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Direct EPR detection of transient and continuous wave signals at 2.5 GHz

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Abstract

Direct detection of free induction decays and electron spin echoes, and the recording of echo-detected EPR spectra and electron spin echo envelope modulation patterns at a microwave frequency of 2.5 GHz is demonstrated. This corresponds to the measurement of the transverse magnetization in the laboratory frame, rather than in the rotating frame as usually done by down-converting the signal (homodyne detection). An oscilloscope with a 6-GHz analog bandwidth, a sampling rate of 20 GigaSamples per second, and a trigger frequency of 5 GHz for the edge trigger and 750 MHz for the advanced trigger, is used in these experiments. For signal averaging a 3-GHz microwave clock divider has been developed to synchronize the oscilloscope with the frequency of the EPR signal. Moreover, direct detection of continuous wave EPR signals at 2.5 GHz is described.

Keywords: Pulse EPR; Continuous wave EPR; Direct digital detection

1. Introduction

In the great majority of EPR experiments, homodyne detection is used to record the signals. The EPR signal from the resonator is down-converted with the signal from the microwave (mw) source (reference signal). The down-converted signal represents the magnetization in the rotating frame, a frame which rotates with the mw frequency around the laboratory *z*-axis oriented along the static magnetic field direction. Both the in-phase signal (dispersion) and the out-of-phase signal (absorption) can be recorded by shifting the phase of the reference signal by 90°, or by using quadrature detection.

In pulse EPR the down-converted transient signal contains frequencies up to about 200 MHz, depending on the off-resonance excitation. In cw EPR, sidebands created by the field modulation (usually 100 kHz) are recorded with a phase sensitive detector (PSD), or the signal with all its harmonics is digitized and processed on a computer. Recently, Hyde and co-workers [1,2] recorded EPR signals by time-locked subsampling, which is instrumentally quite demanding.

In this work we report on the first direct detection of EPR transients, such as FIDs and electron spin echoes without down-conversion, carried out at an mw frequency of 2.5 GHz. This correspond to recording the transverse magnetization directly in the laboratory frame. Direct detection at mw frequencies (at present up to about 6 GHz) has become feasible due to the progress in semiconductor technology [3] used in high-speed oscilloscopes. Manufacturers of high-end oscilloscopes are traditionally early users of new integrated circuit technologies. SiGe semiconductors are now used by leading manufacturers resulting in digitizers with impressive specifications.

Besides the direct recording of the time evolution of transient signals we used direct detection to measure echo-detected field-swept EPR spectra and electron spin echo envelope modulation (ESEEM) traces in two-pulse ESEEM experiments. Moreover, we show in a first attempt that also cw EPR signals can be observed using direct detection.

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2. The spectrometer

2.1. Pulse EPR

2.1.1. Instrumentation

Direct detection of EPR signals is demonstrated at 2.5 GHz on a homebuilt S-band (2–4 GHz) cw/pulse EPR spectrometer [4], adapted for this type of experiments. The main parts of the spectrometer are shown in the block diagram in Fig. 1.

In the pulse mode the signal from the oscillator (KDI Electronics, model CC-24; frequency range, 2–4 GHz; output power, 70 mW) in the mw bridge (JAGMAR, Krakow, model SB-0100A) is fed to the four-channel pulse former unit, which creates the pulse pattern (lengths, phases, and amplitudes of the pulses), and is then guided with an mw power of about 0 dBm to the TWT amplifier (Applied System Engineering, model 117-S, 1 kW output power). After the TWT amplifier the mw signal is fed via a four-port circulator (isolation of ports 1–3, 25 dB) to a homebuilt probehead with an overcoupled bridged loop-gap resonator [5–7] with high pulse-power efficiency [4]. During excitation switch S2 turns the *TWT* on and switch S3 is open to protect the two low-noise preamplifiers (MITEQ, model AFS-302000400-10-10P-6; gain, 32 dB; noise figure, 1 dB, and Avantek, model AFT-6233; gain, 30 dB) against damage caused by the high pulse power. The mw signal is then guided via a 3-GHz bandpass filter (insertion loss, 1 dB; center frequency, 2.7 GHz; bandwidth, 1.5 GHz) to the digitizer.

