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Reconstruction of the first-derivative EPR spectrum from multiple harmonics of the field-modulated continuous wave signal

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ABSTRACT

Selection of the amplitude of magnetic field modulation for continuous wave electron paramagnetic resonance (EPR) often is a trade-off between sensitivity and resolution. Increasing the modulation amplitude improves the signal-to-noise ratio, *S*/*N*, at the expense of broadening the signal. Combining information from multiple harmonics of the field-modulated signal is proposed as a method to obtain the first derivative spectrum with minimal broadening and improved signal-to-noise. The harmonics are obtained by digital phase-sensitive detection of the signal at the modulation frequency and its integer multiples. Reconstruction of the first-derivative EPR line is done in the Fourier conjugate domain where each harmonic can be represented as the product of the Fourier transform of the 1st derivative signal with an analytical function. The analytical function for each harmonic can be viewed as a filter. The Fourier transform of the 1st derivative spectrum can be calculated from all available harmonics by solving an optimization problem with the goal of maximizing the *S*/*N*. Inverse Fourier transformation of the result produces the 1st derivative EPR line in the magnetic field domain. The use of modulation amplitude greater than linewidth improves the *S*/*N*, but does not broaden the reconstructed spectrum. The method works for an arbitrary EPR line shape, but is limited to the case when magnetization instantaneously follows the modulation field, which is known as the adiabatic approximation.

1. Introduction

If the concentration of paramagnetic centers is low and the acquisition time is limited, it may be difficult to achieve a signal-to-noise ratio (*S*/*N*) for a continuous wave (CW) EPR signal that is sufficient for reliable data analysis. Increasing the magnetic field modulation is one way to improve the *S*/*N* [1,2], at the expense of line broadening. Two methods have been used to model the effects of over-modulation on an EPR lineshape. Pseudo-modulation is a mathematical description of magnetic field modulation as a filter that can be applied to experimental or calculated EPR lines [3,4]. Convolution of the filter with the EPR line produces a spectrum that is broadened by over-modulation. The method is applicable within an adiabatic approximation, which means that the magnetization follows magnetic field instantaneously. The effect of the modulation frequency on EPR lineshape is not taken into account. The second approach is based on the solution of the Bloch equations for a single spin 1/2 particle [5,6]. Both modulation amplitude and modulation frequency are taken into account. This method is applicable for inhomogeneously broadened EPR spectra that can be represented as a superposition of Lorentzian lines. Modeling the effects of over-modulation can be used to estimate the linewidth that would have been observed at lower modulation amplitude [7,8]. Bikineev et al. proposed reconstruction of an EPR spectrum, without prior knowledge of the lineshape, by applying the maximum likelihood method to multiple harmonics of an over-modulated signal [9].

In most EPR spectrometers the 1st harmonic spectrum is obtained as the output of a phase sensitive detector operating at the magnetic field modulation frequency. In the limit of low modulation amplitude the 1st harmonic is a good approximation of the first-derivative EPR signal. The 2nd harmonic (second derivative) has been found to be informative for resolution enhancement [10–12] and for saturation transfer EPR [13]. Higher harmonics have not been recorded for two reasons: (i) low *S*/*N* and (ii) if phase-sensitive detection (PSD) is done in hardware, detection of each harmonic would require a separate phase shifter, video amplifier, and digitizer channel. The first problem can be partially solved by over-modulation. If the modulation amplitude is smaller than the linewidth, the *S*/*N* of the *n*th harmonic decreases rapidly with *n*. However, for a strongly over-modulated line the higher harmonics have much higher *S*/*N* [2,14]. It has been shown that simultaneous fitting of multiple harmonics of over-modulated

