

## Field-stepped direct detection electron paramagnetic resonance



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### ABSTRACT

The widest scan that had been demonstrated previously for rapid scan EPR was a 155 G sinusoidal scan. As the scan width increases, the voltage requirement across the resonating capacitor and scan coils increases dramatically and the background signal induced by the rapidly changing field increases. An alternate approach is needed to achieve wider scans. A field-stepped direct detection EPR method that is based on rapid-scan technology is now reported, and scan widths up to 6200 G have been demonstrated. A linear scan frequency of 5.12 kHz was generated with the scan driver described previously. The field was stepped at intervals of 0.01 to 1 G, depending on the linewidths in the spectra. At each field data for triangular scans with widths up to 11.5 G were acquired. Data from the triangular scans were combined by matching DC offsets for overlapping regions of successive scans. This approach has the following advantages relative to CW, several of which are similar to the advantages of rapid scan. (i) In CW if the modulation amplitude is too large, the signal is broadened. In direct detection field modulation is not used. (ii) In CW the small modulation amplitude detects only a small fraction of the signal amplitude. In direct detection each scan detects a larger fraction of the signal, which improves the signal-to-noise ratio. (iii) If the scan rate is fast enough to cause rapid scan oscillations, the slow scan spectrum can be recovered by deconvolution after the combination of segments. (iv) The data are acquired with quadrature detection, which permits phase correction in the post processing. (v) In the direct detection method the signal typically is oversampled in the field direction. The number of points to be averaged, thereby improving the signal-to-noise ratio, is determined in post processing based on the desired field resolution. A degassed lithium phthalocyanine sample was used to demonstrate that the linear deconvolution procedure can be employed with field-stepped direct detection EPR signals. Field-stepped direct detection EPR spectra were obtained for Cu<sup>2+</sup> doped in Ni(diethyldithiocarbamate)<sub>2</sub>, Cu<sup>2+</sup> doped in Zn tetratolylporphyrin, perdeuterated tempone in sucrose octaacetate, vanadyl ion doped in a parasubstituted Zn tetratolylporphyrin, Mn<sup>2+</sup> impurity in CaO, and an oriented crystal of Mn<sup>2+</sup> doped in Mg(acetylacetonate)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>.

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### 1. Introduction

In rapid-scan electron paramagnetic resonance (EPR) the magnetic field is scanned through resonance in a time that is short relative to the electron spin relaxation times [1–3]. The directly detected quadrature signal is obtained using a double-balanced mixer with the reference at the resonance frequency. Deconvolution of the rapid-scan signal gives the absorption spectrum [4,5]. By contrast conventional continuous wave (CW) EPR uses phase sensitive detection at the modulation frequency. For a wide range of samples, rapid scan gives improved signal-to-noise

ratio ( $S/N$ ) relative to CW spectra [1]. The widest scan that we have previously demonstrated for rapid scan EPR was a 155 G sinusoidal scan [6]. As the scan width increases, the voltage requirement across the resonating capacitor and scan coils increases dramatically and the background signal induced by the rapidly changing field increases. An alternate approach is needed to achieve wider scans. We have now developed field-stepped direct detection EPR, which is based on the rapid scan technology, to generate much wider scans. To test the performance of the method, samples were examined with a variety of linewidths and lineshapes. The narrowest linewidth ( $\Delta B_{pp} = 22$  mG) was for degassed lithium phthalocyanine (LiPc), which exhibited rapid-scan oscillations in the signal and required deconvolution to obtain the slow-scan absorption spectrum. Samples with resolved  $g$ - and  $A$  anisotropy include Cu<sup>2+</sup> doped in Ni(diethyldithiocarbamate)<sub>2</sub> (Ni(Et<sub>2</sub>dtc)<sub>2</sub>), Cu<sup>2+</sup> doped in Zn

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tetratolylporphyrin (ZnTTP), perdeuterated 4-oxo-2,2,6,6-tetra-methylpiperidiny-N-oxyl (PDT) in sucrose octaacetate, vanadyl ion doped in Zn p-COOH-tetratolylporphyrin (ZnTTP-COOH), and  $Mn^{2+}$  impurity in CaO. The spectrum of a crystal of  $Mn^{2+}$  doped in  $Mg(acetylacetonate)_2(H_2O)_2$  ( $Mg(acac)_2(H_2O)_2$ ) has well-resolved hyperfine lines and low-intensity forbidden transitions over a sweep width of 6200 G.

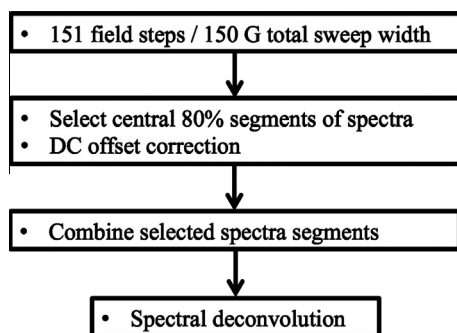
## 2. Approach

To encompass a wide spectrum, multiple triangular scans were acquired with extensive overlap of the field ranges (Fig. 1). In the following description, specific values are given to facilitate understanding, but there is substantial flexibility in choice of parameters. For example to encompass a 150 G scan, 151 scans with widths of 11.5 G were recorded with 1 G offsets between the centers of the scans. Since linearity of a triangular scan is better in the center than at the extremes of the scan, only the central 80% segments of the scans were selected for inclusion in the combined data set. Thus for the example of 11.5 G scans, the central 9.2 G segments were used. The 1 G offset between centers of scans gives an 8.2 G region of overlap of each scan with the previous and following scans. The information from the up- and down-scans and from multiple cycles of the triangular scans is combined. In the direct-detected spectra the y axis values are relative to a DC offset that is different for each scan. To combine successive scans the offset was calculated as the difference between the means of the y-axis values in the overlapping 8.2 G regions. The large spectral overlaps provide accurate determination of the offsets. This offset correction was applied before averaging values from successive scans and combining into the spectral array. Since the scan rate of a triangular scan is constant across the spectrum, linear deconvolution can then be applied to obtain the slow-scan absorption spectrum.

