi} + RS^\downarrow(\omega)e^{j\phi} + U\delta(\omega - \omega_m) + D\delta(-\omega - \omega_m) \quad (6)$$

To understand the separation into $RS^\uparrow(\omega)$ and $RS^\downarrow(\omega)$, one has to examine the evolution of the spin system during the rapid scan. In a rapid scan EPR experiment the excitation power is on constantly and the source frequency f_s is tuned to the frequency of the resonator. Since the Larmor frequency (f_L) of the spins is proportional to magnetic field, it changes sinusoidally through the scan with $f_L = -(\gamma/4\pi) B_{pp} \cos(\omega_m t)$, where B_{pp} is the peak-to-peak amplitude of the scan. The magnetic field, and the Larmor frequency, increase during the first half of the scan ($0 \leq t < \pi/\omega_m$) and decrease during the second half ($\pi/\omega_m < t < 2\pi/\omega_m$). Resonance occurs and spins are excited when $f_L = f_s$. After passing through resonance, f_L continues to increase or decrease. As a result, the Fourier transform of the EPR signal measured for the up-field scan has only frequency components f_s and the down-field scans have only components $-f_s$. As a result, $S(\omega)$ can be divided into separate parts for positive and negative frequencies.

$$S^\uparrow(\omega) = S(\omega) \theta(\omega) = RS^\uparrow(\omega) e^{j\phi} + U \delta(\omega - \omega_m) \quad (7)$$

$$S^\downarrow(\omega) = S(\omega) \theta(-\omega) = RS^\downarrow(\omega) e^{j\phi} + D \delta(\omega - \omega_m) \quad (8)$$

where $S^\uparrow(\omega)$ (Fig. 1c) and $S^\downarrow(\omega)$ (Fig. 1d) correspond to the up-field and down-field scans, including background.

In Eqs.(7,8) $\theta(\omega)$ is the Heaviside function. The $S(0)$ value, which is responsible for any DC offset of the rapid scan signal, can be ignored at this point of the background removal procedure. The zeroth order baseline correction can be performed at the final step of the procedure. Inverse Fourier transformation of Eq.(7) and Eq.(8) produces two time domain signals, where the up-field (Fig. 1e) and down-field (Fig. 1f) components of the rapid scan signal are separated:

$$s^\uparrow(t) = rs^\uparrow(t) e^{j\phi} + U e^{j\omega_m t}, \quad rs^\uparrow(t) = 0 \text{ for } \pi/\omega_m \leq t < 2\pi/\omega_m \quad (9)$$

$$s^\downarrow(t) = rs^\downarrow(t) e^{j\phi} + D e^{-j\omega_m t}, \quad rs^\downarrow(t) = 0 \text{ for } 0 \leq t < \pi/\omega_m \quad (10)$$

Eq. (3) – (10) can be expressed in a compact form by introducing two operators $T^\uparrow$ and $T^\downarrow$:

$$s^\uparrow(t) = T^\uparrow(s(t)) = F^{-1}[F(s(t)) \theta(\omega)] \quad (11)$$

$$s^\downarrow(t) = T^\downarrow(s(t)) = F^{-1}[F(s(t)) \theta(-\omega)] \quad (12)$$

where F and F^{-1} denote Fourier transform and inverse Fourier transform.

The second half-cycle of $s^\uparrow(t)$ (Eq. 9) (Fig. 1e) has no EPR signal and only the U component of the background. U can be obtained by fitting the background in this half-period. Similarly, D can be obtained by fitting the first half-period of the signal $s^\downarrow(t)$ (Eq. 10) (Fig. 1f), which is only background. The background-corrected rapid-scan signals (Fig. 1g, 1h) can be obtained by subtraction, Eq. (13):

$$rs(t) e^{j\phi} = s(t) - U e^{j\omega_m t} - D e^{-j\omega_m t}, \quad 0 \leq t < 2\pi/\omega_m \quad (13)$$

where the complex numbers U and D include information about both the amplitudes and phases of the real and imaginary components of the background (Eq. 4).