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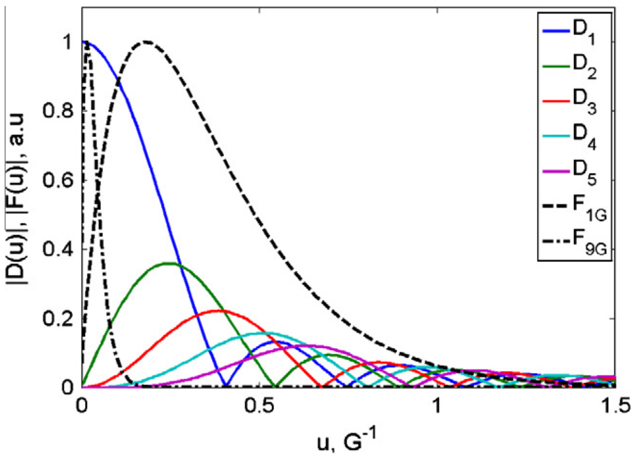

Fig. 1. Comparison of the filter functions $|D_1(u)|$ to $|D_5(u)|$ calculated for a modulation amplitude, h_m, of 3 G (solid lines), with the Fourier transforms of first derivative lineshapes with peak-to-peak linewidths of 1 G (dashed line) or 9 G (dot-dashed line).

spectra could improve the accuracy of the recovered spectrum [15]. The second problem can be solved by using digital PSD, where a single detection channel suffices to obtain multiple harmonics of the spectrum. The *n*th harmonic is denoted as $s_n(B)$. The spectrum $s_n(B)$ can be calculated by multiplication of the digitized signal by the *n*th harmonic of the sinusoidal reference followed by digital low-pass filtering. A few labs have implemented this method [15–18]. Bruker recently announced a Signal Processing Unit, SPU, with the capability to simultaneously digitally detect up to five harmonics [http://www.bruker-biospin.com]. With this innovation multiple harmonics of an EPR spectrum can be routinely measured with a commercial spectrometer.

In this paper a method is demonstrated to process multiple harmonics of an EPR spectrum recorded with over-modulation to calculate the familiar 1st derivative EPR line with improved *S*/*N*, without prior knowledge of the lineshape. Bikineev et al. solved the inverse problem for the entire digitized over-modulated signal [9]. In this paper a simpler and more intuitive way to derive expressions similar to what were obtained in Ref. [9] is shown. The impact on *S*/*N* of the modulation amplitude and of the number of harmonics that are used to reconstruct the spectrum is examined. The problem is solved in the domain that is the Fourier conjugate of the magnetic field domain. The Fourier transform of $s_n(B)$ can be represented as the result of multiplication of the Fourier transform of the 1st derivative spectrum by an analytical function that depends only on the modulation amplitude and number of the harmonic, n. Each function has an oscillatory behavior and can be considered as a filter with a set of zeros (Fig. 1). The filters corresponding to different values of n have maxima and zeros at different positions. If only one harmonic is measured, the information about the Fourier transform of the first derivative spectrum at the position corresponding to the filter's zero is lost. However, other filters have significant intensity at that position, so that the information is preserved if multiple harmonics of the spectrum are available. Appropriate combination of the harmonics permits restoration of the undistorted Fourier transform of the EPR spectrum. The reconstruction procedure is described in this paper and tested by numerical simulation and experiment.

2. Theory

It was shown in [19] that the Fourier transform of the *n*th harmonic EPR spectrum $s_n(B)$ can be written in the following form:

$$S_n(u) = j^n J_n\left(\frac{h_m u}{2}\right) G(u) \tag{1}$$

where $J_n(x)$ is the Bessel function of the first kind, $G(u)$ is the Fourier transform of the absorption (not a derivative) EPR signal $g(B)$, and h_m is the peak-to-peak modulation amplitude. Using the property of the Fourier transform that integration in the *B*-domain is equivalent to division by *ju* in the Fourier-conjugate *u*-domain, Eq. (1) can be rewritten as follows:

$$S_n(u) = j^{(n-1)} J_n\left(\frac{h_m u}{2}\right) u^{-1} F(u) \tag{2}$$

Here $F(u)$ is the Fourier transform of the first-derivative EPR line $f(B)$, where $f(B) = dg(B)/dB$. Using the recurrence relation for the Bessel function:

