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Frequency-agile gyrotron for electron decoupling and pulsed dynamic nuclear polarization

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ABSTRACT

We describe a frequency-agile gyrotron which can generate frequency-chirped microwave pulses. An arbitrary waveform generator (AWG) within the NMR spectrometer controls the microwave frequency, enabling synchronized pulsed control of both electron and nuclear spins. We demonstrate that the acceleration of emitted electrons, and thus the microwave frequency, can be quickly changed by varying the anode voltage. This strategy results in much faster frequency response than can be achieved by changing the potential of the electron emitter, and does not require a custom triode electron gun. The gyrotron frequency can be swept with a rate of 20 MHz/μs over a 670 MHz bandwidth in a static magnetic field. We have already implemented time-domain electron decoupling with dynamic nuclear polarization (DNP) magic angle spinning (MAS) with this device. In this contribution, we show frequency-swept DNP enhancement profiles recorded without changing the NMR magnet or probe. The profile of endofullerenes exhibits a DNP profile with a <10 MHz linewidth, indicating that the device also has sufficient frequency stability, and therefore phase stability, to implement pulsed DNP mechanisms such as the frequency-swept solid effect. We describe schematics of the mechanical and vacuum construction of the device which includes a novel flanged sapphire window assembly. Finally, we discuss how commercially available continuous-wave gyrotrons can potentially be converted into similar frequency-agile high-power microwave sources.

1. Introduction

Dynamic nuclear polarization (DNP) is a powerful tool to increase nuclear magnetic resonance (NMR) sensitivity in which the high polarization of electron spins is transferred to nuclear spins via microwave irradiation that fulfills matching conditions [1–3]. High microwave power levels (>5 W) are required to generate significant DNP enhancements for magic angle spinning (MAS) samples at temperatures >80 K at high magnetic fields (>5 T) [4–6]. Gyrotrons, now widely commercially available, provide the requisite microwave power levels, yet can rarely be tuned quickly or pulsed [7]. Such continuous-wave (CW) gyrotrons permit only CW DNP mechanisms. Similar to the development of NMR and EPR spectroscopy from continuous wave to pulsed regimes, pulsed DNP will provide many advantages over CW approaches [8–12]. Although CW DNP mechanisms yield large signal enhancements for model systems at lower magnetic fields, their performance is sub-optimal with higher magnetic fields, higher temperatures, and more complex samples [13,14]. Pulsed DNP transfers have considerable promise to improve DNP performance where CW mechanisms under-perform [15–18]. Chirped microwave pulses have also recently enabled the first electron decoupling experiments, which attenuate hyperfine interactions and alleviate detrimental paramagnetic relaxation effects [8].

Possible microwave sources which can produce high power levels required for pulsed DNP and electron decoupling with MAS include free electron lasers, slow-wave traveling wave tubes

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(TWTs), gyromonotrons, gyro-TWTs, and gyro-backward wave oscillators (BWOs) [19–24]. Free electron lasers are unrivaled in their tuning range and can also be frequency and phase stable, yet occupy considerable volume making their broad applicability in NMR laboratories across the world limited [25]. Slow-wave TWTs are very promising sources for EPR and DNP below 300 GHz, yet their maximum power levels are lower than gyrotrons, and the inverse scaling of the interaction cavity dimensions with higher frequencies presents considerable micro-fabrication challenges [26,27]. Fast-wave gyro-TWTs have successfully been developed at 140 and 250 GHz, yet their broad dissemination into the ranks of NMR spectroscopists has been hindered by the cost associated with the requisite super-conducting magnets and electron beam power supplies [20,28–30]. We have chosen to instead focus on the development of frequency agile gyrotrons, which fall under the category of gyro-BWOs. Gyrotrons have numerous advantages including higher-power levels (up to 1 MW, 100% duty cycle) and possible widespread dissemination of technology through upgrades of existing and available MAS DNP spectrometers.

