Published in final edited form as:

J Magn Reson. 2014 December ; 249: 126–134. doi:10.1016/j.jmr.2014.10.011.

Digitally generated excitation and near-baseband quadrature detection of rapid scan EPR signals

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Abstract

The use of multiple synchronized outputs from an AWG provides the opportunity to perform EPR experiments differently than by conventional EPR. We report a method for reconstructing the quadrature EPR spectrum from periodic signals that are generated with sinusoidal magnetic field modulation such as continuous wave (CW), multiharmonic, or rapid scan experiments. The signal is down-converted to an intermediate frequency (*IF*) that is less than the field scan or field modulation frequency and then digitized in a single channel. This method permits use of a high-pass analog filter before digitization to remove the strong non-EPR signal at the *IF*, that might otherwise overwhelm the digitizer. The *IF* is the difference between two synchronized X-band outputs from a Tektronix AWG 70002A arbitrary waveform generator (AWG), one of which is for excitation and the other is the reference for down-conversion. To permit signal averaging, timing was selected to give an exact integer number of full cycles for each frequency. In the experiments reported here the *IF* was 5 kHz and the scan frequency was 40 kHz. To produce sinusoidal rapid scans with a scan frequency eight times *IF*, a third synchronized output generated a square wave that was converted to a sine wave. The timing of the data acquisition with a Bruker SpecJet II was synchronized by an external clock signal from the AWG. The baseband quadrature signal in the frequency domain was reconstructed. This approach has the advantages that (i) the non-EPR response at the carrier frequency is eliminated, (ii) both real and imaginary EPR signals are reconstructed from a single physical channel to produce an ideal quadrature signal, and (iii) signal bandwidth does not increase relative to baseband detection. Spectra were obtained by deconvolution of the reconstructed signals for solid BDPA (1,3-bisdiphenylene-2-phenylallyl) in air, 0.2 mM trityl OX63 in water, ¹⁵N perdeuterated tempone, and a nitroxide with a 0.5 G partially-resolved proton hyperfine splitting.

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1. Introduction

Recent advances in arbitrary waveform generators (AWGs) and fast digitizers make it possible to build EPR spectrometers with digital source and detection, which can provide greater flexibility in experimental design and operating frequency than current generation spectrometers. The transition from analog to digital was crucial to improving NMR [1], microwave spectroscopy [2-4], and ion cyclotron resonance [5], and similar advantages await in EPR.

Conventional continuous wave (CW) EPR obtained by phase sensitive detection at a modulation frequency records only the first-derivative of the absorption spectrum. However there are multiple advantages to capturing the signal in quadrature. (i) The dispersion signal can, in principle, be combined with the absorption to improve signal-to-noise (S/N) of CW spectra. (ii) The dispersion signal saturates less readily than the absorption spectrum so it can be used to record spectra of readily saturated spin systems [6, 7]. (iii) In rapid-scan experiments the quadrature signal is used for removal of the periodic background signal and deconvolution [8], and has been shown to improve S/N [9]. These applications of the quadrature signal work better if the phases in the two channels are strictly orthogonal and the relative intensities are matched. In an ideal quadrature EPR signal, real and imaginary components can be transformed to each other with the use of Kramers-Kronig relations. The digital system described in this paper permits reconstruction of an ideal quadrature signal.

The major challenge for signal digitization at an intermediate frequency (IF) is the presence of a reflected or transmitted non-EPR component at the excitation frequency, even if the resonator is carefully tuned. This component may be much stronger than the EPR signal. In the conventional baseband detection method, the non-EPR signal is removed by filtering, but to obtain a quadrature signal two detection channels are required, and it is difficult to obtain ideal orthogonality between the channels [9]. In this paper a general theory is described for detection at an intermediate frequency that is close to baseband and less than the scan or modulation frequency. This allows filtering out the non-EPR component, which otherwise would overwhelm the digitizer, without compromising the absorption and dispersion components of the EPR signal. The approach is general for CW, multiharmonic [10], and rapid scan EPR [8, 11, 12] because these all involve periodic signals. For conventional CW the only frequency of interest is the modulation frequency, ω_{mod} , for which the amplitude would be found for each field position in the spectrum. For multi-harmonic spectroscopy the Fourier coefficients of as many as 10 to 20 harmonics of ω_{mod} would be determined for each field position. Experimental results are reported for the rapid scan method at X-band, which requires a larger number of harmonics of the scan frequency, ω_{scan} , to obtain accurate spectral line shapes than is required for CW EPR. Unlike conventional CW EPR, phase sensitive detection at the modulation frequency is not used in rapid scan EPR.