$$J_n(z) = \frac{(J_{n-1}(z) + J_{n+1}(z))z}{2n},$$

Eq. (2) can be expressed in a form that does not have *u* in the denominator:

$$S_n(u) = D_n(u) F(u) \tag{3}$$

where

$$D_n(u) = \left(\frac{h_m}{4n}\right) j^{(n-1)} \left(J_{n-1}\left(\frac{h_m u}{2}\right) + J_{n+1}\left(\frac{h_m u}{2}\right)\right), n > 0 \tag{4}$$

This rearrangement is done to avoid division by zero at $u = 0$ when using this relationship. The complex function $D_n(u)$ is a filter that converts $F(u)$ into the *n*th harmonic spectrum in the *u*-domain. To make Eq. (3) applicable to experimental data, which always contain noise, a noise term $\sigma_n(u)$ is added to Eq. (3):

$$S_n(u) = D_n(u) F(u) + (1 + j)\sigma_n(u) \tag{5}$$

The standard deviations of the noise in the *u*-domain are assumed to be equal for the real and imaginary parts. The subscript *n* in $S_n(u)$ indicates that the noise might be different for different harmonics. In an experiment the bandwidth of the detection system limits the maximum number of harmonics, N_H, that can be measured without significant intensity attenuation.

Fig. 1 compares the filter functions $|D_n(u)|$, $n = 1, 5$ for modulation amplitude $h_m = 3$ G, with the Fourier transforms, $|F(u)|$, of first-derivative Lorentzian lineshapes with peak-to-peak linewidths (ΔH_{pp}) of 1 and 9 G. For the broad line, the filters overlap extensively with $F(u)$, which is not the case for the narrow line. The $S_1(u)$ functions for those two lines can be obtained by multiplication of the Fourier transforms of the lineshapes $F_{1G}(u)$ or $F_{9G}(u)$ by the filter $D_1(u)$. For the broader line ($\Delta H_{pp} = 9$ G) multiplication by $D_1(u)$ (for $h_m = 3$ G) does not significantly distort $F_{9G}(u)$. The inverse Fourier transform of the product would produce a slightly broadened EPR spectrum. However, for the narrower line ($\Delta H_{pp} = 1$ G) multiplication of $F_{1G}(u)$ by $D_1(u)$ (for $h_m = 3$ G) significantly changes $F_{1G}(u)$, so the Fourier transform of $S_1(u)$ is a severely broadened spectrum.

Because of its oscillating behavior $D_1(u)$ not only acts as a low-pass filter, it also destroys information about $F_{1G}(u)$ in the vicinity of its zeros ($u \sim 0.4, 0.75, \ldots$). Because of zeros in $D_1(u)$, recovering the first-derivative EPR line from the first harmonic spectrum $S_1(u)$ by deconvolution is problematic. One may try to obtain an undistorted line by division $F(u) = S_1(u)/H_1(u)$. However, since the denominator $H_1(u)$ has zeros, small variation in the noise in $S_1(u)$ may be amplified. This situation is known as an ill-posed problem. It can be solved by regularization that produces a distorted but stable solution [20,21].

Fig. 1 not only shows the problem but also suggests a solution. Filter $D_3(u)$ has a maximum at the position of the first zero of $D_1(u)$, which means that the over-modulated 3rd harmonic preserves information about the function $F_{1G}(u)$ at $u \sim 0.4$. In that region $F(u)$ can be obtained by division $S_3(u)/D_3(u)$. Since the denominator is not zero, the solution would be stable. In the same manner other $D_1(u)$ zeros can be 'patched' by the higher harmonics. Thus, the first-derivative EPR signal can be reconstructed based on processing of multiple harmonics of the EPR spectrum in the u-domain. The solution of that problem is sought in the form of a combination:

$$S = \sum_{n=1}^{N_H} \alpha_n S_n = FD + (1+j)\sqrt{\sum_{n=1}^{N_H} |\alpha_n|^2 \sigma_n^2}, \quad D = \sum_{n=1}^{N_H} \alpha_n D_n \tag{6}$$

