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Arbitrary waveform modulated pulse EPR at 200 GHz

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ABSTRACT

We report here on the implementation of arbitrary waveform generation (AWG) capabilities at ~200 GHz into an Electron Paramagnetic Resonance (EPR) and Dynamic Nuclear Polarization (DNP) instrument platform operating at 7 T. This is achieved with the integration of a 1 GHz, 2 channel, digital to analog converter (DAC) board that enables the generation of coherent arbitrary waveforms at K_u-band frequencies with 1 ns resolution into an existing architecture of a solid state amplifier multiplier chain (AMC). This allows for the generation of arbitrary phase- and amplitude-modulated waveforms at 200 GHz with >150 mW power. We find that the non-linearity of the AMC poses significant difficulties in generating amplitude-modulated pulses at 200 GHz. We demonstrate that in the power-limited regime of $\omega_1 < 1$ MHz phase-modulated pulses were sufficient to achieve significant improvements in broadband (>10 MHz) spin manipulation in incoherent (inversion), as well as coherent (echo formation) experiments. Highlights include the improvement by one order of magnitude in inversion bandwidth compared to that of conventional rectangular pulses, as well as a factor of two in improvement in the refocused echo intensity at 200 GHz.

1. Introduction

High field Electron Paramagnetic Resonance (EPR) is an established technique that has provided important insights in many material and biological applications. The use of advanced pulsed and multi-dimensional EPR techniques at high magnetic fields, despite its obvious prospects, is hampered by the limited available microwave power at frequencies above W-band (>100 GHz) where high-power amplifiers >150 mW are not available, or are prohibitively expensive. The limited microwave power available for high-field EPR results in low nutation frequency ω_1 values of at most 4.2 MHz at 180 GHz and 2.1 MHz at 275 GHz, even when using an efficient T_{011} single mode resonator [1,2]. This hampers the feasibility or quality of important pulsed EPR experiments, including double electron-electron resonance (DEER) at high fields. The low ω_1 available at high field/frequency of a few MHz is in stark contrast to the 70 MHz ω_1 routinely achieved at X-band frequencies where DEER and other pulsed EPR experiments are routinely performed.

EPR experiments are typically limited by the available pulse bandwidth, hence the push for higher power and shorter pulses. Amplitude and phase modulated microwave pulses, generated by an arbitrary waveform generator (AWG), have proven a viable solution to the limitations in the available pulse bandwidth. AWG-generated waveform-modulated pulses allow for high level of control over spin manipulations which results in a dramatically improved pulse performance at a given microwave power. Owing to such capabilities, AWG pulses have been successfully applied for decades in nuclear magnetic resonance (NMR) [3–5], and have become integral to virtually all modern NMR spectroscopy and imaging experiments. In contrast, only recent advances in high speed electronics permitted the implementation of AWGs in pulsed EPR experiments [6–9]. There are numerous recent applications detailing the use of AWGs in pulsed EPR experiments at conventional, X-band (~9.5 GHz) and Q-band (~35 GHz), frequencies that showcase the gains afforded by arbitrary amplitude and phase modulation of microwave pulses [7,9,6,10–13]. However, AWG-controlled pulsed EPR at higher frequencies have not been demonstrated to date.

The application of AWGs to pulsed EPR spectroscopy is expected to have an even greater impact at higher magnetic fields. The rational is twofold: (1) the available microwave power (50–200 mW) and thus the pulse bandwidth (~1 MHz) is significantly less compared to lower microwave frequencies and (2) the EPR spectral width is typically much wider due to the increased g-factor resolution. For instance the spectral width of a simple

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nitroxide radical is ~1 GHz at 7 T and spans a few GHz or more for common transition metal ions. This discrepancy between the typical pulse excitation bandwidth (~1 MHz) and the width of the EPR spectra (~few GHz) significantly limits the sensitivity of high field pulse EPR experiments, as well as presents an opportunity for significant sensitivity gains by AWG implementation. The cost of overcoming the pulse bandwidth limitation without increasing microwave power is an increased pulse length. This poses a limitation on the shaped-pulse utility for systems with short relaxation times (compared to the required pulse length) or strong electron spin-spin couplings (compared to the inverse pulse length), and requires a compromise between the length of the best performing shaped pulse and the relaxation time or the electron spin-spin coupling strength.

To this end we integrate a homebuilt AWG system with 1 GHz bandwidth into a 200 GHz microwave bridge with dual EPR and Dynamic Nuclear Polarization (DNP) capabilities for the purpose of confronting the pulse bandwidth limitation [14]. We implement the AWG into the 12 GHz pulse forming network of the microwave bridge. The AWG features two digital to analog converter (DAC) boards that drive the I and Q channels of an IQ mixer. The IQ mixer mixes the DAC outputs with the 12 GHz microwave. The output microwave pulses are then up-converted to 200 GHz by an amplifier multiplier chain (AMC). This design achieves amplitude and phase modulation at 200 GHz, similar to other systems designed for rotational spectroscopy at sub-THz frequencies [15,16].