2. Theory

The signal in an EPR spectrometer after the mixer and before analog filtering can be expressed mathematically as:

$$s(t) \propto [\{r_y + m_y(t)\} \sin(\omega_0 t) + \{r_x + m_x(t)\} \cos(\omega_0 t)] \cos(\omega_0 t + \omega_{IF} t + \varphi) \quad (1)$$

where m_x and m_y are the rotating frame components of the net EPR magnetization in-phase and 90° out-of-phase with one circularly polarized component of B_1 , r_x and r_y are the components of the non-EPR reflection or transmission signal, ω_0 is the excitation frequency, ω_{IF} is an intermediate frequency to which ω_0 is down-converted, and φ is an adjustable phase setting. B_1 in the rotating frame is defined to be along the x axis. Multiplication by $\cos(\omega_0 t + \omega_{IF} t + \varphi)$ in Eq. (1) represents the analog mixing of the resonator output with a reference, which produces signals at $2\omega_0 + \omega_{IF}$ and at ω_{IF} . Eq.(1) can be used to describe three types of signal detection: (i) baseband detection if $\omega_{IF} = 0$, as is conventionally used in EPR spectrometers; (ii) detection at the excitation frequency with post processing in a computer, which can be represented with Eq. (1) by deletion of the $\cos(\omega_0 t + \omega_{IF} t + \varphi)$ term; or (iii) down-converting the signal to an intermediate frequency, ω_{IF} .

2.1 Conventional detection at baseband

The standard EPR bridge employs phase sensitive detection at baseband (method i). This is achieved by mixing with a reference at ω_0 . The mixing produces signals at two frequencies, baseband and $2\omega_0$. The latter is filtered out by a low-pass filter. For example, substitution of $\omega_{IF} = 0$ and $\varphi = 0$ into Eq. (1) shows that the signal $\{r_y + m_y(t)\}$ is lost as the result of baseband detection and filtering:

$$[r_y + m_y(t)] \sin(\omega_0 t) \cos(\omega_0 t) \propto \{r_y + m_y(t)\} \sin(2\omega_0 t) \xrightarrow{\text{Low-Pass Filter}} 0. \quad (2)$$

The signal r_x becomes a DC offset that is removed by the high-pass filter. The removal of r_x is possible due to the separation of the lowest frequency component of the periodic EPR signal from DC in the frequency domain. In the standard CW experiment the only EPR component is at ω_{mod} . In a rapid scan experiment the lowest frequency component of the signal is at ω_{scan} . Both ω_{scan} and ω_{mod} typically are in the kHz range.

In a conventional spectrometer either $m_x(t)$ or $m_y(t)$, or a mixture, is detected. To enable detection of the second component, the signal is split into two physically independent channels and the phase of the reference signal (φ) for one of the channels is shifted 90°. This is equivalent to changing $\cos(\omega_0 t)$ to $\sin(\omega_0 t)$ in Eq.(1) (and using $\omega_{IF} = 0$). By analogy to Eq. (2), $\{r_x + m_x(t)\}$ is removed by baseband detection. Combination of the components from the two channels generates a complex quadrature signal:

$$c(t) = m_x(t) + j\lambda [m_x(t) \cos \varphi + m_y(t) \sin \varphi], \quad (3)$$

where λ is a real number describing the difference in gain between the two physical channels that are nominally in quadrature. If the two channels are perfectly matched, $\lambda = 1$, $\varphi = -90^\circ$, and $c(t)$ is an ideal quadrature signal. For a real phase shifter, φ changes with frequency and for real hardware λ is not exactly 1.

2.2 Detection at ω_0

For detection at the excitation frequency (method ii) a mixer is not used [13], and the $\cos(\omega_0 t + \omega_{IF} t + \varphi)$ term in Eq. (1) is omitted. This method has the advantage of reducing the number of components in the bridge, and produces undistorted quadrature signals. A single physical channel that carries $s(t)$ is digitized and separation of $m_x(t)$ from $m_y(t)$ is carried out in a computer by means of digital phase-sensitive detection. For CW, multiharmonic, or rapid scan experiments the RF or microwave power is on continuously and a very intense reflection:

$$r(t, \omega) = r_y \sin(\omega t) + r_x \cos(\omega t), \quad \omega = \omega_0, \quad (4)$$

has to be digitized along with the EPR component [14]. Because of a very small separation in the frequency domain, ω_0 vs. $\omega_0 + \omega_s$, filtering of the unwanted signal is not possible. For CW $\omega_s = \omega_{\text{mod}}$ and for rapid scan $\omega_s = \omega_{\text{scan}}$. These frequencies typically are orders of magnitude smaller than ω_0 . In addition, method (ii) requires a digitizer with sampling rate that is sufficient to avoid aliasing. The sampling rate can be reduced by time-locked sub-sampling (band-pass sampling) [15], but the bandwidth of the digitizer still must exceed the signal bandwidth, which is of the order of $\omega_0/2\pi$. This method also requires processing very large amounts of data, which becomes less practical at high frequencies such as X-band.