Here (and in subsequent equations) the argument u of the functions S, D, α_n and σ is omitted. The coefficients $\alpha_n = |\alpha_n| exp(j\varphi_{\alpha n})$ are the complex weighting factors and $\varphi_{\alpha n}$ are the phases. The fact that the sum of two sets of random numbers having standard deviations σ_1 and σ_2 results in a set with standard deviation equal to $\sqrt{\sigma_1^2 + \sigma_2^2}$ is used to derive Eq. (6).

The function $F(u)$ can be found from Eq. (6) as follows:

$$\frac{S}{D} = F + (1+j)\text{Err}, \quad \text{Err} = \sqrt{\frac{\sum_{n=1}^{N_H} |\alpha_n|^2 \sigma_n^2}{\sum_{n=1}^{N_H} \alpha_n D_n}} \tag{7}$$

Division of $S(u)$ by $D(u)$ (Eq. (7)) gives the desired function $F(u)$ plus a term that originates from the noise, which is $(1 + j)$ Err(u). A set of weighting factors $\alpha_n(u)$ is sought that minimizes function Err(u), at each value of u. Although the numerator of Err(u) depends only on $|\alpha_n(u)|$, the denominator depends on $\alpha_n(u)$, which are complex. For a given set of $\alpha_n(u)$, Err(u) is minimized when the denominator is maximized. This can be achieved when all the terms in the sum are real and positive, which requires

$$\alpha_n D_n = |\alpha_n D_n| \tag{8}$$

This is achieved when $\varphi_{\alpha n} = -\varphi_{Dn}$, where $\varphi_{\alpha n}(u)$, $\varphi_{Dn}(u)$ are the phases of the complex functions $\alpha_n(u)$ and $D_n(u)$, respectively. Since the phases of the weighting functions are defined by Eq. (8), the goal is to find the set of $\gamma_n(u) = |\alpha_n(u)|$ for which the error term is minimized. This occurs when all derivatives of Err(u) with respect to $\gamma_n(u)$ are equal to zero.

$$\partial\left[\sqrt{\sum_{n=1}^{N_H} \gamma_n^2 \sigma_n^2 \Big/ \sum_{n=1}^{N_H} \gamma_n |D_n|}\right] \Big/ \partial\gamma_k = 0, \quad k = 1, N_H \tag{9}$$

The solution of Eq. (9) is

$$\gamma_n = C|D_n|/\sigma_n^2 \tag{10}$$

where C is an arbitrary constant. The result, that the weighting factor of a particular harmonic in the sum Eq. (6) is proportional to $|D_n(u)|$ and inversely proportional to the noise variance, is quite reasonable. The larger the amplitude of the filter and the smaller the noise level, the better information about $F(u)$ that is preserved in $S_n(u)$. If the noise level is the same for all harmonics, Eq. (10) simplifies to Eq. (11).

$$\gamma_n = C|D_n| \tag{11}$$

3. Experimental

3.1. Samples

Lithium phthalocyanine (LiPc) prepared electrochemically following procedures in the literature [22,23] was provided by Prof. Swartz, Dartmouth University. A single very small crystal was used for the measurements. A sample in a 4 mm tube was open to the air. The EPR spectrum of the LiPc crystal had a Lorenzian lineshape with ΔH_{pp} = 0.77 G. An 0.1 mM solution of ^{15}N-4-hydro-3-carbamoyl-2,2,5,5-tetramethylpyrrolin-1-yloxy-d_{12} (mHCTPO) in water in a 4 mm quartz tube was degassed and sealed. The CW EPR spectrum of mHCTPO has two widely separated lines as a result of hyperfine interaction of the unpaired electron with the ^{15}N nucleus. Each nitrogen hyperfine line consists of two partially overlapping lines with about 0.27 G peak-to-peak linewidth, due to about 0.5 G hyperfine splitting by the proton at the 4-position of the ring [24]. The spectrum of the low-field nitrogen hyperfine line was measured in this study.

