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Integration of a versatile bridge concept in a 34 GHz pulsed/CW EPR spectrometer

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ABSTRACT

We present a 34 GHz continuous wave (CW)/pulsed electron paramagnetic resonance (EPR) spectrometer capable of pulse-shaping that is based on a versatile microwave bridge design. The bridge radio frequency (RF)-in/RF-out design (500 MHz to 1 GHz input/output passband, 500 MHz instantaneous input/output bandwidth) creates a flexible platform with which to compare a variety of excitation and detection methods utilizing commercially available equipment external to the bridge. We use three sources of RF input to implement typical functions associated with CW and pulse EPR spectroscopic measurements. The bridge output is processed via high speed digitizer and an in-phase/quadrature (I/Q) demodulator for pulsed work or sent to a wideband, high dynamic range log detector for CW. Combining this bridge with additional commercial hardware and new acquisition and control electronics, we have designed and constructed an adaptable EPR spectrometer that builds upon previous work in the literature and is functionally comparable to other available systems.

1. Introduction

The past sesquidecade has witnessed widespread applicability of pulse electron paramagnetic resonance (EPR) spectroscopy techniques [1] throughout scientific disciplines, from its founding realm of physics to the fields of chemistry, materials science, biology and medicine. Commercialization of spectrometers at multiple operating frequencies, in combination with pulse sequences designed to manipulate and extract information from spin systems, has produced a mature field where formerly esoteric, but now routine experiments can investigate the molecular dynamics of paramagnetic species. A new generation of experiments, however, exquisitely capable of manipulating spin systems with heretofore unrivaled excitation bandwidths, has been made possible by microwave pulse shaping technologies (for a recent review of pulse shaping in EPR spectroscopy, see Spindler et al. [2]). Arbitrary waveform generators (AWGs) equipped with nanosecond timing resolution, built onto existing commercial [3,4] or custom-built spectrometers [5–10], have been used to demonstrate that pulse shaping in EPR spectroscopy presents several advantages over traditional experiments (i.e., those restricted to rectangular-like pulses).

Shaped microwave pulses, in which the carrier's phase, frequency or amplitude are arbitrarily modulated, and related instrumental requirements have recently found applications in several well-known EPR spectroscopy experiments. The double electron-electron resonance (DEER) experiment, for example, has benefitted from shaped pulses as demonstrated from increased modulation depths by pumping at larger, more selective bandwidths [11,12]. The original four-pulse DEER sequence [13] itself has been newly modified for the inclusion of Carr-Purcell pulse trains [6,14–16], for pre-polarization of high-spin systems [17] and also for the use of an entirely new dipolar pathway in the experiment [18]. Optimal control theory has been employed in Fourier Transform-EPR to account for the spectrometer response function [3]. Finally, three-dimensional experiments, using ultra-wideband pulses to excite large hyperfine splittings, also have been demonstrated [19]. Most of these experiments were performed at either X-band (approximately 9.5 GHz) or Q-band[1] (34 GHz in the EPR community) operational frequencies.

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[1] Q band is not standardized, but common usage refers to a range of 33–50 GHz. The EPR community generally refers to Q band as approximately 34 GHz.

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The Q-band frequency is uniquely advantageous for measurements using the nitroxide radical, a common spin label/probe [20] used to investigate biomolecule dynamics in conjunction with EPR spectroscopy. In this frequency band, neither the Zeeman interaction nor the hyperfine interaction outright dominates the nitroxide spectrum so that an intermediate regime exists [21]. High-field EPR spectroscopy (frequencies at or above 95 GHz (W-band)) requires careful data analysis due to orientation selection effects, whereas at lower frequencies (X-band or lower) the spectrum narrows considerably, to the point of negligible g--anisotropy, so that care must be taken to avoid band overlap in dual-frequency experiments (e.g. DEER), necessitating a compromise in excitation bandwidths to collect spectra free from artifacts. For multi-frequency microwave experiments targeted towards elucidating hyperfine couplings (e.g. electron double resonance (ELDOR)-detected nuclear magnetic resonance (NMR)), the increase in the nuclear Zeeman frequency at Q-band, relative to X-band, aids in shifting signals away from the central hole of the spectrum [22,23]. As a final example, pulsed EPR techniques used to detect low frequency hyperfine couplings, namely electron spin echo envelope modulation (ESEEM) and hyperfine sublevel correlation spectroscopy (HYSCORE), suffer from a reduction in modulation depths at higher frequencies, and the necessity of larger B_1 fields to excite forbidden transitions, but an advantage may be obtained through resolution of closely spaced multi-nuclear peaks. Additionally, in certain situations, the 'cancellation limit' is achieved at Q-band [24,25], whereby maximum modulation depth is achieved. As such, Q-band offers several advantages over both X- and W-bands, and presents a desirable middle-ground to develop pulse shaping capabilities.