2.3 Detection at ω_{IF} that exceeds signal bandwidth

In method (iii) the microwave signal is translated to an intermediate frequency before detection. The sampling rate requirement for the digitizer can be reduced enough to just satisfy the Nyquist criterion for the signal after downconversion to the IF , which reduces the amount of data to be processed. Detection at an IF also has the advantage that the digitized signal can be processed to obtain both m_x and m_y signals. To permit quadrature detection, ω_{IF} traditionally is selected to be larger than all frequency components of the signal. As was noted for method (i), there are strong reflected signals $r(t, \omega_{IF})$ (Eq. 4), which may overwhelm the digitizer and limit the dynamic range available for the EPR signal. Because $r(t, \omega_{IF})$ and $m_x(t)$ and $m_y(t)$ are very close in the frequency domain, the reflected signal cannot be removed by filtering.

2.4 Detection at near baseband ω_{IF}

We demonstrate a method to remove the strong reflected signals without compromising the EPR signal, which uses ω_{IF} that is small relative to the fundamental frequencies ω_{mod} or ω_{scan} (Eq. 5). Mixing with $\omega_0 + \omega_{IF}$ (Eq. 1), where ω_{IF} is near baseband,

$$0 < \omega_{IF} < \omega_s, \quad \text{where } \omega_s \text{ is either } \omega_{\text{scan}} \text{ or } \omega_{\text{mod}} \quad (5)$$

generates signals at $2\omega_0 + \omega_{IF}$ and at ω_{IF} . Low-pass filtering removes the components at $2\omega_0 + \omega_{IF}$. The non-EPR reflection $r(t, \omega_{IF})$ is now sufficiently well separated from the EPR signal in the frequency domain, that it can be removed by a high-pass filter before digitizing.

This down-conversion to IF and analog filtering modifies the EPR signal described by Eq. 1, into one that is described by Eq. 6.

$$s(t) \propto -m_y(t) \sin(\omega_{IF}t) + m_x(t) \cos(\omega_{IF}t) \quad (6)$$

which preserves both $m_y(t)$ and $m_x(t)$, and therefore, can be post-processed to obtain $\alpha(t)$ with $\lambda = 1$ and $\phi = -90^\circ$ (Eq. 3). Transformation of real $s(t)$ into complex quadrature $\alpha(t)$ (Eq. 3) is described in detail below.

To see the relationships between the coefficients in Eq. (6) and the coefficients after Fourier transformation, the sine and cosine functions can be replaced by complex exponents

$$\begin{cases} \cos(\omega_{IF}t) = \{ \exp(j\omega_{IF}t) + \exp(-j\omega_{IF}t) \} / 2, \\ \sin(\omega_{IF}t) = -j \{ \exp(j\omega_{IF}t) - \exp(-j\omega_{IF}t) \} / 2 \end{cases},$$

to give, after rearrangement,

$$s(t) \propto c(t) \exp(j\omega_{IF}t) + \bar{c}(t) \exp(-j\omega_{IF}t), \quad (7)$$

where $\bar{c}(t)$ denotes the complex conjugate of $c(t)$. Fourier transformation of Eq.(6) or (7) gives:

$$S(\omega) \propto C(\omega + \omega_{IF}) + \bar{C}(-\omega - \omega_{IF}), \quad (8)$$

in the frequency domain, where $C(\omega)$ is the Fourier transform of $\alpha(t)$. The $\alpha(t)$ in Eq.(7) describes a periodic quadrature response to sinusoidal variation of the external magnetic field:

$$c(t) = m_x(t) + jm_y(t) = \sum_{n=-N}^N C_n \exp(jn\omega_s t). \quad (9)$$

In Eq.(9) C_n are the complex Fourier coefficients and N is the number of detectable harmonics in the EPR signal. Using Eq.(9), Eq.(8) can be rewritten as follows:

$$S(\omega) \propto \sum_{n=-N}^N C_n \delta(\omega - n\omega_s - \omega_{IF}) + \sum_{n=-N}^N \bar{C}_n \delta(\omega + n\omega_s + \omega_{IF}), \quad (10)$$