As digitizing front-end, a high-speed oscilloscope (LeCroy, Wavemaster 8600A) was used. Instruments of this class consist nowadays basically of a personal computer (PC) platform with specialized hardware to acquire analog signals. In case of the Wavemaster 8600A, the digitizing front-end is built with several custom designed integrated circuits in SiGe technology, which are able to fill the large (24 MegaSamples per channel) high-speed CMOS acquisition memory at the maximum sampling rate of 20 GS/s. The link from the digitizing part to the PC is made with a standardized fast serial bus (Gigabit Ethernet), in order to move the collected data quickly to the system memory.

Key parameters of this 4-channel digitizer are an analog bandwidth of 6 GHz, a fixed input impedance of 50 Ohm, an adjustable full-scale range from 16 mV to 8 V with a resolution of 8 bits. Critical timing specifications are a single shot sampling rate of 10 GS/s using all 4 channels (or 20 GS/s by using only 2 input channels), an internal clock accuracy of 1 ppm, a trigger uncertainty of typical 2.5 ps, and a sampling rate accuracy of ±1 ppm. The acquisition memory has a size of 24 MSamples per channel. The bandwidth of the basic trigger circuit used to trigger on edges is maximum 5 GHz. This bandwidth drops to 750 MHz if, as in our case, the trigger is realized in two steps.

The internal PC of the oscilloscope is based on an Intel Pentium 4 processor with a clock rate of 860 MHz. The system-memory (RAM) size is 512 Mbytes. The operating system is Windows 2000. The software driver controlling the digitizing front-end is based on Microsoft Component Object Model (COM), an architecture that allows one to reuse the compiled code and to exchange data between different programs running simultaneously. An extensive set of software functions to manipulate acquired data is installed. We mainly used

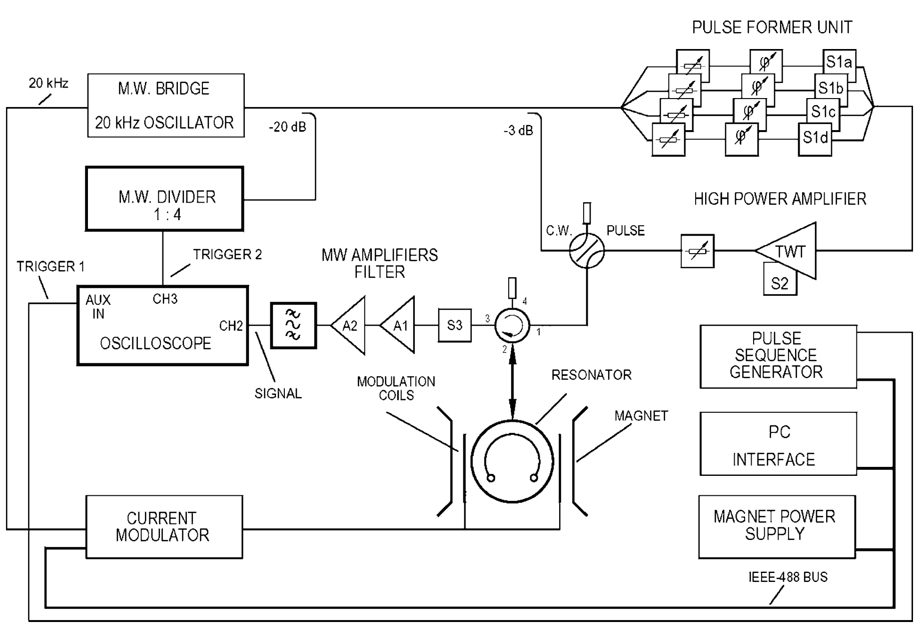

Fig. 1. Overall block diagram of the EPR spectrometer for direct detection.

Fast Fourier Transform (FFT) algorithms, averaging and measurement parameter functionalities.

In our experiments, we used two types of triggers. Trigger 1 is provided by the pulse sequence generator. For Trigger 2, mw power from the oscillator is guided via a directional coupler (−20 dB) to the mw-clock divider, that consists mainly of a 2.5-GHz low-power divide-by-four prescaler (ON Semiconductor, type MC12095). The 625-MHz signal of the prescaler output (rectangular signal with 0.6 V amplitude) is fed to input channel Ch3 of the oscilloscope. Data transfer and communication between the spectrometer PC and peripheral instruments (pulse sequence generator, magnet power supply, etc.) is done via an IEEE 488 bus. In the experiments presented in this work the data were not only recorded, but also accumulated, stored and processed by the oscilloscope, which was still local controlled. Pulse sequence generator, interface, and resonator are described elsewhere [4].