The goal of the work presented here was to create a fully-functional, combined pulsed/continuous wave EPR spectrometer intended for routine use in the National Institute of Standards & Technology's (NIST) Center for Nanoscale Science & Technology (CNST) user facility that integrates pulse shaping and operates at 34 GHz (Ka-band, which encompasses 26.5–40 GHz per IEEE definitions [26]). Herein, we report a versatile design for a high-power 34 GHz spectrometer built using a custom commercial pulse/CW bridge architecture and outfitted with additional electronic components. The NIST spectrometer uses a commercial resonator designed for CW and pulsed experiments, with a relatively large active volume (3 mm outer diameter tubes) for sample access. Practical considerations, including the spectrometer design and performance, are presented and illustrate the feasibility and performance of the spectrometer system built with this approach.

2. Instrument design

Fig. 1 shows the basic block diagram of our spectrometer system, with components used for CW (blue), pulsed mode (red), and both modes (purple). The component list is provided in Table 1.[2] For clarity, the block diagram specifically omits microwave switches (Tx Mute and Rx Mute) and bandpass filters in the up/down conversion stages in the bridge. Additional details on the bridge layout and architecture are in Supporting Information (Fig. S6).

The highlight of our system is the versatile bridge design (Fig. S6) loosely based on modern radar bridges that was proposed and built by Smiths Interconnect (formerly Millitech), expert in microwave engineering, under contract to the US Government. Adoption of this bridge layout impacted our overall instrument architecture and guided our procurement of the external components required to create a fully-functioning EPR spectrometer system. Additional NIST-built electronics completed the system; details of select function modules of the hardware are provided in SI. The most notable consequence of the bridge design is that we use three separate external sources of radiofrequency (RF) excitation, a voltage-controlled oscillator (VCO), an RF generator, and an AWG, to carry out resonator tuning (VCO), CW (RF generator) and pulsed mode (AWG) operation. The output frequency of the bridge ranges from 33.2 GHz to 35.3 GHz with an instantaneous bandwidth of 500 MHz. When the resonator bandwidth exceeds 500 MHz, or when an AWG is used to pre-distort pulses to compensate for limited resonator bandwidth, the 500 MHz bandwidth of the bridge can be limiting. The actual bridge operating frequency is determined by the sum of the bridge RF input frequency (500 MHz to 1 GHz), a first-stage upconverter local oscillator (LO) fixed at 3.5 GHz, and the second, programmable upconverter synthesizer frequency settable over a 29.2–30.8 GHz range in 20 MHz steps. A careful accounting of these numbers verifies the stated 33.2–35.3 GHz operating range of the bridge: 500 MHz + 3.5 GHz + 29.2 GHz = 33.2 GHz; 1 GHz + 3.5 GHz + 30.8 GHz = 35.3 GHz. There are three excitation paths available within the bridge: low power CW, pulse mode with an internal 10 W solid state power amplifier (SSPA), and pulse mode using an external 150 W traveling wave tube (TWT) amplifier. The TWT amplifier was built and tested to our specifications to have WR-28 waveguide in/out along with pre-shipment testing over our operating range of 33.2 –35.2 GHz Motorized waveguide switches inside the bridge direct the transmit path to the software-selected amplifier. The bridge has waveguide connections allowing use of any reflection-based resonator either home-built or from commercial suppliers. The receive path gain (typically 31.25 dB) in the bridge is frequency-dependent and varies from 29 dB to 34 dB over the usable frequency range. Addition of the 150 W TWT amplifier necessitated use of a robust protection switch [27], with a peak power rating of 200 W, to protect the low noise amplifier (LNA) in the receive path. The RF switch isolation was specified at 65 dB over the operating band; we measured 82 dB at 34.25 GHz. The pulsed and CW modes are distinguished principally by the excitation source and detection method used. A voltage-controlled oscillator (VCO) sweeps the frequency over a maximum range of 500 MHz for tuning to the resonator's resonant frequency, resulting in the intuitive power vs frequency scan displayed by the control software. This traditional tuning method was chosen for its simplicity although it has been demonstrated that an AWG chirp pulse (i.e. a pulse solely modulated using a linear frequency sweep) response could be used for this function [8]. The resonator's calculated resonant frequency is marked in software, and then measured using a frequency counter in the transmit (Tx) path of the bridge. Software then calculates the frequency setting for the bridge synthesizer and RF generator for CW operation and, in pulse mode, the AWG.

The main benefit of the NIST spectrometer is that the bridge is a commercial transceiver with IF in/out in the 0.5 –1 GHz range, which allows for customization and experimentation with the excitation/detection scheme. It permits a wide-variety of user-defined equipment to generate excitation signals (VCO, RF Generator, commercial AWG) and process the bridge output RF signal (detectors, demodulators, digitizers) without change to the microwave bridge. As an example, we performed an exercise to detect a Hahn echo of coal using a CW RF generator at the bridge input and formed rectangular-shaped pulses using a microwave switch in the bridge (Tx Mute, Fig. S6), which allowed us to use our bridge like more conventional bridges that employ pulse-switches to generate microwave pulses. The echo was detected by attenuating and phase shifting the RF Generator output to provide the demodulator LO signal. After we had all parts on hand, the entire experiment

[2] Certain commercial equipment, instruments, or materials are identified in this paper to specify the experimental procedure adequately. Such identification is not intended to imply recommendation or endorsement by the National Institute of Standards and Technology, nor is it intended to imply that the materials or equipment identified are necessarily the best available for the purpose.