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Skew Projection of Echo-Detected EPR Spectra for Increased Sensitivity and Resolution

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Abstract

The measurement of EPR spectra during pulsed EPR experiments is commonly accomplished by recording the integral of the electron spin echo as the applied magnetic field is stepped through the spectrum. This approach to echo-detected EPR spectral measurement (ED-EPR) limits sensitivity and spectral resolution and can cause gross distortions in the resulting spectra because some of the information present in the electron spin echo is discarded in such measurements. However, Fourier Transformation of echo shapes measured at a series of magnetic field values followed by skew projection onto either a magnetic field or resonance frequency axis can increase both spectral resolution and sensitivity without the need to trade one against the other. Examples of skew-projected spectra with single crystals, glasses and powders show resolution improvements as large as a factor of seven with sensitivity increases of as much as a factor of five.

Keywords

Echo-Detected EPR; Electron Spin Echo; Pulsed EPR

Introduction

The continuous-wave (CW) electron paramagnetic resonance (EPR) spectrum contains a wealth of information about a spin system and its spin Hamiltonian and is a representation that is familiar and convenient to most EPR spectroscopists. During pulsed EPR measurements, it is often desirable to measure a 'CW-like' EPR spectrum of intensity versus field or frequency in order to verify sample integrity, sample orientation or the species being measured. CW-like spectra generated by pulsed methods can have advantages for the measurement of precise spectral line positions because of the absence of saturation and passage effects and because of the ability to edit spectra based on relaxation times. Occasionally, the entire EPR spectrum of interest can be measured by Fourier Transformation of the free induction decay (FID) or spin echo signal. But typically, the spectral width exceeds the useful bandwidth of the spectrometer and so another approach,

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known as echo-detected (ED) EPR or echo-induced EPR is used to measure a CW-like spectrum [1].

ED-EPR originated in the early days of pulsed EPR when the analog boxcar integrator was the most advanced real-time signal processing technique available. Briefly, the electron spin echo is integrated within a time window centered on the echo and the value of the integral is plotted as a function of the applied magnetic field (B) with the spectrometer frequency (ω_s) held constant. The spin echo can generally be represented as back-to-back FIDs although modified by relaxation and the spectrometer response characteristics. Thus, the ED-EPR signal intensity is:

$$I_{ED}(B) = \int_{-t_w/2}^{t_w/2} FID(t, B, \omega) dt \quad (1)$$

where $FID(t)$ is the functional form of the experimental FID, t_w the width of the integration window, t the time relative to the center of the echo, B the applied magnetic field, and ω the microwave frequency. The integral in eqn. (1) can be formally evaluated in terms of the Fourier transform (FT) of the echo, $EPR_{FT}(B, \omega)$, as:

$$I_{ED}(B) = t_w \int_{-\infty}^{\infty} EPR_{FT}(B, \omega + \delta\omega) \text{Sinc}(\delta\omega t_w) d(\delta\omega) \propto EPR_{FT}(B, \omega) \otimes \text{Sinc}(\delta\omega t_w) \quad (2)$$

where $\text{Sinc}(x) = \text{Sin}(x)/x$ and $\otimes$ indicates a convolution of two functions. The ED-EPR signal measured at each field position is the convolution of the EPR spectrum detected by the spectrometer with a *Sinc* function.

One readily-apparent consequence of the convolution is that the ED-EPR spectrum approaches the EPR spectrum only for spectral features much broader than $(\gamma t_w)^{-1}$; while narrow lines are transformed into *Sinc* functions which have long, extended ripples. Interference between the ripples from adjacent or overlapping spectral lines can change the apparent number and position of lines in a spectrum [2].

A less apparent consequence of ED-EPR impacts the sensitivity. The echo or FID shape describes the portion of an EPR spectrum that is close to resonance. That portion of the EPR spectrum can be obtained by an FT of the FID or echo shape. Yet, conventional ED-EPR measures just a single value, I_{ED} , at each magnetic field value; the information about the EPR spectrum at other nearby field/frequency values is discarded. That information could be used two different ways. The same location in the EPR spectrum appears in independent measurements at several nearby magnetic fields and can be combined to increase the S/N ratio of that location in the EPR spectrum. In addition, portions of the FT spectrum lie between the magnetic field values where measurements are made. That spectral information can provide better lineshapes and line positions, increasing the spectral resolution. In fact both improvements can be achieved in the same spectrum, improving sensitivity and resolution simultaneously.

The technical limitations in signal processing technology that led to classic ED-EPR have been overcome in current pulsed EPR spectrometers. It is now possible to digitize the entire spin echo shape and signal average it at rates appropriate for many paramagnetic centers. We describe a two-dimensional (2D) data acquisition and processing scheme that provides increased spectral fidelity, resolution and sensitivity while yielding a 1D, CW-like EPR spectrum. This new approach is particularly well-suited for measurement of high-resolution EPR spectra that extend over a broad spectral range extending far beyond the available microwave B_1 field.