3.2. Spectroscopy

Experiments were done with a Bruker E500T spectrometer using 10 kHz magnetic field modulation. The resonator was a critically-coupled EN4118X-MD5, which has $Q \sim 2000$ for the empty resonator. The SPU unit, although designed to measure up to five harmonics, currently only outputs the 1st and 2nd harmonics. To obtain the higher harmonics, phase-sensitive detection was done numerically in a PC. The field-modulated EPR signal was digitized with a LeCroy Wave Runner 44Xi-A oscilloscope. The input to the scope or SPU was filtered with a 4th order Butterworth low-pass filter (Krohn-Hite 3955). The cut-off frequency of the filter was 100 kHz, so up to 10 harmonics of the modulation frequency could be measured. The signal was over-sampled at a rate of 2 MS/s to compensate for the low 8 bit vertical resolution and minimize the quantization error. An HP 3110A function generator was used to synchronize data acquisition by the LeCroy and the spectrometer's software, XEPR. The output of the function generator was connected to the 'EXT TRIG' port on the SPU and to the trigger input of the LeCroy. After the trigger, XEPR initiated a sweep of the external magnetic field and measurement of the 1st harmonic EPR spectrum. The same signal was sent to the SPU and the LeCroy. Data from the LeCroy were transferred to the PC and the harmonics of the spectra were calculated using a Matlab program. The numerical demodulation method described in [18] was implemented. The 1st harmonic spectra measured with the XEPR software and by digital demodulation of the digitized modulated signal were in good agreement, which confirmed that digital phase-sensitive detection is equivalent to the analog data processing.

Spectra of the LiPc sample were recorded and harmonics calculated for 21 modulation amplitudes between 0.2 and 4 G. For each modulation amplitude, data were recorded three times. Harmonics were processed as described above to obtain the 1st derivative EPR spectra. The result was three reconstructed EPR spectra at each h_m. Spectra of mHCTPO were recorded and harmonics calculated for nine values of the modulation amplitudes between 0.13 and 1.12 G. Measurements were repeated three times.

3.3. Results

For comparison of the signals obtained by the standard method and the proposed reconstruction method, parameters were selected that broadened the signal to the same extent. In the standard method, broadening and S/N are affected both by the modulation amplitude and the characteristics of the low-pass filter. In the proposed method, broadening and S/N are determined only by the filtering that is selected in the post-processing.

For the traditionally detected 1st harmonic EPR spectra $s_1(B)$ of LiPc the modulation amplitude h_m was 377 mG (about 50% of ΔH_{pp}), which caused about 6% increase in ΔH_{pp}. The experimental data were filtered with a low-pass 4th order Butterworth filter in the PC software to suppress high frequency noise. The cut-off frequency was selected so that the line was just slightly broadened. In the proposed method $f(B)$ were filtered with the same low-pass filter but with a lower cut-off frequency. It was adjusted so that over-filtering produced 6% broadening, analogous to the effect of