Gyrotrons are especially appealing due to the experimental feasibility of implementing chirped pulses for time-domain DNP and electron decoupling, rather than hard pulses which are more commonly employed in NMR spectroscopy of spin ½ nuclei. For instance, we previously calculated that 13 MW of microwave power are required to generate sufficient electron Rabi frequency (ω_{1e}) for a hard pulse to excite the 800 MHz nitroxide lineshape at 7 T, given current widely available MAS DNP probes [31]. Furthermore, the wavelength of high-frequency microwaves is smaller than the sample geometries currently employed in MAS DNP experiments leading to severe inhomogeneity of the electron Rabi frequency, and would lead to a concomitant poor performance of hard pulses. Notably, frequency chirped pulses such as adiabatic rapid passages remain effective with a high degree of ω_{1e} inhomogeneity [9,10]. Microwave resonance structures and focusing strategies (i.e. TE_{01} resonators and Teflon lenses) are being developed by our group and others, and could provide both uniform and intense ω_{1e} fields required for pulsed DNP. However, we note that their applicability will most likely be restricted to sample-limited applications, as larger samples currently provide higher sensitivity in MAS DNP experiments. Gyrotrons which exhibit fast frequency tuning, or pulsing, include those described by Idehara et al., Alberti et al., and the device we present herein [32–34]. In this paper we describe the mechanical, vacuum, and electrical design of a frequency-agile gyrotron which has previously been employed in pulsed electron decoupling experiments [8]. We also measure frequency swept DNP enhancement profiles of various polarizing agents using the gyrotron. Importantly, the DNP enhancement profiles of an endofullerene, N@C_{60}, indicate that the gyrotron has the frequency and phase stability required to perform time domain DNP transfers such as the integrated solid effect. Finally, we conclude with a discussion of how currently available spectrometers could possibly be upgraded to provide similar frequency agility and a concomitant acceleration of the field of MAS DNP into the pulsed regime.

2. Design

2.1. Overview

The gyrotron is shown within the context of the DNP-MAS NMR spectrometer (Fig. 1), of which many components were custom-built such as the NMR probe, cryostat, heat-exchanger, and corrugated waveguide transmission line. Corrugated transmission line transmits microwave power from the gyrotron to the NMR probe. A cryostat insulates the NMR superconducting magnet and facilitates cryogenic MAS <6 K [35,36]. The DNP NMR probe includes a four-channel transmission line circuit resonating at 300.184 MHz (^{1}H), 75.495 MHz (^{13}C), 30.427 MHz (^{15}N), and 121.516 MHz (^{31}P) [37,38]. A Tecmag Redstone spectrometer (Tecmag Inc., Houston TX), drives each channel and includes an arbitrary waveform generator (AWG) to generate shaped microwave pulses.

The potential waveform from the AWG is amplified 1000:1 by a low capacitance, high voltage Trek 5/80-L linear amplifier (Trek, Lockport, NY). The amplifier output is connected to the gyrotron anode, as shown in Fig. 2c and 3a. An electron beam is emitted from a magnetron injection gun (MIG), and compressed by the magnetic field gradient into the interaction cavity. A portion of the electron beam power is deposited into the TE_{52q} cylindrical resonator. Microwaves are directed out of the gyrotron by the internal mode converter while the electron beam continues up through the gyrotron body. Finally, the remaining electron beam energy is absorbed at the grounded collector.

2.2. Electrical isolation and frequency agility

The amplifier driven by the AWG is connected to the anode by a low-capacitance wire (pseudo-colored in yellow for clarity, Fig. 3a). This high-voltage wire is isolated to reduce stray circuit capacitance. The cathode, which emits the electron beam, is connected to a separate high-voltage, high-power (4 kW) supply (Fig. 2c and 3b) (Spellman, Hauppage, NY). Note that the capacitance of the cathode power supply is very large to maintain a stable potential, yet prevents the generation of quickly-swept microwave waveforms via control of only the cathode potential. The anode amplifier has a low power and voltage requirement which permits a fast slew rate of 1000 V/μs due to a low internal capacitance. Therefore the potential of the anode can be changed quickly and results in microwave output frequency agility of up to 20 MHz/μs. This allows for frequency jumps from the DNP matching condition to the electron spin resonance for electron decoupling [8,31], and should permit coherent electron spin manipulation with adiabatic chirped pulses.

Ceramic breaks allow for electrical isolation between different sections of the gyrotron (Fig. 2c). Vacuum ion pumps must be grounded to function properly and are electrically isolated from the collector and anode. The collector is also grounded so that the electron beam colliding with its surface does not accrue a negative charge. Note that the collector must be kept electrically separated from the anode to permit fast microwave frequency tuning.

The microwave output frequency is partially determined by the acceleration potential of electron emission. The electron beam is generated by a barium impregnated tungsten ring within the MIG and carries 190 mA of current. The potential between the anode and cathode is maintained between 9 and 17 kV. This high potential accelerates electrons to relativistic speeds. The associated increase in electron mass results in a lower microwave frequency according to the cyclotron frequency equation:

$$\Omega = \frac{eB_0}{m} \tag{1}$$

where Ω is the cyclotron resonance frequency, e is the charge of the electron, B_0 is the magnetic field at the interaction cavity, and m is the relativistic electron mass [24]. Within the interaction cavity the electron beam deposits power into a cylindrical microwave mode. This TE_{52q} mode supports a continuous tuning bandwidth over a frequency range of 197.2–198.4 GHz, which can be controlled with 1 MHz precision by adjusting the potential across the MIG. Here, the q subscript refers to axial modes present along the long axis of the cylindrical resonator (Fig. 4a) [7,22].