where $\delta(\omega)$ is the delta-function. In Eq.(10) ω is a continuous variable because $S(\omega)$ is obtained by Fourier transformation of the continuous infinite signal $s(t)$. Periodic signals measured in an experiment are discretely digitized and have finite duration. Data processing requires Discrete Fourier transformation to give $S(\omega)$ in the discrete form $S(\omega_m)$. The range

for the integer number m and the frequency increment depend on the sampling rate and signal period. When the periodic signal is measured at baseband, the period for averaging is the same as the scan period:

$$P_{aver}=P_s=\frac{2\pi}{\omega_s}, \quad (11)$$

For detection with ω_{IF} near baseband, the selection of the averaging period is not arbitrary. Averaging only works if $s(t)$ is periodic. To ensure periodicity, and therefore to enable averaging, the following constraints must be imposed:

$$P_{aver}=kP_s=lP_{IF}. \quad (12)$$

In Eq.(12) P_{aver} is the period to be averaged, P_{IF} is the period of the intermediate frequency, k and l are positive integer numbers. To permit signal averaging without discontinuities, if down-conversion is done to a near baseband intermediate frequency (see Eq.5), it is convenient to choose ω_s to be an integer multiple of ω_{IF} :

$$\omega_s=K\omega_{IF}. \quad (13)$$

In this case the averaged signal period becomes equal to the IF period, with $l=1$ in Eq. (12):

$$P_{aver}=P_{IF}=KP_s \quad (14)$$

and the frequency increment for discrete $S(\omega_m)$ is ω_{IF} . As a result, Eq.(10) can be transformed to:

$$S_m=S(m\omega_{IF}) \propto \sum_{n=-N}^N C_n \delta(m-nK-1) + \sum_{n=-N}^N \overline{C}_n \delta(m+nK+1), \quad (15)$$

In Eq.(15) the delta function was changed to a discrete unit function: $\delta(0)=1$ and $\delta(m \neq 0)=0$. Because $s(t)$ is a real function,

$$S_m=\overline{S}_{-m}, \quad (16)$$

which means that the coefficients for the positive and negative frequencies contain the same information. Data analysis in the frequency domain can be done using only the non-negative frequencies:

$$S_m \propto \sum_{n=-N}^N C_n \delta(m - nK - 1) + \sum_{n=-N}^N \overline{C}_{-n} \delta(m - nK + 1), m \geq 0 \quad (17)$$

The summation order in the second term in Eq. (17) was reversed by changing the subscript on the coefficient to -n. If $K > 2$, Eq. (17) allows for separate determination of Fourier coefficients C_n for negative and positive frequencies:

$$\begin{cases} C_n = \frac{S_{nK+1}}{S_{nK-1}}, n \geq 0 \\ C_{-n} = \frac{S_{nK-1}}{S_{nK+1}}, n \geq 0 \end{cases} \quad (18)$$

When the coefficients C_n are found, inverse Fourier transformation gives the EPR signal in complex quadrature form $\alpha(t)$. This is the signal for a single period that would have been obtained by detection at baseband with balanced quadrature channels. In Eq. (18) some points in S are not used to find C_n and C_{-n} , but in the experimental data these points include only noise. For example, for $K = 8$ the points $S_1, S_2, \dots, S_6$, and S_8 are not used. Omitting these points improves the S/N and is equivalent to averaging K cycles of P_s . Since the signal is periodic and the noise is not, the signal only contributes at $(nK \pm 1)\omega_{IF}$.

2.4.1 Rapid scan with $f_{IF} = 5$ kHz, $K = 8$ —To understand the steps in the data analysis it is useful to consider a specific case (Fig. 1). The following rapid scan example is given for $f_{IF} = 5$ kHz ($f = \omega/2\pi$), which is the frequency that was used for the experiments. For $K = 8$, $f_{scan} = 40$ kHz (Eq. 13). Fig. 1a is a graphical representation of the S coefficients in Eq. (18), in the linear frequency domain. The data consist of pairs of components with frequencies of $40 \pm 5, 80 \pm 5$ kHz, etc. For example with $n = 1$ (Eq. 18), $C_1 = S_9$, and for the example shown, C_9 is the Fourier coefficient at 9 times IF . Similarly the complex conjugate of C_{-1} is equal to S_7 , at 7 times IF (Fig. 1a). The complex conjugates of S_{nK-1} are taken, and the results are moved to the corresponding negative frequencies (Fig. 1b). All frequencies are then shifted by one unit of IF (Fig. 1c) such that the data are now centered at 0. The signal-containing points are now positioned at nK , ($n \neq 0$). All other points contain noise. The subarray of signal-containing points is extracted to generate a new array that is $1/8^{\text{th}}$ as long. This array is Inverse Fourier transformed to produce one full cycle of the complex baseband rapid scan signal.