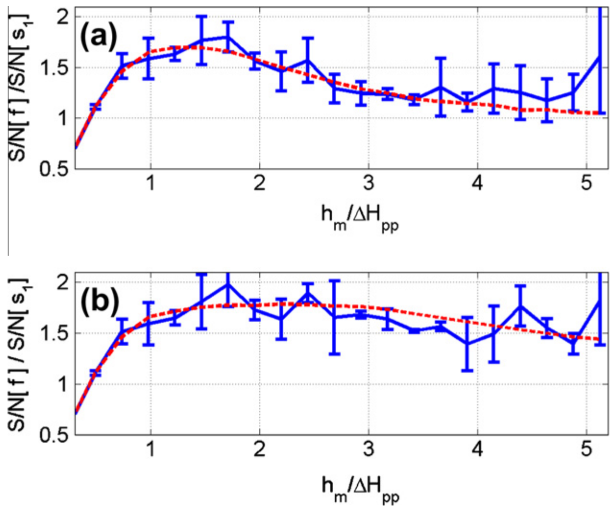

Fig. 2. Ratio of the *S*/*N* for *f*(*B*) to *S*/*N* for $s_1(B)$ as a function of the ratio of the modulation amplitude (h_m) to the peak-to-peak first derivative linewidth (ΔH_{pp}) for the LiPc sample. Blue solid lines with error bars represent experimental results for three measurements and dashed red lines are results of numerical simulations. The *S*/*N* comparison was made for *f*(*B*) spectra reconstructed from $N_H = 5$ (a) and $N_H = 10$ (b) harmonics and $s_1(B)$ obtained at constant low modulation amplitude.

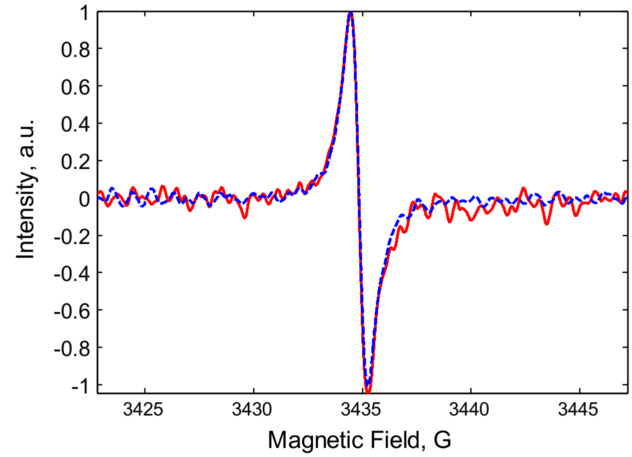

Fig. 3. Comparison of the traditional first harmonic EPR spectrum $s_1(B)$ of LiPc measured with $h_m/\Delta H_{pp} \sim 0.5$ (red line) and *f*(*B*) reconstructed from $N_H = 10$ with $h_m/\Delta H_{pp} \sim 2.4$ (blue dashed line).

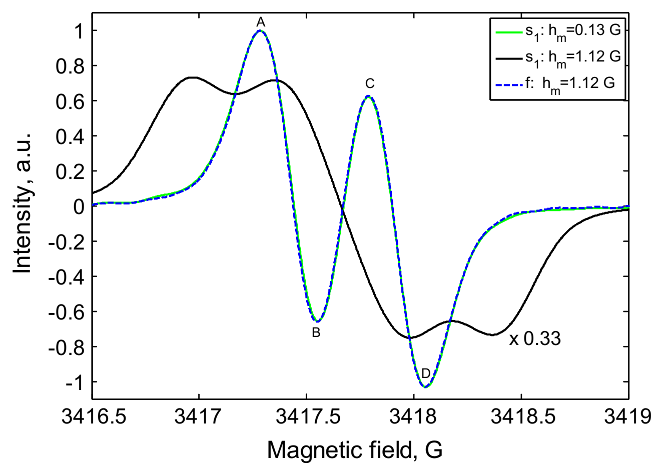

Fig. 4. Comparison of $s_1(B)$ measured with $h_m = 0.13$ G (solid green) with *f*(*B*) (dashed blue) recovered from spectra at harmonics $n = 1$–10, measured with $h_m = 1.12$ G ($s_1(B)$, solid black). To facilitate comparison of the lineshapes the amplitude of the over-modulated $s_1(B)$ spectrum measured with $h_m = 1.12$ G is decreased by a factor of 3.

over-modulation on the traditionally-detected signal. This approach was used to permit comparison of *S*/*N* for $s_1(B)$ and *f*(*B*) spectra that are broadened by the same amount.