Theory

The EPR spectrum is inherently a 2D function of frequency and magnetic field. The 2D EPR spectrum has considerable redundancy and most measured spectra are simply a slice through this 2D spectrum at a constant frequency or field. The typical CW-EPR spectrum is a 1D slice in which B varies with ω constant, and in FT-EPR ω varies with B constant. Sometimes 1D spectra are measured at widely different fields or frequencies, for example, at X-band, Q-band and W-band, to aid in their interpretation. In each case, the EPR spectrum is a small portion of a much larger 2D spectrum.

For non-interacting spins, the EPR spectrum is simply the sum of responses from packets of identical spins. The properties of the spectrum can be deduced from the properties and behavior of a single spin packet in the context of the Bloch equations [3, 4]. Our discussion will focus on one of these spin packets and its position in the EPR spectrum. Spin packet positions are relatively immune to experimental artifacts and can be used to determine the spin Hamiltonian parameters. Lineshapes and intensities, on the other hand, are easily distorted and are more susceptible to experimental and instrumental artifacts.

The CW absorption signal, S_i , and the FID, F_i , of a spin packet, i , that follows the Bloch equations are:

$$S_i(B, \omega_s) \propto T_2 \frac{1}{1 + \left(\frac{E_i(B)}{\hbar} - \omega_s \right)^2 T_2^2} \quad (3)$$

$$F_i(t, B, \omega_s) \propto \text{Exp} \left(-\frac{t}{T_2} + it \left(\frac{E_i(B)}{\hbar} - \omega_s \right) \right)$$

where the initial magnetization, $M_{0,i}$, of the spin packet parallel to the applied magnetic field is taken as unity, $E_i(B)$ is the transition energy, and the FID is mixed with ω_s for detection. The absorption line of an individual spin packet is related to its FID by the Fourier transform. The corresponding absorption, A , and FID, V , signals from many spin packets are:

$$A(B, \omega_s) = \sum_i M_{0,i} S_i(B, \omega_s) = \sum_i M_{0,i} T_2 \frac{1}{1 + \Delta\omega_i^2 T_2^2}$$

$$V(t, B, \omega_s) = \sum_i r \left(\frac{E_i(B)}{\hbar} - \omega_s \right) M_{0,i} F_i(t, B, \omega_s) = \sum_i r(\Delta\omega_i) M_{0,i} \text{Exp} \left(-\frac{t}{T_2} + it \Delta\omega_i \right) \quad (4)$$

where $M_{0,i}$ is the equilibrium magnetization of spin packet i , $\Delta\omega_i = (E_i(B)/\hbar - \omega_s)$ is the resonant frequency offset of the spin packet, and $r(f)$ is the response function of the spectrometer at a frequency difference, f , from the microwave frequency. For simplicity, T_2 is assumed to be independent of spin packet. The summations in eqn. (4) can be replaced by integrals over the distribution of spin packets.

The 2D spectrum—The full EPR spectrum is a 2D surface with field as one axis and frequency as the other. However, most EPR measurements take only a 1D slice through that surface, for an exception, see [5–7]. Although eqns. (3) and (4) suggest that ω_s is constant in a CW absorption spectrum, it is not required; a few swept-frequency spectrometers without a resonator have been demonstrated. Figure 1 shows three hypothetical FT-EPR spectral slices obtained by Fourier Transformation of the FID or spin echo shape at progressively larger B . There are two absorption EPR lines in each spectrum which shift to larger ω . In all three spectra, the corresponding features line up along a direction, indicated by the grey lines, that is skewed with respect to the field and frequency axes. The spectra can be projected along this skew direction onto a line at constant field, indicated here as B_0 to produce a frequency-domain spectrum at constant B_0 . Alternatively, projection onto a constant frequency line at ω_0 produces a field-domain spectrum at constant ω_0 .

A pulsed measurement provides a window into that 2D surface. The window shape is the result of the spectral response function, or useful bandwidth, of the pulsed EPR spectrometer, $\mathcal{r}(f)$ in eqn. (4), which is relatively limited, typically less than 100–200 MHz. After the FT, only spin packets whose $\Delta\omega$ falls within that bandwidth are seen (and need to be retained) in each horizontal slice in Figure 1, while noise outside that bandwidth can be safely rejected. Also, because a spin packet appears in a slice only when its $\Delta\omega$ falls within the bandwidth, each spin packet appears only in slices measured in the limited range of magnetic fields, typically less than 5 mT wide, where its $\Delta\omega$ falls within the spectrometer response bandwidth.

Skew Direction—For the vast majority of EPR spectra, the frequency of a spin packet $\omega = E(B)/\hbar$ depends almost linearly on B , at least, within the spectrometer response window. A linear approximation is accurate in many cases, giving $E(B_0 + dB) \approx E(B_0) + E(B_0)/B dB$ so that

$$A(B, \omega) \cong A\left(B + dB, \omega + \frac{\partial E}{\partial B} \frac{dB}{\hbar}\right) \cong A\left(B + \hbar \frac{\partial B}{\partial E} d\omega, \omega + d\omega\right). \quad (5)$$

A peak measured at B_i is shifted in frequency by $E(B)/B (B_i - B_0)/\hbar$ from its position at B_0 . The peaks fall on a line at a skew ‘angle’ of $\arccot(E(B)/B)$ from the B axis.