2.1.2. Trigger for direct detection

For direct detection and averaging (processing) of data of consecutive pulse experiments, the oscilloscope was synchronized with the frequency of the mw oscillator by the two triggers mentioned above. The trigger and detection scheme of a 0°, 90°, and 180° echo is shown in Fig. 2. The first trigger (Trigger 1), fed to the auxiliary input (AUX IN) of the oscilloscope, is the positive edge of a pulse from the pulse sequence generator. It has to be properly set with respect to the driving pulses of mw switch S1a–d, which creates the pulse sequence. The second trigger (Trigger 2, called qualified trigger in LeCroy terms), is set by the first zero-crossing of the divide-by-four prescaler output after Trigger 1. The vertical line in Fig. 2 shows a trigger example of three different phases of the electron spin echo, applied for phase-cycling data accumulation [8] in directly detected pulse EPR.

The pulse pattern generator that drives the mw switches S1a–d, S2, and S3 is not synchronized with the mw frequency. Therefore, Trigger 2 is activated after Trigger 1 within a time uncertainty of maximum 1.6 ns (one clock cycle of Trigger 2). This uncertainty of the starting time during accumulation of FIDs or echoes has virtually no influence on the averaged signal amplitudes. It would be more straightforward to use the mw signal as Trigger 2, but the bandwidth of the qualified-trigger circuit used for data averaging is limited to 750 MHz.

The amplified transient signal from the resonator is fed to input channel Ch2 of the oscilloscope. Using only channel Ch2 and Ch3, the oscilloscope allows for a maximum sampling rate of 20 GS/s. In all the experiments the signal-to-noise ratio is improved by using exponential averaging with a weighting factor of 1:31.

The oscilloscope has the capability to record and display a measurement parameter over time, similar as a strip chart recorder. This feature is called ‘trend mode’ and was used to record echo-detected EPR spectra and ESEEM time traces. When the oscilloscope is controlled by the PC of the spectrometer, such sweeps can directly be recorded and averaged on the oscilloscope, synchronized with the increments of the B_0 field.

2.2. Continuous wave EPR

For the direct detection of cw EPR signals the switch after the TWT amplifier is turned to ‘cw’ and the mw source is locked to the resonator by an automatic frequency control (AFC) loop. The static magnetic field is modulated with a frequency of 20 kHz and an amplitude of up to 6 mT, by guiding a 20-kHz signal from the PSD in the mw bridge via the current modulator to the modulation coils. As in the case of pulse EPR, the cw EPR signal is amplified by the mw preamplifiers A1 and A2 and is fed via the 3-GHz bandpass filter to input channel Ch2 of the oscilloscope. Since in cw experiments only low mw power is used, protection switch S3 is kept closed.

It was tempting to use the time signal acquired by the oscilloscope to demonstrate the feasibility of direct cw EPR detection. We used a 10-MS acquisition memory size with a sampling rate of 10 GS/s, to record a 1-ms time window of cw EPR data at a static magnetic field of 89 mT. FFT of these data leads to a magnitude spectrum of the EPR signal and the AFC signal.

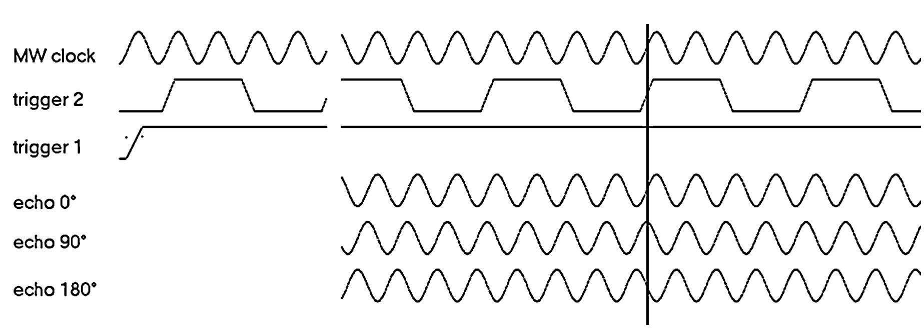

Fig. 2. Timing diagram of the oscilloscope trigger: Trigger 1, edge trigger; Trigger 2, clock/4. The vertical line shows a trigger example for three different phases of the electron spin echo applied for data accumulation under phase cycling in directly detected pulse EPR.