3. Experimental section

3.1 Samples

A small particle of 1,3-bisdiphenylene-2-phenylallyl (BDPA, Sigma-Aldrich, St. Louis, Missouri) in air in a capillary tube was supported in a 4 mm o.d. quartz tube. Tris[8-carboxyl-2,2,6,6-benzo(1,2-d:5-d)-bis(1,3)dithiole-4-yl] methyl sodium salt (trityl OX63) [16] was provided by Professor Howard Halpern, University of Chicago. A 0.2 mM aqueous solution of trityl OX63 in a 4 mm o.d. $\times$ 3 mm i.d. quartz tube had a height of 3 to 4 mm. The sample was purged with N_2 for 5 min and then flame sealed. The sample reduced the

resonator Q to about 60. Nitroxide ^{15}N -PDT (perdeuterated 4-oxo-2,2,6,6-tetramethylpiperidiny- ^{15}N -oxyl) was purchased from CDN isotopes (Quebec, Canada). A 6 mM solution of ^{15}N -PDT in water was mixed with superabsorbent polymer (SAP) (cross-linked polyacrylate sodium salt, Sigma-Aldrich #436364) in a 10:1 mass ratio. Superabsorbent polymers (SAP) consist of cross-linked polyacrylic acid or polyacrylate salts. These polymers can absorb a large amount of water relative to the volume of the polymers. When an aqueous solution is mixed with SAP, a gel is formed. The pH of the gel can be adjusted to pH ~ 5 by using a buffered solution. Samples in 1 mm capillary tubes were sealed in air with a torch and monitored by X-band EPR for more than 500 days. A capillary supported in 4 mm OD quartz tube reduced the resonator Q to about 225. The stability of these pH-controlled samples is good for long-term use. ^{15}N -mHTCPO was provided by Prof. Halpern, University of Chicago [17]. A 0.1 mM solution of ^{15}N -mHTCPO in 80/20 EtOH/H₂O in a 4 mm o.d. $\times$ 3 mm i.d. quartz tube had a height of 3 mm, resulting in 3×3 mm cylindrical shape, which reduced the resonator Q to about 150 [18]. The sample was degassed by six freeze–pump–thaw cycles and then flame sealed.

3.2 Hardware

The digital rapid scan EPR system is built around a Bruker E500T spectrometer with a Bruker X-band Flexline ER4118X-MD5 dielectric resonator [18, 19]. For low-loss samples the resonator Q is about 9000 and the efficiency is 3.8 G/ W [19]. The resonator efficiency decreases approximately as $1/Q$ [19]. The Xepr software controls the magnetic field, and data are digitized with a Bruker SpecJet II digitizer, which has a sampling rate up to 1 GHz. The sinusoidal scans are generated with the recently described scan driver [20]. The scan coils are constructed from 200 turns of Litz wire (255 strands of AWG44 wire). The coils have about 7.6 cm average diameter and were placed about 4 cm apart. The coil constant is 37.7 G/A [20]. Mounting the coils on the magnet, rather than on the resonator, reduces the oscillatory background signal induced by the rapid scans. The placement of highly conducting aluminum plates on the poles of the Bruker 10" magnet reduces resistive losses in the magnet pole faces. The dielectric resonator decreases eddy currents induced by the rapidly-changing magnetic fields relative to resonators with larger amounts of metal.

The block diagram of the system is shown in Figure 2. The source is a Tektronix arbitrary waveform generator (AWG 70002A) with two 8-bit DAC outputs at 25 Gsamples/s, which permits generating waveforms with 2.5 samples/cycle at 10 GHz. Amplifiers in the signal path give a maximum microwave power of 235 mW. An adjustable attenuator (0 to 50 dB) controls the power to the resonator. The signal from the resonator, after amplification, is mixed with the amplified signal from the second AWG DAC channel. The frequency difference between the two synchronized microwave outputs from the AWG creates the approximately 5 kHz IF . A high pass filter at 25 kHz (-3dB) removes the non-EPR signal at the intermediate frequency, but preserves the spectral information that is in the harmonics. After an additional 20 dB gain and a 5 MHz low pass filter (Krohn-Hite 3955 LP Butterworth dual-channel filter) that is set to remove high frequency noise, the signal is detected in the Bruker SpecJet II digitizer. The timing of the data acquisition was synchronized by an external clock signal from the AWG. To generate the sinusoidal rapid scans a square-wave marker signal from the AWG was converted to a sine wave by a low

pass filter (at 29 kHz). The period of the rapid scans was exactly $1/8$ of the period for the IF . The scan coils are resonated with a capacitor [20]. Timing of the excitation frequency, reference frequency, IF , and rapid scan cycles were selected to give integer numbers of cycles for each frequency. The timing diagram for the signals from the AWG is shown in Fig. 3 for a particular example.