The ratio of the *S*/*N* for reconstructed *f*(*B*) as a function of $h_m/\Delta H_{pp}$ for LiPc to that of $s_1(B)$ traditionally obtained with modulation amplitude that gives only 6% broadening is shown in Fig. 2 for three independent experimental data sets (blue[1] solid curves with error bars) and compared with numerical simulations (red dashed). The noise level was assumed to be the same for all harmonics. For $h_m < \sim 0.37\Delta H_{pp}$ the modulation is smaller than selected for $s_1(B)$ so the *S*/*N* obtained by reconstruction from multiple harmonics is poorer than for $s_1(B)$. However, it is the same as would have been obtained by traditional detection at the same modulation amplitude. To benefit from the multiple harmonics, higher modulation amplitudes are needed. The simulations show that for $N_H = 5$ the $[S/N(f)]/[S/N(s_1)]$ ratio has a maximum of 1.7 at $h_m/\Delta H_{pp} \sim 1.2$ and decreases slowly for increasing modulation amplitudes. The decreasing *S*/*N* at higher modulation amplitudes arises from noise amplification if higher harmonics are not included. For $N_H = 10$ $[S/N(f)]/[S/N(s_1)]$ is relatively constant at about 1.75 for $h_m/\Delta H_{pp}$ between 1.5 and 3. Experimental results are in a good agreement with the simulations (Fig. 2). The comparison of $s_1(B)$ and *f*(*B*) shown in Fig. 3 demonstrates the *S*/*N* improvement that can be obtained by using multiple harmonics.

Recovery of *f*(*B*) from multiple harmonics of the over-modulated EPR spectrum of the proton hyperfine-split low-field ^{15}N hyperfine line of mHCPO also was tested (Fig. 4). mHCTPO was synthesized to be used for EPR oxymetry [24]. The ratio $K = (A - D)/(C - B)$ between inner and outer peak-to-peak heights (see Fig. 4) is sensitive to the oxygen concentration. Parameter *K* increases when oxygen broadens the overlapping lines. Over-modulation causes broadening of the lines that is indistinguishable from that due to oxygen. Thus O_2 measurements can be compromised if the modulation amplitude is too large. Since in the general case the concentration of O_2 is not known, the modulation amplitude in a conventional experiment must be set low enough that it does not broaden the oxygen-free spectrum, which may result in *S*/*N* in the presence of O_2 that is not sufficient for reliable data analysis. Fig. 4 demonstrates that with the method described in this paper the minimally broadened lineshape (*f*(*B*), dashed blue) can be recovered from a severely over-modulated spectrum ($s_1(B)$, black solid). The recovered spectrum is in excellent agreement with $s_1(B)$ recorded at low modulation amplitude.

4. Discussion

In a conventional CW EPR experiment only the 1st harmonic signal is measured. In this paper a method is described that utilizes information that is contained in multiple harmonics of the field-modulated EPR signal. The 1st derivative spectra reconstructed by using the proposed algorithm not only show improved *S*/*N* but also are not broadened by over-modulation. It is also important that the method is applicable to an EPR signal of an arbitrary shape, provided that the magnetization instantly follows the magnetic field, which is typical for CW in the absence of power saturation or passage effects. This approach frees a spectroscopist from the

[1] For interpretation of color in Figs. 1–4, the reader is referred to the web version of this article.

difficult trade-off between S/N and lineshape distortion in selecting modulation amplitude.

Insensitivity to the modulation amplitude comes with a cost. The S/N of the recovered 1st derivative EPR spectrum becomes more sensitive to the characteristics of the low-pass filter. This sensitivity occurs because D(u), which is in the denominator of the calculation of $F(u)$ (Eq. (7)), decreases with increasing u, resulting in amplification of the noise at higher frequencies. Selection of a lower cut-off frequency of the filter efficiently reduces noise, but over-filtering can broaden the EPR spectrum. In comparison with the broadening caused by over-modulation, the effect of over-filtering is reversible, since it is done in software. The filter characteristics can be selected to optimize S/N or resolution, without doing another measurement.

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