3. Results

3.1. Pulse EPR

A screen shot of the on-resonant FID of lithium phthalocyanine powder directly recorded at 2.508 GHz with 20 GS/s is shown in Fig. 3A. The signal observed after a 30-ns mw $\pi/2$ pulse and a deadtime of 300 ns consists of 2×10^5 data points and represents the decay of the transverse magnetization during the first 10 μs in the laboratory frame. Fig. 3B, trace F5, shows the zoom of a 20-ns time window of the FID (grey area in Fig. 3A) together with the magnitude spectrum of this time window obtained by FFT (trace F3). The repetition rate of the pulse experiments was determined by the data acquisition and process time of the oscilloscope, and is specified to be 100 Hz for 1000 data points.

Fig. 4A shows a screen shot of a directly detected two-pulse echo experiment on γ-irradiated calcium formate powder recorded at 2.508 GHz with 20 GS/s. The echo represents the refocusing of transverse magnetization in the laboratory frame. It is created with the sequence $\pi/2$–τ–π–τ-echo, using the pulse lengths $t_{\pi/2} = 20$ ns and $t_\pi = 40$ ns, and a pulse power of 2.5 W. An interpulse delay of $\tau = 300$ ns is used, a value for which the nuclear modulation effect is minimum. Protection switch S3 is closed immediately before the echo is formed. On the rising flank of the echo some cavity ringing is visible. Even after suppression of the two excitation pulses by switch S3 (80 dB), they can still be observed. This pulse leakage, which depends on the isolation of switch S3, is caused by mw power reflected by the overcoupled resonator [4]. Fig. 4B shows a zoom of a 10-ns time window at the echo maximum (grey area in Fig. 4A). If in more complex pulse sequences unwanted transient signals have to be eliminated, phase cycling can be done [8] by using different phase settings for the mw channels in the pulse former unit, in the same way as in an experiment which uses down-conversion.

The echo-detected EPR spectrum of γ-irradiated calcium formate powder recorded with direct EPR at 2.508 GHz by using the 'trend mode' of the oscilloscope, is shown in Fig. 5. The same two-pulse echo sequence as in Fig. 4 is used. The measurement parameter was the rms voltage of a 50-ns time window centered at the echo maximum. It represents one data point in the trend plot. The accumulation time for this sweep amounts to 98 s.

Fig. 6 shows a directly detected time-domain trace of a two-pulse ESEEM experiment on γ-irradiated calcium formate powder recorded at 2.508 GHz and a magnetic field of 88.9 mT, recorded with the pulse sequence used in Fig. 4. A deep echo modulation caused by a large number of weakly coupled protons is observed with oscillation frequencies at the proton Larmor frequency of 3.78 MHz and at twice this frequency.

At 2.5 GHz, the S/N ratio of the recorded FIDs and electron spin echoes is considerably lower than at higher frequencies [4]. With our spectrometer the S/N ratio using homodyne detection was about the same as the one found with the direct detection method, considering a 10 times larger receiver bandwidth. The receiver gain was the same for both methods. The signal-to-noise ratio is determined by the insertion losses between resonator and mw amplifier A1 and depends on the overall receiver bandwidth, the noise figure of the amplifier A1, and the performance and temperature of the resonator.

3.2. Continuous wave EPR

We now demonstrate that with an acquisition memory of 10-ms per channel of the oscilloscope, the harmonics of the EPR signal can simultaneously be computed. Fig. 7 shows a 200-kHz section of the power spectrum of a directly detected cw EPR signal of γ-irradiated calcium formate powder. The input amplitude of the signal after 62 dB amplification was 1.5 V_{pp}. The data were recorded at a fixed magnetic field of 89 mT and an mw frequency of 2.499 GHz. A modulation

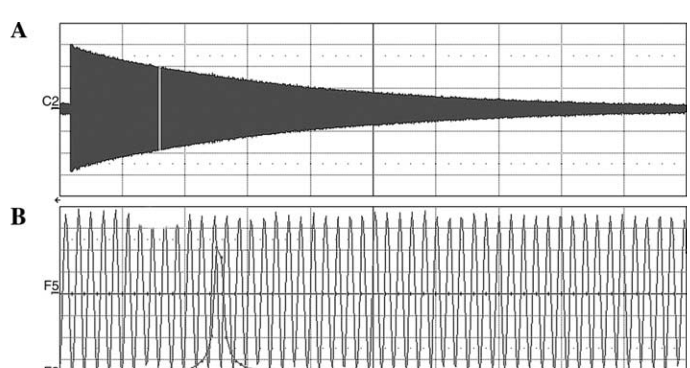

Fig. 3. Screen shot of the on-resonant FID of lithium phthalocyanine powder, recorded with 20 GS/s at 2.508 GHz; room temperature. (A) Horizontal resolution, 1 μs/div; vertical resolution, 50 mV/div. (B) Trace F5: Zoomed 20-ns window (grey time interval) of (A); horizontal resolution, 2 ns/div; vertical resolution, 10 mV/div. Trace F3: Magnitude spectrum of trace F5; horizontal resolution, 1 GHz/div; vertical resolution, 10 mV/div.