The experimental signal was passed through a 4-pole high-pass Butterworth filter to remove the component at the IF , with minimum impact on higher frequencies that contain EPR signal. The amplitudes of frequency components of the EPR signal were preserved, but the filter introduces frequency-dependent phase shifts. The Butterworth filter was designed with “Filter Lite” software from Nuhertz Technologies, Phoenix, AZ. The software outputs tabular data describing the impact of the filter on the phase and amplitude of the frequency components of the signal which was stored in the data reconstruction program. The corrections were read from the stored file and applied to the data in the software, prior to the data reconstruction described in section 2.4.1.

3.3 Resonator tuning and data acquisition

3.3.1 Resonator tuning—With the AWG 70002A a chirp pulse waveform from 9.6 to 9.7 GHz was generated in channel 1 DAC as the excitation and a continuous waveform at 9.6 GHz was generated in channel 2 DAC as the reference. The signal after the mixer is detected with a LeCroy 400 MHz digital scope (model 44Xi-A). In the scope, a Fourier transform was applied to convert the signal from time domain to frequency domain. The resonator reflection dip in the frequency domain was displayed on the scope, in essentially real time. The resonator was adjusted to critical coupling. The actual resonator frequency, relative to the reference, is read from the scope display and used to program the outputs from the AWG.

3.3.2 Data acquisition—The AWG is programmed to output continuous waveforms for the excitation and reference. The waveforms were designed in Matlab and transferred to the AWG. The excitation microwave frequency was matched with the resonator, with a clock rate that is 2.5 times the resonator frequency. For a frequency of about 9.6 GHz, a difference of exactly one cycle between the number of cycles for the excitation and the reference frequencies corresponds to a difference of about 5 kHz, which is then the IF (Fig. 3). The rapid scans were generated with a frequency that is exactly 8 times the IF . The trigger for the digitizer occurs once per IF period. The AWG also provides the clock signal at about 200 MHz for the SpecJet II. Within the SpecJet II the clock frequency is divided by two, so the digitization occurs at about 100 MHz. The frequencies are exactly synchronized by the AWG and all frequencies shift proportionately with the resonator frequency. Data were acquired on and off resonance.

3.4 Data analysis

The data analysis process is outlined in Fig. 4. The experimental data are many averages of the spectrum with a time window equal to $1/IF$ (Fig 5a). The off-resonance signal that contains only unwanted information, including digital clutter, is subtracted from the on-resonance signal. The high pass filter introduces known phase shifts that can be corrected in

postprocessing using the known characteristics of the filter (section 3.2). The data are Fourier transformed into the frequency domain. Analysis as described in section 2.4.1 reconstructs the quadrature-detected rapid scan spectrum in the time domain (Fig. 5b). Deconvolution generates the absorption spectra in the field domain, from the quadrature rapid scan signal (Fig. 5c). The $n = 0$ term (Eq. 9) is the DC offset of the signal and is generated in the baseline correction procedure [21].

3.5 Spectroscopy

The performance of the digital spectrometer has been tested with four samples. Solid samples of BDPA in air have Lorentzian lineshapes with first derivative peak - to- peak widths of 0.4 to 0.8 G and $T_1 \sim T_2$ in the range of 80 to 160 ns [22]. These relaxation times are sufficiently short that rapid-scan passage effects are not observed for the 40 kHz 10 G scans used in this study. Rapid scan data for the full 8 sinusoidal cycles at 40 kHz that occur within one IF period are shown in Fig. 5a. The relative contributions of m_x and m_y change sinusoidally in the course of an IF cycle. These data contain both the real and imaginary signals, which are reconstructed by the data analysis algorithm. After reconstruction, a time-domain full cycle rapid scan signal including both the real and imaginary components is obtained as shown in Fig. 5b. Averaging up- and down-cycles and combining real and imaginary produces the absorption spectrum in the field domain, as shown in Fig. 5c. The full-width at half height of 1.3 G is in reasonable agreement with the expected linewidth. The signal-to-noise is excellent for this strong sample.