In the high-field approximation, a net hyperfine field, A , and the g -factor determine peak position, $E(B) = g\beta B + \hbar A$, for many typical EPR spin packets, so that $E(B)/B = g\beta$. In the limit that hyperfine interactions produce the shape of the spectrum, then $g = \hbar\omega/B\beta$ and it can be appropriate to use the same g -factor for all spin packets so that every point in the spectrum is projected at the same skew angle. This limiting case is appropriate for spectra dominated by hyperfine interactions as in the diamond example given later. Even when the g -factor does vary across a spectrum, a constant skew angle can be used for sufficiently narrow spectra. The small variation in g -factor will not produce noticeable broadening of a spin packet in the projected spectrum as long as the fractional variation in the g -factor, $\delta g/g$, times the spectral response bandwidth of the spectrometer is small compared to spin packet width. A 1% variation in g -factor with a 100 MHz spectral response bandwidth gives only 1 MHz additional broadening. However, the spin packet position will shift from its correct value by roughly $\delta g/g$ times the difference in fields when it is projected to a much different magnetic field. This shift is minimized by projecting frequency-domain spectra onto a magnetic field near the center of the measured signals in the 2D spectrum.

Constant g -factor—The skew projection is relatively simple when the entire spectrum can be represented by a constant g -factor. Projection onto the frequency axis at constant B_0 yields $A_{\omega p}$, a frequency-domain spectrum ‘measured’ at B_0 ,

$$A_{\omega p}(B_0, \omega) = \sum_n A\left(B_n, \omega + \frac{g\beta}{\hbar}(B_0 - B_n)\right). \quad (6)$$

The $A_{\omega p}$ spectrum is readily obtained by shifting the frequency-domain spectrum in each field slice by $g\beta(B_n - B_0)/\hbar$ and then making a sum projection onto the frequency axis. This simple projection is illustrated in Figure 2 with the diamond sample discussed later. A detailed description with high-resolution figures showing the intermediate steps is given in the Supplemental Information. The spin echoes measured at different values of B were Fourier Transformed to give EPR intensity as a function of EPR frequency. Each spectrum is arranged as a slice with B increasing in the vertical direction. Because of the limited

response function for the excitation and detection conditions used, signals from the sample are observed only when they fall in a ~50 MHz window around ω_s . As B is incremented from bottom to top of Figure 2 three groups of resonances from a nitrogen hyperfine interaction ‘walk’ through this response window, basically following a straight line, indicated by the orange arrows, from low frequency and field toward higher frequency and field. Each point along one of those lines contains the ‘same’ EPR signal but different noise so that summing all the points along one of those lines, *i.e.*, making a slanted or skewed projection, sums signals from the same spin packets, increasing the signal to noise ratio (SNR). The projection can be made onto a line at constant magnetic field, as shown in Figure 2, or onto a vertical line of constant frequency. The summed intensity from each point along that dashed line at 345.4 mT in Figure 2 corresponds to the spectral intensity at a resonance frequency as indicated by the red arrows.

Some data processing packages lack the ability to directly make the required skew projection indicated by the orange arrows. Instead, we can consider it as a two-step process. For a frequency-domain projection, as in Figure 2, each horizontal, or field, slice is shifted or sheared by $\Delta B g \beta / \hbar$ where ΔB is the difference between the field of the slice and the dashed line. Typical shifts are indicated by the green arrows. Then in the second step, the sheared spectrum is projected directly onto the frequency axis as indicated by the red arrows of Figure 2. In this two-step process, the original rectangular 2D spectrum shears into a parallelogram which is trimmed into the rectangle shown in Figure 3 and then is projected onto the frequency axis. Each slice generally needs to be shifted by a non-integer number of points, potentially introducing a shift error of as much as $\pm 1/2$. That $\pm 1/2$ point error can be made arbitrarily small by liberal zero-filling of the FID or echo before Fourier transformation. Increasing the number of points in the FID or echo by a factor of eight seems to be more than adequate. The goal is to ensure that the sharpest peaks and edges are represented by several points after the Fourier transformation.

The 2D spectrum can also be projected onto a vertical, or field, axis at a frequency ω_0 to give a field-domain spectrum ‘measured’ at a fixed frequency of ω_0 . The spectrum is

$$A_{B_p}(B, \omega_0) = \sum_n A \left(B_n + \frac{\hbar}{g\beta} (\omega_0 - \omega), \omega_0 \right). \quad (7)$$

The projections in eqns. (6) and (7) are simple to perform because they involve only a shift of each slice but no rescaling or stretching of slices. In both types of projection, adjacent slices are shifted by the same increment in frequency or field, as appropriate. This procedure corresponds to a simple skew projection of the 2D spectrum which can be considered as a shear transform to convert the 2D spectrum from a rectangle to a parallelogram which is projected onto the appropriate axis. The increment or step size between successive values of B_n can be much larger than the EPR linewidth as long as the field step size is small compared to the width of the spectral response function $r(f)$ so that each peak appears in multiple slices.