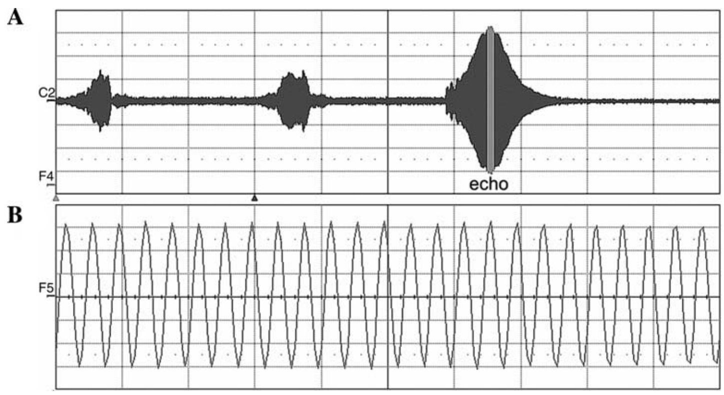

Fig. 4. Screen shot of the two-pulse echo of γ-irradiated calcium formate powder, recorded with 20 GS/s at 2.508 GHz; temperature, 25 K. (A) Horizontal resolution, 100 ns/div; vertical resolution, 50 mV/div. (B) Zoomed 10-ns window (grey time interval) of (A) at echo maximum; horizontal resolution, 1 ns/div; vertical resolution, 50 mV/div.

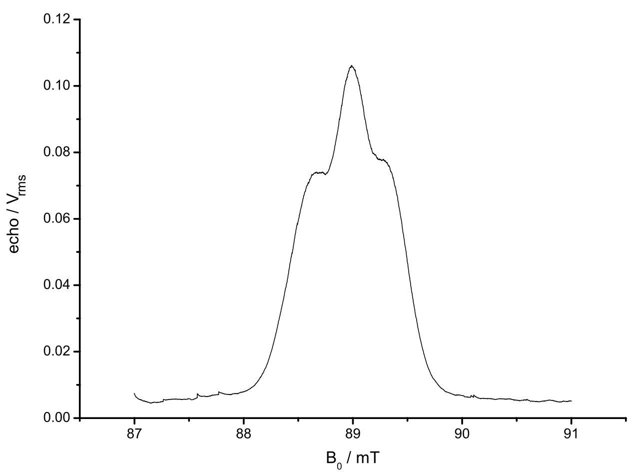

Fig. 5. Echo-detected EPR spectrum of γ-irradiated calcium formate powder. Microwave frequency, 2.508 GHz; temperature, 25 K. For each field setting the data were directly recorded on the oscilloscope by measuring the rms voltage of the echo signal during 50 ns at the echo maximum.

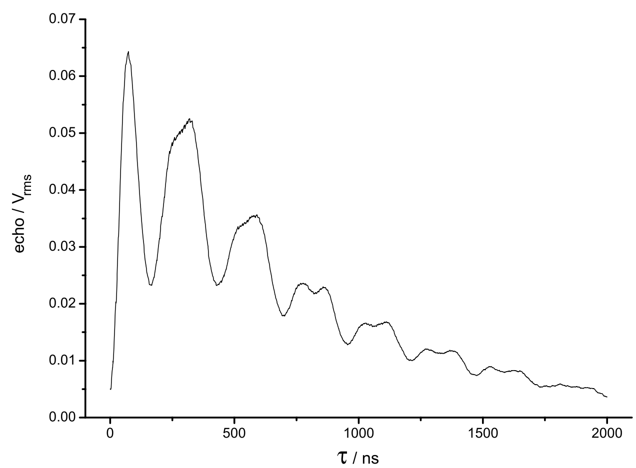

Fig. 6. Two-pulse electron spin echo envelope modulation of γ-irradiated calcium formate powder as a function of the interpulse time τ. Microwave frequency, 2.508 GHz; magnetic field, 88.9 mT; temperature, 25 K. For each τ value the data were directly recorded on the oscilloscope by measuring the rms voltage of the echo signal during 50 ns at the echo maximum.

frequency of 20 kHz and a modulation amplitude of 2 mT were used.