2.2 Correction for non-orthogonality for quadrature channels

The two quadrature channels of the detector often are not exactly orthogonal. The amplification in the two channels is a little different, and the 90° phase shifter in the bridge is not exact and varies with frequency. If the two quadrature channels are not orthogonal, the deconvolution algorithm may create artifacts [4]. In addition, non-orthogonality introduces errors when the two channels are combined to improve signal-to-noise. The separation of the up-field and down-field signals in the frequency domain can also be used to restore orthogonality of the real and imaginary components of the rapid scan signal. The discrepancy in gains can be represented by a factor of $(1+\alpha)$ and the deviation from orthogonality as a phase angle $e^{j\beta}$, where both α and β may be positive or negative Eq. (14).

$$s(t) = \text{real}(rs(t)) + j(1+\alpha) \text{imag}(rs(t)e^{j\beta}) \quad (14)$$

Assuming that $|\alpha|, |\beta| \ll 1$, Eq.(14) can be simplified to

$$s(t) \approx rs(t) + j\alpha \text{imag}(rs(t)) + j\beta \text{real}(rs(t)) \quad (15)$$

It can be shown that the combination of the up-field half-cycle of $s^\uparrow(t)$ (Eq. (11) and the down-field half-cycle of $s^\downarrow(t)$ (Eq. (12) forms a signal with precise orthogonality of the two components.

$$s^Q(t) = s^\uparrow(0 \leq t < \pi/\omega_m) + s^\downarrow(\pi/\omega_m \leq t < 2\pi/\omega_m) \quad (16)$$

with the amplitude and phase slightly different from that of undistorted full cycle $rs(t)$ signal. As guidance in the proof one can use Appendix 1 in ref. [6]. Practical application of Eq.(16) is not limited by lineshape or scan rate. The only limitation is that the signal must decay to zero by the end of the half cycle. Since phase is arbitrary, a small change in phase is not a concern. Provided that $|\alpha|, |\beta| \ll 1$, the change in signal amplitude that occurs due to the correction for non-orthogonality has little impact on signal quantitation. The $T^\uparrow/T^\downarrow$ transformation eliminates half of the noise in the frequency domain and achieves the same improvement in signal-to-noise for the absorption signal as would have been obtained by using the Kramers-Kronig transformation to combine the absorption and dispersion channels. The residual noise in the two channels is now correlated so no further improvement in signal-to-noise would be obtained by combining the absorption and dispersion channels.

The procedure for background subtraction of experimental data is the following. (i) Based on the known scan frequency and time per data point, calculate the number of data point for each sinusoidal scan cycle. (ii) Identify a point in the data array that corresponds to the beginning of a sinusoidal cycle. This can be done by deconvolving the data, and checking that the positions of the peaks in the up-field and down-field scans coincide. Steps (i) and (ii) define the first and last elements of the array $s(t)$, Fig. 1a. (iii) Perform a complex Fourier transform to obtain $S(\omega)$, Fig. 1b. (iv) Separate $S(\omega)$, into arrays $S^\uparrow(\omega)$ and $S^\downarrow(\omega)$ that contain the positive and negative frequencies, respectively, Fig. 1c and 1d. (v) Perform reverse Fourier transforms independently for $S^\uparrow(\omega)$ and $S^\downarrow(\omega)$, to obtain $s^\uparrow(t)$ and $s^\downarrow(t)$, respectively, Fig. 1e and 1f. (vi) Fit the half-sinusoid in the second half of $s^\uparrow(t)$, extrapolate into the first half cycle, and subtract from $s^\uparrow(t)$ to obtain the baseline corrected signal for the up-field half cycle of the scan, Fig. 1g. (vii) Perform the analogous fitting procedure for the first half of $s^\downarrow(t)$, extrapolate, and subtract from the second half to obtain the baseline corrected signal for the down-field half cycle of the scan, Fig. 1h. (viii) Perform sinusoidal

deconvolution [4] to obtain the slow scan spectra. (viii) Combine the up-field and down-field scans to obtain the final spectrum. (ix) To correct the phase, multiply the original data by $e^{i\phi}$ (Eq. 1) and repeat the deconvolution and background subtraction process. The steps are implemented in a MatLab procedure with the array index for first point of a cycle and phase correction as adjustable parameters.

3. Experiment

3.1 Samples

Xanthine oxidase, hypoxanthine, superoxide dismutase, horse heart ferricytochrome c, and diethylenetriaminepentaacetic acid (DTPA) were purchased from Sigma-Aldrich (St. Louis, MO). Dr. Gerald Rosen at the University of Maryland generously supplied the spin trap, 5-tert-butoxycarbonyl-5-methyl-1-pyrroline N-oxide (BMPO) [7]. Solutions were made in a 50 mM sodium phosphate solution (with 1 mM DTPA added), buffered to a pH~7.4. Superoxide was generated by a 2 μ M hypoxanthine/0.04 units/mL Xanthine Oxidase solution ($O_2^{\cdot -}$ flux of ~2 μ M/min measured by SOD-inhibited reduction of ferricytochrome C). The BMPO (50 mM) formed an adduct with the superoxide that was detected with EPR [7].