Dominant g-factor—For broad spectra or low-frequency EPR, the g -factor can vary considerably across the 2D spectrum and a more complex projection is required. For a simple spin Hamiltonian containing only the electron Zeeman interaction, the spin packet position is determined solely by the g -factor, $E_f(B) = g\beta B$ and the orange lines in Figure 2 are not parallel, but converge on the origin at $\omega=0$, $B=0$. The g -factor at any point in the 2D spectrum is $g = \hbar\omega_s(\beta B)$ which can be approximated as $\hbar\omega_s(\beta B_n)$ when the width of the spectral response, $r(f)$, is small compared to ω_s . In this limit, the skew-projected spectra become

$$A_{\omega p}(B_0, \omega) = \sum_n A\left(B_n, \omega - \omega_s \left(1 - \frac{B_0}{B_n}\right)\right) = \sum_n A\left(B_n, \Delta\omega + \omega_s \frac{B_0}{B_n}\right) \quad (8)$$

$$A_{Bp}(B, \omega_0) = \sum_n A\left(B_n \left(1 + \frac{\omega_0 - \omega}{\omega_s}\right), \omega_0\right) = \sum_n A\left(B_n \frac{\omega_0 - \Delta\omega}{\omega_s}, \omega_0\right). \quad (9)$$

where $\Delta\omega = \omega - \omega_s$ is the typical frequency axis in FT-EPR spectrometers. The frequency-domain projection in eqn. (8) involves shifting the frequencies of each slice. But in contrast to eqn. (6), the shift between adjacent slices changes with magnetic field, so that eqn. (8) no longer represents a simple skew projection. Rather, the original 2D spectrum is sheared into a distorted parallelogram, in which two opposite sides are curved rather than straight, before it is projected onto the frequency axis. The field-domain projection of eqn. (9) requires rescaling the frequency axis in each slice. In effect, each Fourier Transform slice is stretched and shifted so that the 2D spectrum becomes a trapezoid which is then projected onto the field axis.

Results and Discussion

In the following section, three examples compare skew EPR to classical ED-EPR. All three samples are described in detail in the Experimental section. In the first example, the simultaneous increase in both resolution and sensitivity with skew EPR is shown in a sample with isotropic g -factor. Each step in the data processing and manipulation is illustrated for this sample in the Supplemental Information. The second example illustrates the use of skew EPR in mixtures of broad and sharp signals. In ED-EPR, sinc artifacts from sharp lines can interfere with and obscure adjacent spectral features; skew EPR maintains spectral fidelity. The final example illustrates the different projection methods on a broad spectrum with sharp lines and high dynamic range.

For each example, the echo signal was digitized and stored. All the ED-EPR and skew EPR spectra were generated later from the same stored data. This procedure means that the spectra resulted from data with identical signal, noise and instrumental artifacts. The differences between spectra for each sample result entirely from differences in digital signal processing. To make comparisons easier, each ED-EPR and skew EPR spectrum has been normalized to the most intense peak in each spectrum.

First Example: N in Diamond

The first example of skew EPR is the isolated nitrogen center in single-crystal diamond. The spectrum arises from ~40 different orientations of a substitutional nitrogen atom in 10 diamond crystals. The EPR spectrum is dominated by the nitrogen hyperfine splitting, which produces three lines. The center line with $m_I = 0$ is relatively sharp and narrow because it has no first-order hyperfine shift and the g -factor is isotropic. The outer lines with $m_I = \pm 1$ show an axial hyperfine interaction that has some apparent sharp structure. With the small number of crystals in the sample, the lineshape has not reached the ‘powder’ limit. This sample provides a good test of resolution.

Figure 4a–c show the ED-EPR spectrum for integration windows of 48 ns, 96 ns and 336 ns, respectively, centered on the echo. Figure 4d–e shows skew EPR spectra based on eqn. (7) with $\omega_0 = 9.7000$ GHz obtained from Fourier transforms of the full echo and half echo taken from the max, respectively. Note that the skew EPR spectra have been shifted to a microwave frequency that may be more ‘convenient’ than the original $\omega_s = 9.6984$ GHz. The integration windows used for Figure 4a–b have widths of 48 and 98 ns equal to the

FWHM of the echo at the $m_I = \pm 1$ and $m_I = 0$ features, respectively. These narrow integration windows cause considerable broadening of the ED-EPR spectra. The integration window for Figure 4c at 336 ns is the narrowest that gives ED-EPR spectral resolution similar to the skew EPR spectrum. Increasing the width of the integration window further does not increase the amplitude or resolution of the spectrum, but does increase the noise. The structure on the $m_I = \pm 1$ peaks progressively sharpens from Figure 4a–c. This structure is real and appears symmetrically on both peaks. An expanded region of the high-frequency portion of the diamond spectrum, Figure 5, shows that each slice of the 2D spectrum, Figure 3, contains a mixture of signals from different spin packets and carries high-resolution information about the overall shape of the spectrum in Figure 4d.