## 3. Methods

### 3.1. Samples

LiPc prepared electrochemically was provided by Prof. Swartz, Dartmouth College [7,8]. A small crystal was placed in a capillary tube. The tube was extensively evacuated and then flame sealed. The capillary tube containing LiPc was placed in a 4 mm outer diameter quartz tube beside a second capillary tube filled with



**Fig. 1.** Block diagram of post processing procedure for spectral reconstruction in field-stepped direct detection, using typical parameters. For example, data could be acquired at 151 field positions in 1.0 G increments over 150 G. Each scan is 11.5 G wide and the linear scan frequency is 5.12 kHz, which corresponds to a scan rate of 118 kG/s. From each of the scans the central 80% is selected. The DC offset between scans is calculated by comparing signal intensity at the comparable fields in overlapping segments of successive scans and this correction is applied prior to combining the spectra.

water to a height of 1 cm to lower the Q of the resonator to about 1000. The bandwidth of the rapid scan signal for this sample is so large that a lowered Q is required to decrease broadening of the signal.

The preparation of  $Cu^{2+}$  doped in  $Ni(Et_2dtc)_2$  was described in [9]. The preparation of  $Cu^{2+}$  doped in ZnTTP and of  $VO^{2+}$  doped in ZnTTP-COOH were described in [10]. The sample of nitroxide PDT in sucrose octaacetate was prepared as previously reported [11]. Calcium oxide was purchased from Sigma–Aldrich (part number 248568, St. Louis, MO).  $Mn^{2+}$  is an impurity in the reagent CaO powder. The sample was handled under nitrogen gas and placed in a 4 mm outer diameter quartz tube. The tube was evacuated on a high vacuum system for about 6 h, then flame sealed.  $Mg(acac)_2(H_2O)_2$  was prepared and characterized as described in [12,13]. The crystal doped with  $Mn^{2+}$  was grown from acetonitrile. Sample heights were 6–7 mm, to ensure uniform  $B_1$  and scan field along the full lengths of the samples.

### 3.2. EPR spectroscopy

A Bruker E500T spectrometer was used to record CW and field-stepped direct detection spectra with a Bruker Flexline ER4118X-MD5 dielectric resonator, which can excite spins over a sample height of about 1 cm. The Q of the resonator is  $\sim 9000$  for nonlossy samples [2]. A Bruker SpecJet II fast digitizer was used. The 10 ns timebase was selected for LiPc and for  $Mn^{2+}$  in  $Mg(acac)_2(H_2O)_2$  and the 40 ns timebase was used for the other samples. The phase difference between the quadrature detection channels was calibrated with a small sample of solid BDPA (1:1  $\alpha,\gamma$ -bis(diphenylene- $\beta$ -phenylallyl): benzene) radical [14]. The deviation between the Kronig–Kramers transformation of the absorption signal and the observed dispersion signal showed that a phase correction of  $7^\circ$  was required. The amplitude difference between quadrature detection channels was calibrated with a small degassed sample of solid LiPc. There was a 7% amplitude difference between the I and Q channels. The corrections were applied in the post-processing of the field-stepped direct detection signals.

The linear scans were generated with the previously described scan driver [15]. The scan coils were constructed from 60 turns of Litz wire (255 strands of AWG44 wire). The coils have about 8 cm average diameter, were placed about 4 cm apart, and have a coil constant of 17.3 G/A. Mounting the coils on the magnet, rather than on the resonator, reduces the oscillatory background signal induced by the rapid scans [6]. The placement of highly conducting aluminum plates on the poles of the Bruker 10" magnet reduces resistive losses in the magnet pole faces that arise from induced currents [1]. The dielectric resonator decreases eddy currents induced by the rapidly-changing magnetic fields relative to resonators with larger amounts of metal. The scan frequency of 5.12 kHz was selected because the background signal induced by the rapidly varying field is relatively small at this scan frequency. Since the linearity is high over more than 90% of the scan at 5.12 kHz, the use of only the central 80% is conservative. Data were acquired in blocks of 3 cycles at each field step. For the spectra used in this study, the scan rate is 118 kG/s, which is  $2 \times fs \times B_m$  G/s where  $fs$  is the scan frequency and  $B_m$  is the scan width.

The incident powers were converted to  $B_1$  using the known resonator efficiency of  $3.8 \text{ G/W}^{1/2}$  at Q of 9000 and the dependence of efficiency on  $\sqrt{Q}$  when Q is decreased [16]. The power selection was relatively conservative to prevent distortion of the lineshape by power saturation at higher  $B_1$ . The modulation frequency for the CW spectra of LiPc was 10 kHz and the modulation frequencies for other samples were 100 kHz. The modulation amplitudes were selected to be about 20% of  $\Delta B_{pp}$  for the narrowest feature in each

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