Electrochemically prepared x-LiPc was graciously provided by Prof. Harold M. Swartz (Dartmouth Medical School) [8]. Multiple small crystals were placed in three quartz 3-mm OD tubes with 0.5 mm wall thickness. The amounts of sample in the three tubes were different. One tube was extensively evacuated and then flame sealed. The samples in the other two tubes were equilibrated with a 2% O_2 in nitrogen gas mixture then flame sealed. The three tubes were arranged in a row with the evacuated sample in the middle. Thus, the center-to-center distances between samples in adjacent tubes were 3 mm. The line between the centers of the tube was approximately aligned with the direction of the magnetic field gradient.

3.2 Spectroscopy

Rapid scans at X-band were obtained on a Bruker E500T transient spectrometer using a dielectric resonator. The scan parameters for spin-trapped superoxide were $B_{pp} = 55$ G and $F_m = \omega/2\pi = 50645$ Hz. Rapid scans at 250 MHz were obtained on the locally-designed and built system [9]. The scan parameters for the LiPc sample (250 MHz) were $B_{pp} = 15$ G and $F_m = 1200$ Hz in the presence of a gradient of 10 G/cm. The sinusoidal rapid scan driver has a feed-back circuit similar to what was designed for linear scans [10] and includes interchangeable capacitors to resonate the circuit including the scan coils. Details of the design of the rapid scan driver and coils will be described separately. The 250 MHz cross-loop resonator has a design similar to that reported in [11].

4. Results

4.1 Background subtraction for rapid scans of BMPO-OOH at X-band

Application of the background subtraction procedure to rapid scan data for spin-trapped superoxide (BMPO-OOH) at X-band is shown in Fig. 2 for a case in which the background is large compared with a relatively weak EPR signal (Fig. 2a). The background oscillation is about 90° out of phase from the scan waveform (Fig. 2a). The up-field and down-field components of the signal can be separated using Eqs. (11,12). The up-field signal $s^{\uparrow}(t)$ is shown in Fig. 2b and the down-field signal $s^{\downarrow}(t)$ is shown in Fig. 2c. For each scan direction the half cycle in which no EPR signal is expected were fitted with sinusoids to determine the complex numbers U and D. The real and imaginary components of the signal, after subtraction of the calculated complex background signal (Eq. (13)), are shown in Fig. 2d.

Additional details can be seen when the simulated background signals are subtracted for the individual half-scan, $s^{\uparrow}(t)$ (Fig. 2b) and $s^{\downarrow}(t)$, (Fig. 2c) separately (Fig. 3). The spectra show that the separation of up-field and down-field components is not complete. The up-field signal $s^{\uparrow}(t)$ has weak residual contributions from the down-field signal, and vice-versa. This observation indicates that the assumption of orthogonal signals in the real and imaginary channels is not valid. To correct for the non-orthogonality, the half-cycle that contains the residual signal can be zeroed or deconvolution can be done for each half cycle separately.

The resulting spectrum after sinusoidal deconvolution [4] and combination of the up-field and down-field scans is shown in Fig. 4. The amplitude of the background signal in the real and imaginary channels was about 1.5 to 2.0 times larger, respectively, than the EPR signal in the experimental data, and was reduced to less than the random noise level by the subtraction procedure.

For sharp signals such as those for BMPO-OOH it might be argued that the sinusoidal background could be defined even in the presence of the signal. However, one important application of sinusoidal rapid scans is to EPR imaging where some spectra are substantially broadened and might be difficult to distinguish from background. A demonstration of the application of the background and non-orthogonality corrections is shown in Fig. 5 for a phantom composed of three tubes of LiPc. The correction procedure removed the sinusoidal background without introducing artifacts. The spectra obtained from the up-field (Fig. 5a) and down-field (Fig. 5b) scans are in good agreement and can be combined to give the average signal (Fig. 5c) with improved S/N.