The FWHM of the center, $m_I = 0$, peak is (a) 0.753 mT, (b) 0.439 mT, and (c) 0.191 mT in the ED-EPR spectra and (d) 0.190 mT and (e) 0.185 mT in the skew EPR spectra. The increase in resolution with longer integration window in the ED-EPR spectra is accompanied by a reduction in SNR because increasing the integration window includes more noise but little additional signal. The ED-EPR spectra have SNRs of: (a) 146, (b) 121, and (c) 64; while the skew EPR spectra have a SNR of (d) 241 and (e) 158. The SNR was calculated as the ratio of the peak intensity of the $m_I = \pm 1$ feature to the RMS noise in the DC corrected baseline between 350.5 and 353.5 mT. The SNR calculated from the amplitude of the $m_I = 0$ peak shows a more dramatic contrast: (a) 244, (b) 241 and (c) 184 for the ED-EPR, and (d) 694 and (e) 462 for the skew EPR from the same experimental data.

Second example: 4-methyl, 2,6-di-*t*-butyl Phenoxy Radical

The ED-EPR and two skew EPR spectra of the 4-methyl, 2,6-di-*t*-butyl phenoxy radical are shown in Figure 6a–b. The ED-EPR spectrum was obtained by integration of the echo with a 40 ns window (roughly the echo FWHM) centered on the echo. The skew EPR spectrum was generated from half the echo starting at the center and extending to longer times. The two skew EPR spectra show the field-domain projections at $\omega_0 = 9.7000$ GHz using a constant g -factor of $g = 2.0094$ or a g -factor determined by the field position. The skew EPR spectra show the expected 4 line spectrum from the ~ 1.1 mT isotropic hyperfine interaction of the 4-methyl group broadened by the ~ 0.17 mT isotropic hyperfine interaction from the protons at the 3 and 5 positions [8, 9 (p. 195, radical 920)]. The four lines are close to the expected intensity ratio of 1:3:3:1. In addition to the phenoxy radical a sharp feature from the so-called E' center in the irradiated fused-silica sample tube is clearly resolved.

The ED-EPR spectrum is not easily interpreted. The ‘sinc wiggles’ from the E' centers obscure the two high field peaks of the phenoxy radical and the resulting spectrum appears to have three poorly-resolved lines with intensity ratios of 1:3:5. The E' center has far fewer spins than the phenoxy radical and has an EPR spectrum that is only ~ 0.2 mT wide. Yet, artifacts from the E' center dominate a large portion of the ED-EPR spectrum, making it difficult to recognize the major radical species.

The phenoxy radical EPR spectrum is dominated by hyperfine interactions so that skew projections based on eqns. (6) and (7) are appropriate. On the other hand, the difference in the center of the phenoxy radical and E' center spectra are determined by their g -factor differences, making skew projections based on eqns. (8) and (9) appropriate. Fortunately, the fractional difference in g -factors, $\Delta g/g \sim 0.0025$, and the fractional width of the spectrum, $\Delta\omega/\omega_s \sim 5$ mT/350 mT = 0.014, are small enough that there is little difference in projections based on these two sets of equations as shown in Figure 6b–c. In both spectra, the sharp line from the E' centers has clearly resolved g -anisotropy ($g_{\parallel} = 2.0034$ and $g = 2.0045$) [10].

Third example: Ti(III) in TiO₂

The final example, Ti(III) ions in single crystal TiO₂, is shown in Figure 7a–d and Figure 8a–b. Figure 7 compares two ED-EPR spectra using different integration windows with skew EPR spectra, while Figure 8 compares frequency-domain spectra constructed using eqns. (6) and (8).

The ED-EPR spectra, Figure 7a–b, were obtained with a 32 ns integration window centered on the echo and a 120 ns integration window taken from the echo max. As seen with the diamond spectra, an increase in the integration window improves peak resolution but is accompanied by a loss in SNR. The FWHM of the peak at 360.2 mT for the two windows is: (a) 0.72 mT and (b) 0.31 mT. The SNR for that peak is: (a) 60 and (b) 44.

Figure 7c–d shows the field projected skew EPR spectra at $\omega_0 = 9.7000$ GHz generated using eqns. (7) and (9), respectively. For comparison, the FWHM of the peak at 360.2 mT for the skew spectra is: (c) 0.106 mT and (d) 0.110 mT. The corresponding SNRs are (c) 65 and (d) 70 which are very modest improvements but accompany tremendous increases in resolution. The peaks in Figure 7c–d appear at the same B , regardless of the projection method used. This is a consequence of projecting onto a frequency ω_0 very close to ω_s . The relatively narrow $r(f)$ prevents broadening of the lines by differences in g -values.