At X-band 0.2 mM trityl-OX63 in deoxygenated water has $T_1 = 15 \mu\text{s}$ and $T_2 = 6.4 \mu\text{s}$ [23]. These relaxation times are long enough that the signal exhibits rapid-scan oscillations when a 40 kHz, 10 G scan width is used. These oscillations are captured accurately in the digital scans (Fig. 6a). In the deconvolved spectrum (Fig. 6b) the ^{13}C hyperfine lines with splittings of 2.4 and 3.4 G are visible, and in good agreement with the literature values of 2.3 and 3.3 G [24]. The full width at half-height of the partially degassed trityl-OX63 signal is 0.22 G.

As an example of wider scans, a 40 G scan width was used to encompass both ^{15}N hyperfine lines of 6 mM ^{15}N -PDT in superabsorbent polymer (SAP). Although the macroscopic viscosity of the gel is high, the local microscopic viscosity is low. The X-band EPR signal was in the rapid tumbling regime. These experiments indicate that SAP can be used to prepare EPR samples in which small molecule solutes are tumbling freely, but the sample does not flow readily within the tube. The digital rapid scan spectrum (Fig. 7a) accurately reports the known nitrogen hyperfine splitting of 22.4 G.

To check the resolution of the spectra, a sample of 0.1 mM mHCTPO in 80:20 ethanol:water was obtained. The 0.47 G partially-resolved proton hyperfine splitting is well defined [17], as shown in the Fig. 7b.

4. Discussion

There has been a continuing evolution of the use of digital technology in EPR since the early days of signal digitization. X-band pulsed EPR has recently been performed using microwaves generated with an AWG [13, 25]. One other lab, in parallel with our efforts, has

digitally generated the incident RF and directly digitized the CW EPR signal at 300 MHz [26, 27]. The current work makes the major step to CW at X-band, which was not feasible until the latest developments in digital technology. Down-conversion and subsampling techniques, which are also extensively used in NMR [1] and MRI, have been used by the Hyde lab for recording multiharmonic X-band CW EPR [15, 28, 29] [30], by the Ohio State lab for L-band CW EPR [14], and by the NCI lab to digitize an FID [26]. An AWG was used to control pulse timing in a 26.5-40 GHz pulsed EPR spectrometer [31]. These experiments have all used a traditional EPR spectrometer with substitution of the normal detection system by newer digital detection components. The programmability of an AWG permits direct synthesis of the excitation and reference frequencies, which removes the need for up- and down-conversion and thereby simplifies the spectrometer. Detection at an IF near baseband permits removal of the reflected signal at f_0 . The experimental data demonstrate the performance of the algorithm using detection at $\omega_{IF} < \omega_s$ for rapid scan EPR and samples with linewidths as narrow as 0.22 G and scan widths up to 40 G.

The experiments are designed with exactly integer numbers of cycles for excitation, reference, and scan frequencies. This ensures that the signal is fully periodic with no discontinuities. In the example f_{scan} is denoted as 40 kHz. This number is not exact and scales with the actual resonator frequency. If the IF is changed substantially, a different high-pass filter would be needed and the resonating capacitor in the coil driver circuit would need to be changed. All other aspects of the digital system can be varied over a wide range of frequencies.

A major advantage of this method is the removal of the non-EPR component of the signal at ω_{IF} prior to digitization. For a reflection resonator this is reflected source power and leakage through the circulator. For a cross-loop resonator it is leakage through the resonator. This component may be orders of magnitude larger than the EPR signal. If this unwanted component is not removed, it may require low sensitivity settings for the digitizer which would limit the vertical resolution that is available for the EPR component. Detection at $\omega_{IF} < \omega_s$ and removal of the component at ω_{IF} , as demonstrated in this paper for rapid scan, is valid for any periodic signal.

These experiments were designed as a proof of principle for AWG excitation and detection at near baseband ω_{IF} . Thus a comparison of signal-to-noise with conventional detection was not attempted. Even so, it is valuable to consider sources of noise in the digital instrumentation. There are digital clutter signals, which were cleanly removed by subtraction of off-resonance signals. The time jitter of the AWG is stated by the vendor to be too small to measure, and the experimental results obtained in this paper are consistent with that assertion. The phase noise for the current model of the AWG is stated to be about -100 dBc at 100 kHz offset at 9-10 GHz, which is significantly poorer than conventional CW sources that have phase noise about -140 dBc at 100 kHz offset. The AWG manufacturer has suggested that the phase noise could be reduced by using a low phase noise external clock generator, which can be implemented in future work. In addition, phase noise in the detected signal could be substantially decreased by use of a bimodal resonator. Thus it seems reasonable to propose that system optimization will result in signal-to-noise performance with AWG and digital signal processing comparable to conventional spectrometer, but with

greatly enhanced flexibility for experimental design based on software rather than hardware changes.