In the following we describe the integration of the AWG unit into a 200 GHz solid-state source powered EPR/DNP spectrometer platform. We showcase broadband manipulation of up to 20 MHz bandwidth of the EPR spectrum at 200 GHz using phase-modulated chirp pulses that largely exceeds the bandwidth possible with standard rectangular pulses at the available microwave power. Using phase modulated pulses we demonstrate broadband inversion and coherent echo formation on electron spins in a BDPA/poly styrene mixture, and in the P1 centers of a ^{13}C enriched diamond sample. Finally, we present the performance and limitations of the 200 GHz IQ mixer and AMC-based microwave bridge for generating both amplitude and phase modulated pulses.

2. Results

2.1. Hardware setup and design

The conventional approach for implementing arbitrary phase and amplitude modulated pulses at X-band frequencies is to mix the arbitrary waveform with a carrier frequency at (or close to) the final operating X-band frequency of around 9.5 GHz using an IQ mixer [7,8]. The drop in power due to insertion loss of the 12 GHz IQ mixer (~7–9 dB) is compensated for by further amplification after mixing, culminating in the final high-power amplification stage of the ~1 kW TWT amplifier. However, the absence of a microwave amplifier operational at high frequencies (> ~100 GHz) prevents us from replicating this approach at 200 GHz, where the power drop due to the insertion loss of a ~200 GHz mixer cannot be compensated for by subsequent amplification. Instead, we integrate the AWG into the spectrometer at the ~12 GHz base frequency, before the AMC. To achieve this, an additional channel that includes the IQ mixer for mixing the AWG waveform with the 12 GHz base signal was added to the pulse-forming unit of our spectrometer. The schematics of the pulse-forming unit is presented in Fig. 1, with the IQ mixer used for AWG integration shown on top right of the figure.

The overall design of the 200 GHz quasi optics (QO) bridge for dual EPR and DNP operation was described in detail in a recent publication [14]. The system utilizes three digitally programmable, continuous wave (CW) ~12 GHz synthesizers to operate (i) the main microwave transmitter channel source for pulsed and CW EPR and (ii) the second transmitter channel for pump-probe Electron Double – Resonance (ELDOR) experiments, as well as (iii) to generate the LO (local oscillator) reference for the 200 GHz sub-band mixer in the heterodyne receiver system. The microwave output of the main ~12 GHz CW transmitter source (i) is sliced, and if desired mixed, with coherent AWG waveforms produced with a fast (1 GHz) DAC board for phase and amplitude modulation. The generation of this ~12 GHz AWG waveform occurs in the pulse-forming unit before it is sent to the ×16 amplifier multiplier chain (AMC) chain to produce the pulsed and shaped output at 200 GHz. The induction mode-selected 200 GHz EPR signal is routed via the QO bridge to the 200 GHz sub-band mixer, where it is down-converted to an intermediate frequency of 3 GHz. The 3 GHz signal is amplified using a 46 dB gain low-noise amplifier, before being down converted to a DC signal by mixing with a coherent 3 GHz signal from a reference arm, and then digitized for detection.

2.2. Pulse forming unit

The pulse forming unit operating at ~12 GHz frequency consists of three main modules (Fig. 1). In the AWG module (highlighted in green in Fig. 1) the CW signal from the transmitter source is mixed, using the IQ mixer (IQ0618LXP by Marki microwave), with the AWG waveform. The digital to analog converter (DAC) board used for arbitrary waveform generation in this work consists of an Ethernet accessible FPGA board (Altera Stratix II by Altera) that drives two independent DAC boards with 14-bit resolution and 1 GHz bandwidth that form two analog output channels that are used to produce the real and imaginary DC – 1 GHz waveforms. In addition, there are three digital ECL (emitter-coupled logic) channels synchronized with the analog ones, by virtue of operating at the same high frequency clock, which can be used to trigger/control other devices, such as microwave switches and digitizers. The AWG can be set to generate the programmed waveform, either immediately after finishing the data transfer or upon receiving an external trigger. This DAC board was previously used in a digital X-band EPR spectrometer constructed in our lab [8] and was designed by the Martinis group at UCSB [17]. The shaped ~12 GHz waveform output after the IQ mixer passes through a low pass filter (FLP-1740 by Marki microwave), mainly to suppress the leakage signal at the 2nd harmonic of the carrier frequency (~24 GHz). It is important to ensure careful calibration of the power level of the shaped pulses such that the input power of the full-amplitude shaped pulse is sufficient to operate the AMC at saturation while the leakage at carrier and image frequencies is below the power threshold for engaging the AMC. Subsequently the shaped signal is routed into the phase cycling unit (highlighted in blue in Fig. 1). The manually selectable bypass channel, selected by a manual SP2T switch, (SM-2min by RLC electronics) in the AWG module is installed to carry out experiments that do not require AWG operation with the same transmitter source as used for AWG, and to maintain backward compatibility with existing pulse sequences and operating procedures. The bypassed signal is routed into the same phase cycling module as the shaped signal.

The signal generated from the AWG module is routed via a fast <10 ns SP2T (F9120AH by General Microwave) switch to either a bypass channel (0° phase shift) or through a voltage controlled phase shifter hardware that is set nominally for an 11.25° phase shift at the ~12 GHz operating frequency, thus resulting in a 180° degree phase shift at ~200 GHz (following x16 multiplication in the AMC). While phase cycling can of course be achieved without relying on an analog phase shifter unit by digitally reprogramming the waveform produced by the AWG, it is beneficial to retain the hardware-based phase cycling capability, especially when