There are major differences between the two frequency-domain spectra in Figure 8a–b based on eqns. (6) and (8), respectively. Differences in peak positions grow toward the ends of the spectra, appearing to originate at the g -value used in eqn.(6). Figure 8b, based on eqn. (8) for spectra dominated by g -value differences, preserves the apparent g -values in the ED-EPR spectrum. For example, in the ED-EPR, Figure 7b, the peak at 370.3 mT has an apparent g -value of 1.873; and in Figure 8b, has a g -value of 1.872. In contrast, that peak in Figure 8a, based on eqn. (6), has a g -value of 1.866. The EPR spectrum of most of the Ti(III) ions is dominated by the g -anisotropy so the skew projections based on eqns. (8) and (9) are appropriate and make the CW-EPR and ED-EPR spectra consistent. The position of the spectral features is determined by the g -factor for this sample and the fractional width of the spectrum is significant, $\Delta B/B_0 \sim 12\%$, making the difference between Figure 8a and b noticeable.

Resolution of skew spectra

In ED-EPR one limit on the spectral resolution is the field increment of the acquisition. An increase in spectral resolution requires a proportionate increase in acquisition time. The spectral resolution of skew EPR is limited by the field increment of the acquisition only when it exceeds the spectrometer response function. As long as the field increment is much less than $r(f)$, the skew projection fills in the points between field steps with points from the Fourier transform of the echo, resolving lineshapes narrower than the field step size. It is remarkable that the lineshape E' -center is reproduced even though the g -anisotropy, ~ 0.34 mT, is comparable to the magnetic field step of 0.2 mT used in the measurement. In the TiO₂ spectra, the pair of lines flanking 353.1 mT are well-resolved and separated by about 0.2 mT even though the field step size used in the measurement is 0.176 mT.

The resolution in ED-EPR also depends on the width of the integration window, as seen in the diamond and TiO₂ examples, and any increase in window width comes at the expense of SNR. On the other hand, processing the echo signal to produce the skew EPR spectrum can increase resolution without impacting the acquisition time while increasing SNR. Peak resolution can be further improved in skew EPR through application of resolution enhancement window functions, as used in NMR, to sharpen lines at the expense of SNR.

Which equations to use

Two different methods to process the echo and generate a skew EPR spectrum were presented. The methods are valid in different limiting conditions: eqns. (6) and (7), when the g -factor is constant in the spectral range; and eqns. (8) and (9), when the g -factor varies across the field range and dominates the spectrum.

The differences between the two skew methods are readily apparent only in the frequency-projected skew EPR spectra, as shown in Figure 8, but not when projected onto a field axis with small frequency shift. In the phenoxyl radical and TiO_2 examples, field-projected spectra constructed using both processing methods are basically indistinguishable as a consequence of using $\omega_0 - \omega_s$ and the limited spectrometer response function $r(f)$.

Full versus half echo

Both the full echo and half of the echo, taken from the maximum, can be processed to produce a skew EPR spectrum. If the phase memory time of the signal is long compared to the width of the echo measured out to the extreme tails, processing the full echo gives an advantage of $\sim 2^{1/2}$ in SNR, as seen in the diamond example. The Fourier transform of the full echo contains a large frequency-dependent phase shift that requires a large first-order phase correction before it can be skewed, but phasing is easy because the imaginary part of the EPR signal vanishes when phased correctly. On the other hand, a dispersion-like signal remains in the correctly phased Fourier transform of the half-echo, but the first-order correction is relatively small. In either case, the same phase correction applies to all field slices and the phasing parameters can be determined from the strongest features in the 2D spectrum.

Experimental

EPR Measurements

X-band pulsed EPR experiments were carried out on an E680 pulsed EPR spectrometer (Bruker BioSpin) using an EN 4118X-MD4-W1 resonator in a Flexline cryostat. The two-pulse echo was measured using the pulse sequence (p_1 - τ - p_2 - τ -echo) with a four-step phase cycle where the first pulse, p_1 , had phases (x, -x, x, -x), the second pulse, p_2 , (x, x, -x, -x) and both quadrature components of the signal were summed (+, -, +, -) to produce the quadrature echo signal [11]. In some measurements, a CYCLOPS cycle was superimposed on this four-step cycle to give a 16-step cycle that removed all image peaks from the spectrum.

The digitizer was started in advance of the peak of the spin echo and continued with a 4 ns dwell time until the echo signal had completely disappeared. The spin echo was acquired at one magnetic field value, then the field was incremented by a constant amount and the echo was acquired at the new field. The echo shapes were stored as successive rows of a 2D dataset. This dataset was processed to produce the skew EPR spectrum. The same dataset was also processed by integrating the signal in each row over a time window to produce the conventional ED-EPR spectrum for any desired integration window for direct comparison with the skew EPR spectrum. Data processing was carried out with Xepr (Bruker BioSpin) and with programs written in MatLab (MathWorks).

EPR SAMPLES

N in Diamond—Ten synthetic diamonds approximately 0.4 mm across were placed in a 3mm EPR quartz tube with random orientations. The diamonds contain the isolated, substitutional nitrogen center, P1, with $S=1/2$ and the substitutional Ni center, W8, with $S=3/2$ [12, 13]. Measurements were made at 70 K where only the P1 center was observed.