The FFT of a 1-ms time window sampled at 10 GS/s shows besides the dominating carrier frequency sidebands representing the first harmonic at 20 kHz and the second harmonic at 40 kHz of the EPR signal. In addition, the 70-kHz sidebands generated by the frequency modulation of the mw oscillator used for the AFC loop are visible.

The 10 MegaSamples have been truncated to the closest power of 2, which resulted in a transformation of 2^{23} data points. The Nyquist frequency of 5 GHz is divided into 2^{22} frequency bins of 1.19 kHz each. A rectangular window was applied. This frequency resolution is more than is needed for spectral information, but it was chosen to reduce the noise floor [9]. The noise floor in dBm depends on $\log(N/2)$ (N: number of FFT data points). By using 2^{23} samples it was found to be

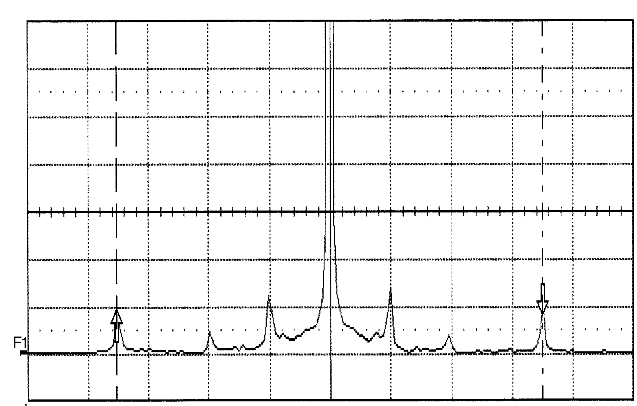

Fig. 7. Screen shot of the magnitude spectrum of a directly detected cw EPR time trace of γ-irradiated calcium formate powder. Microwave frequency, 2.499 GHz; magnetic field, 89.0 mT; temperature 25 K; modulation frequency, 20 kHz; modulation amplitude, 2 mT. Horizontal resolution, 20 kHz/div; vertical resolution, 10 mV_{rms}/div.

−87 dBm for a single acquisition. With such a low noise floor, spurious signals originating from the oscilloscope (e.g., feed through from the reference clock and the harmonics) appear and could mask echo signals. In our case the spikes did not coincide with the EPR signal, since we were only interested in the small frequency range of 200 kHz centered at 2.5 GHz. The computation time was approximately 1 s. For comparison, a measurement with a spectrum analyzer (Agilent E4402B) using a frequency range of 200 kHz and a resolution bandwidth of 1 kHz showed a noise floor of −92 dBm. The time required to sweep the frequency range was 500 ms. The FFT delivers by far too much data, since just a fraction of the transformed data contains useful information. This situation is considerably improved using higher modulation frequencies.

4. Conclusions

For the first time we demonstrated that direct EPR detection is feasible in the mw frequency range. We illustrated this new way of detecting EPR signals by recording an FID and a two-pulse echo in the time domain, as well as by measuring an echo-detected EPR spectrum and a two-pulse ESEEM time trace. With the spectrometer used for these experiments, such measurements can be carried out up to 4 GHz, whereas the upper limit of the oscilloscope is 6 GHz.

The advantage to use an oscilloscope as front-end lies in its versatility. It is also an appropriate tool to control the signals to tune the spectrometer, whether in the time or, by using FFT, in the frequency domain. Together with a digitizing front-end, which cannot be surpassed by homebuilt designs, the built-in data manipulation capabilities of such an oscilloscope allows the experimenter to process data without transferring them to a host computer. Even custom functionality can be implemented on the oscilloscope platform (by writing for examples Mathlab scripts) to enhance data processing. The feasibility to record cw data would suggest to use the same detection instrumentation for both pulse and cw EPR. The strength is at the same time also its weakness. As an instrument designed to be used primarily by electronic engineers, significant processing power of the oscilloscope is used to quickly update the data on-screen. Repetition rates of 100–200 Hz can be achieved for acquisition of less than 1000 data points.

It is expected, that in the near future high-speed oscilloscopes with an analog bandwidth in the mw X-band frequency range (8–10 GHz) become available, highlighting the trend seen throughout instrumentation to digitize as close to the signal source as possible.

With direct EPR detection the signal from the spin system is, after suitable amplification, directly recorded without any conversion in between. This opens the vast field of digital signal processing of the EPR mw raw data, including extensive filtering, FFT, and in-phase and out-of-phase detection.

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