5. Discussion

In addition to the examples shown in Figs. 4 and 5, the background correction procedure has been used for a variety of other samples and consistently reduces the sinusoidal background to less than the noise level. In applying this method it is important to know which half cycles correspond to the up and down-field scan directions, which can be determined by changing the center field and noting the direction in which the signals shift. It also is important to define the real and imaginary channels such that in the up-field scan the dispersion signal goes positive before it goes negative. Data should be acquired in the linear response regime, without signal saturation, because the absorption saturates more readily than the dispersion.

The background subtraction method also provides a method to correct for nonorthogonality of the detection system. In pulse EPR experiments which use quadrature detection, the problem of non-orthogonality of the quadrature channels is solved by phase cycling. The phases of the pulse change with 90° increments and the echo signal are summed or subtracted to restore orthogonality of the signal.

For samples with narrow well-resolved lines it might be possible to fit the background sinusoid in the presence of signal. However, for samples with broad lines or in an imaging experiment with signals broadened by a gradient, it is much better to have a procedure that does not depend upon distinguishing signal from background. A procedure based on fitting an underlying background sinusoid also would not correct for non-orthogonality of channels.

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Research Highlights

- Rapid scan EPR signals are separated from sinusoidal background in the frequency domain.
- The sinusoidal background signal is fitted and subtracted.
- This background subtraction method does not require recording an off-resonance signal.
- This procedure also corrects for non-orthogonality of the quadrature detection channels.
- Signal to noise is improved by removing half of the noise in the frequency domain.

Fig. 1.

Separation of the sinusoidal background from the rapid scan EPR signal. (a) Full cycle of a rapid scan signal, $I(t)$ and $Q(t)$ including the sinusoidal background, which may be out of phase from the scan. The first half of the rapid scan signal corresponds to the up-field scan and the second half corresponds to the down-field scan.

(b) The Fourier transform of the signal in (a) is $S(\omega)$. The sinusoidal background in the time domain is transformed into two spikes in the frequency domain, at the positive and negative scan frequencies, respectively. The intensities of these two spikes are much larger than the intensity of the rapid scan signal.

(c) and (d) The frequency domain signal in (b) is divided into two halves, one for positive frequencies $S^{\uparrow}(\omega)$ (c) and the another for negative frequencies $S^{\downarrow}(\omega)$ (d) Magnitudes of signals in the time domain, (b) – (d), are displayed.

(e and f) The signals in (c) and (d) are inverse Fourier transformed to produce time domain signals, (e) and (f), respectively. In (e), $s^{\uparrow}(t)$, the first half of the signal contains up-field rapid scan + background, but the second half contains only background. Since the signal is a full cycle of the sinusoid, the background in the second half can be fitted, extrapolated into the first half, and subtracted. Similarly, the first half of the signal in (f), $s^{\downarrow}(t)$, does not contain a rapid scan signal, but the second half contains the down-field half cycle + background. The background in the first half can be fitted, extrapolated into the second half and subtracted. Alternatively, the full cycle backgrounds from (e) and (f), can be summed and subtracted from the data in (a).

(g) and (h). Background subtracted up-field (g) and down-field (h) scans.

Fig. 2.

Application of background subtraction procedure to spectra of BMPO-OOH at X-band. The signals in the two channels are shown in blue and green. a) Experimental data for a full cycle of sinusoidal scan overlaid on the magnetic field scan waveform (black). b) Up-field scan, $s^{\uparrow}(t)$, c) Down-field scan $s^{\downarrow}(t)$. For both the up and down scans, the fitted background (solid red) was extrapolated into the half-cycle that includes the EPR signal (dashed red). d) Results after background subtraction (Eq. (13)).

Fig. 3.

Subtraction of the calculated background signals from the up-field (Fig. 1b) and down-field scans (Fig. 1c) separately gives the spectra shown in Fig. 2a and 2b, respectively. The spectra in the two channels are shown in blue and green. These spectra show the residual signals in the half cycles that are expected to be only background, which occur due to non-orthogonality of the channels. These are removed by zeroing the half cycle that should only contain background.

Fig. 4. Absorption spectrum of BMPO-OOH after deconvolution and combination of the up- and down-field scans. The characteristic hyperfine splittings are well resolved.

Fig. 5. Spectra at 250 MHz of 3 samples of LiPc in the presence of a magnetic field gradient, after correction for the sinusoidal background and non-orthogonality of the channels. a), b) Spectra obtained by scanning up-field and down-field. c) Average of spectra in a) and b).