The P1 center has four symmetry-related, but usually magnetically-inequivalent, sites with appreciable nitrogen hyperfine anisotropy but no detectable g -anisotropy. The EPR spectrum consists of a single sharp line for the hyperfine line with $m_I=0$ flanked by a pair of broad lines with $m_I=\pm 1$. These broader hyperfine lines resemble an axial powder pattern, but the small number of crystals in the sample produces several sharp features from incomplete 'powder averaging'.

2D EPR measurements were made at 70 K with $\tau=500$ ns, the four-step phase cycle and a repetition rate of 490 Hz. Both microwave pulses at $\omega_s=9.6985$ GHz had a turning angle of $\pi/2$ and a nominal width of 16 ns to reduce spin echo decay from instantaneous diffusion. The entire echo signal was recorded in 240 points starting shortly after the second microwave pulse. Measurements were made at 256 field values starting at 337.5 mT with an increment of 0.06275 mT.

4-methyl, 2,6-di-*t*-butyl Phenoxy Radical—A single crystal of 4-methyl, 2,6-di-*t*-butyl phenol was X-irradiated and stored several years at room temperature to allow decay of all free radicals except the 4-methyl, 2,6-di-*t*-butyl phenoxy radical [8]. The crystal (approximately $2\times 1\times 0.5$ mm) was sealed in a 3mm EPR quartz tube. The EPR spectrum consists of a broad 1:3:3:1 quartet from the hyperfine coupling of the protons of the 4-methyl group with unresolved splittings from many other protons. The EPR tube contains a small amount of E' centers which have a narrow EPR line with some g -factor anisotropy and peak intensity comparable to the radical.

2D EPR measurements were made at room temperature with $\tau=120$ ns, the four-step phase cycle with CYCLOPS and a repetition rate of 263 Hz. Microwave pulses p_1 and p_2 at $\omega_s=9.7140$ GHz had turning angles of $\pi/2$ and π with nominal widths of 16 and 32 ns respectively. The echo signal was recorded in 256 points starting shortly before the peak of the echo. Measurements were made at 51 field values starting at 340 mT with an increment of 0.2 mT.

Single-Crystal TiO₂—A TiO₂ (rutile) crystal approximately $1\times 1.5\times 9$ mm was heated under vacuum until it became light bluish-grey in color from the production of a variety of Ti(III) centers. The crystal was placed in a 4 mm EPR tube and mounted at an arbitrary orientation in the EPR spectrometer with the magnetic field away from the crystal axes. The low-temperature EPR spectrum contains a large number of sharp lines from a number of interstitial and substitutional Ti(III) flanked by lower intensity hyperfine and superhyperfine lines from natural abundance ⁴⁷Ti (7.4%, $I=5/2$) and ⁴⁹Ti (5.4%, $I=7/2$), as well as other unidentified paramagnetic centers.

2D EPR measurements were made at 16 K with $\tau=500$ ns, the four-step phase cycle and a repetition rate of 4.90 kHz. Microwave pulses p_1 and p_2 at $\omega_s=9.7095$ GHz had turning angles of $\pi/2$ and π with nominal widths of 8 and 16 ns respectively. The echo signal was recorded in 512 points starting shortly before the center of the echo. Measurements were made at 256 field values starting at 335 mT with an increment of 0.176 mT.

Spectral Processing

The ED-EPR and the skew EPR spectra were both generated using in-house Matlab processing programs. The raw 2D echo shape versus field spectra were read by Matlab directly from the spectrometer datafiles with no additional processing. A zero-order phase correction was applied to ensure a proper absorption signal in ED-EPR. The in-phase part of the echo was integrated over a square window to produce the ED-EPR spectrum. The processing used to generate the skew spectrum is outlined here and illustrated on the diamond data in the Supplementary Information.