Acknowledgements

Partial support of this work by National Science Foundation grant MRI 1227992 (SSE and GRE), National Institutes of Health NIBIB EB000557 (GRE and SSE), and K25 EB016040 (MT) is gratefully acknowledged. OX63 and ^{15}N -mHCTPO were provided by Professor Howard Halpern, University of Chicago. Solutions of OX63 and ^{15}N -mHCTPO used in this study were prepared by Joshua Biller (University of Denver) and Deborah Mitchell (University of Denver), respectively.

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Research Highlights

- Arbitrary waveform generator based X-band EPR spectrometer.
- Signal is down-converted to intermediate frequency near baseband.
- EPR signal is digitized and converted to quadrature from single physical channel.
- The method is demonstrated for rapid scan of 4 organic radicals.
- The method is applicable for any periodic signal.

Figure 1.

Graphical description of the algorithm for $f_{IF} = 5$ kHz and $K = 8$ (Eq. 13), showing only the first two harmonics. (a) Fourier transform of the IF signal (Eq. 15). The Fourier coefficients for negative and positive frequencies are interdependent, so that only positive frequencies are used. Red and blue colored bars represent S_{nK+1} and S_{nK-1} coefficients in Eq. (17). The black dashed line denotes the position of the strong 5 kHz signal that was filtered out. (b) The complex conjugates of S_{nK-1} coefficients are taken and mirror-inverted into the negative half of the frequency domain. (c) All coefficients are shifted in the negative direction by 5 kHz. The result is the Fourier transform of the complex quadrature signal $c(t)$ (Eq. 9).

Figure 2.

Block diagram for digital EPR spectrometer. KH refers to a Krohn-Hite 3955 LP Butterworth dual-channel filter. 1) microwave power amplifier: Mini circuits ZX60-14012L-S+; 2) microwave power amplifier: Aydin AWA 8596B; 3) microwave power amplifier: MITEQ AMF 4s 9092-20; 4) low noise amplifier: HD27028, noise figure = 1.8dB; 5) amplification in KH filter; 6) low pass filter with a cutoff frequency of 29 kHz; 7) low pass filter with a cutoff of 5 MHz ; 8) 4 pole high pass Butterworth filter (-3dB) at 25 kHz. This proof-of-principle experiment was conducted with available components. The design has not been optimized.

Figure 3.

Timing details for AWG outputs. The synchronization of the five outputs from the AWG is sketched for a sampling frequency of 24.135575 Gs/s. The timing is selected to have an integer number of cycles for each output. The lengths of the outputs from channels 1 and 2 differ by 1 cycle, which corresponds to the IF . The output from marker 1 is sent through a low-pass filter with a cutoff of 29 kHz frequency to convert the square wave into a sine wave that generates the sinusoidal rapid scan. The scan frequency is exactly 8 times IF . Marker 2 synchronizes the SpecJet II digitization, and Marker 3 triggers the oscilloscope. The clock output provides the external clock signal for the Specjet II. For the examples shown in this paper, the IF was about 5 kHz. The exact value of IF changes with resonator tuning because that changes the excitation frequency.

Figure 4.
Schematic sequence of data analysis as described in the text.

Figure 5.

X-band rapid-scan data for solid BDPA in air. a) Experimental data for the time corresponding to one IF cycle obtained with power = 0.6 mW ($B_1 \sim 90$ mG) and 102400 scans, which required about 20 s. One IF cycle encompasses 16 passages through resonance, including both the up-field and down-field sinusoidal scans. b) Reconstructed quadrature-detected rapid scan spectrum including both up and down scans - real (blue) and imaginary (red). c) Deconvolved field-domain spectrum.

Figure 6.

X-band rapid-scan data for 0.2 mM OX63 in water with 0.6 mW power ($B_1 \sim 7$ mG) and 1024000 scans which required 200 s. a) Reconstructed quadrature-detected rapid scan spectrum including both up and down scans - real (blue) and imaginary (red), including the rapid-scan oscillations. b) Deconvolved spectrum.

Figure 7.

X-band rapid scans. a) Spectrum of 6 mM ^{15}N -PDT in superabsorbent polymer obtained with 0.6 mW power ($B_1 \sim 15$ mG) and 102400 scans, which required 20 s. b) Spectrum of 0.1 mM mHCTPO in 80:20 ethanol:water obtained with 0.6 mW power ($B_1 \sim 10$ mG) and 2048000 scans, which required 400 s.