1. The full echo or half-echo starting at the peak is windowed, typically with a Blackman window centered on the echo maximum, although other windowing functions can be used to enhance either sensitivity or resolution. The windowed data is zero-filled, typically increasing its length by a factor of eight, and a complex Fourier transform is applied along the time dimension to generate a 2D frequency-domain spectrum. A first-order phase correction is applied to recover the EPR absorption spectrum. The phase correction is based on the strongest signals in the spectrum because every frequency slice receives the same phase correction.
2. Each frequency-domain slice is windowed because only a finite band of frequencies is excited and detected by the spectrometer. Only noise lies outside that band and it can safely be deleted. Typically a tapered cosine window is used in each slice to remove noise outside the spectrometer response function, but other windows including Gaussian, Lorentzian, trapezoid and matched filters can be applied. Windowing at this stage has no effect on spectral resolution; it only affects sensitivity and SNR.
3. The frequency-domain skew EPR spectrum is generated from this 2D dataset by offsetting each field slice and making a sum projection onto the field axis as described above and in the Supplemental Information. The 2D spectrum is zero-filled in the frequency direction so that shifting does not cause signal to wrap-around or shift off the end. Each field slice is shifted by $g\beta(B_n - B_0)/\hbar$ and then summed onto the field axis, to generate a 1D frequency-domain spectrum. Eqns. (6) and (7), show that there is a one-to-one mapping of points in the skew projected spectra in this limit and that there is a linear relation between the field and frequency of corresponding points. This makes it easy to generate the field-domain skew projection from the frequency-domain projection. Simply calculate the field at each point from the frequency using $\hbar\omega = g\beta B$ and adjust for any difference between $g\beta B_0/\hbar$ and the desired ω_0 . The required shift of $g\beta(B_n - B_0)/\hbar$ is often a non-integer number of points. The liberal zero-filling used in step 1) before Fourier transformation ensures that the shift can be rounded to the nearest integer without significant impact on the spectrum.
4. When the g -factor varies across the field range, each field slice has a different width in the final projection and needs to be stretched or compressed according to eqn. (8). This change in width can be accomplished by fitting a spline or other curve to the frequency-domain spectrum and resampling it. However, MatLab has only a minor speed penalty for making Fourier transforms on data that are not exactly a power of two in length. We found it convenient to zero-fill in step 1) so that the total length of a slice in the time domain produced the desired increment between points in the frequency domain after the Fourier transform. Each echo was zero-filled to a different number of points so that the Fourier Transform produces slices with different numbers of points in each slice but with the desired frequency increment between points. The frequency-domain skew EPR spectrum is constructed by making a sum projection onto the frequency axis. This spectrum was found to be a convenient starting point for generating the field-domain spectrum of eqn. (9). Each point in the frequency-domain spectrum maps to a frequency at a field of B_0 given by $B_0\omega_0/\omega$ and the field-domain spectrum can be obtained by re-plotting against these field values. The points in the new spectrum are no longer equi-distant apart, but this is accommodated by many data manipulation packages. The intensity of each point can be adjusted by the varying field increment if desired.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Highlights

- Echo-Detected EPR discards much of the signal information
- FT of echoes retains full information in a 2D spectrum
- Skew projected spectra have better resolution and sensitivity
- Resolution is better than the B_0 step size

Figure 1. Skew Example

Three hypothetical frequency-domain spectra obtained by Fourier transform of a FID or echo at progressively higher fields are shown in black. The pairs of features seen in the individual spectra correspond to the same features and points can be summed together along the grey lines. The resultant skew EPR spectra at a constant frequency, ω_0 , or a constant field, B_0 , are shown in blue.

Figure 2. Simple Skew Projection

An illustration of skew projection on the diamond sample. B_0 , yellow dashed line, was selected near the center of the spectrum. Each signal in the zero-filled FT is projected along the orange arrows at an angle given by Eqn. 6, until it intersects B_0 . The points of intersection are the resonant frequencies, red arrows. The green arrows indicate the shift of each slice needed for direct projection onto the frequency axis.

Figure 3. Simple Sheared Spectrum

The sheared spectrum ready for projection onto the frequency axis to produce the skew projected spectrum.

Figure 4. Diamond Field Projection

ED-EPR and skew EPR spectra of diamond generated from echo signals collected at $\omega_s = 9.6985$ GHz. The ED-EPR spectra were generated using an integration window of (a) 48 ns (blue), (b) 96 ns (green), and (c) 336 ns (red). The field-domain skew EPR spectra were generated with $\omega_0 = 9.7000$ GHz and a g value of 2.0062 using (d) the full echo (cyan), or (e) half of the echo (magenta).

Figure 5. A Portion of the Diamond Spectrum

A stacked plot showing the field slices from 340.95–342.8 mT of Fig. 3 that contribute to the high frequency hyperfine feature.

Figure 6. Phenol Field Projection

D-EPR and skew EPR spectra of 4-methyl, 2,6-di-*t*-butyl phenol generated from an echo signal collected at $\omega_s = 9.7140$ GHz. The ED-EPR spectrum was generated using an integration window of (a) 40 ns (blue). The field-domain skew EPR spectra were generated with a $\omega_0 = 9.7000$ GHz using (b) a constant g value of 2.0094 (green), or (c) a g -value calculated at each field position (red).

Figure 7. TiO₂ Field Projection

ED-EPR and skew EPR spectra of a TiO₂ (rutile) crystal generated from an echo signal collected at $\omega_s = 9.7095$ GHz. The ED-EPR spectra were generated using an integration window of (a) 32 ns (blue), and (b) 120 ns (green). The field projected skew EPR spectra were generated with a $\omega_0 = 9.7000$ GHz using (c) a constant g -value of 1.9770 (red), or (d) a g -value calculated at each field position (cyan). The inset shows the expanded region between 352.2–354.0 mT for spectra (b), (c) and (d).

Figure 8. TiO₂ Frequency Projection

The frequency-projected skew EPR spectra of a TiO₂ (rutile) crystal generated with a $B_0 = 350.9$ mT using (a) a constant g -value of 1.9770 (blue), or (b) a g -value corresponding to each field position (green).