Time Domain Measurement of Electron Spin Relaxation at High Fields and Dynamic Nuclear Polarization at Sub-Millimeter Wavelengths

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Abstract **We describe a 395 GHz pulsed electron paramagnetic resonance (EPR) setup, and initial results of relaxation measurements and cw EPR at these frequencies in samples used for liquid- and solid-state nuclear magnetic resonance enhanced by dynamic nuclear polarization (DNP). Depending on the amount of spin – orbit coupling, the spin lattice relaxation becomes significantly faster at higher fields and frequencies, which has consequences for some DNP applications at high fields and frequencies. We will discuss the requirements for (sub)millimeter-wave sources and components for DNP and pulsed EPR at even higher frequencies and fields, as even higher magnetic fields will become available in the near future.**

Index Terms**—Submillimeter wave propagation, gyrotrons, submillimeter wave technology, Nuclear magnetic resonance, Paramagnetic resonance.**

I. Introduction

Biological Magnetic Resonance applications typically require high sensitivities and high spectral resolution, especially in case it is necessary not to stray too much from physiological conditions. For nuclear magnetic resonance (NMR), an increase of the magnetic field and the operating frequency can partly achieve both these goals. These are limited by the availability of superconducting magnets. The critical field and mechanical strain properties of superconducting materials however pose a limit on the magnetic fields that can be generated. Even at the currently available highest superconducting magnetic fields of 23 Tesla, only a tiny fraction ($<10^{-4}$) of the nuclear spins participate in the signal. One way to increase the NMR signal is by increasing the nuclear spin polarization with the help of electron spins. The much larger spin polarization of the electrons can be transferred to the nuclear spins through Dynamic Nuclear Polarization (DNP), which can achieve signal enhancements by orders of magnitude[1]. This requires the excitation of magnetic dipole transitions in the electron spin system, or the combined nuclear-electron spin system, which at current NMR fields are in the millimeter and submillimeter range (250-800 GHz). While the NMR operating frequencies are limited by the availability of superconducting magnets at high magnetic fields, electron spin resonance (ESR) applications are limited in frequency by the availability of suitable microwave sources.

In this paper we will show experimental set-up and techniques and results of electron spin relaxation measurements by pulsed EPR in the (sub)millimeter range at frequencies of 336 GHz and 395 GHz using solid state sources, as well as the experimental setup for DNP in the solid state and in liquids using a high-power gyrotron source. These frequencies are considerably higher than are commercially available EPR frequencies. Also the set-up for the in-situ EPR in the DNP set-up will be described. Within that context we discuss the requirements for sources at even higher frequencies that are necessary to address important outstanding questions in biology with magnetic resonance. With the upcoming introduction of high T_c superconductors for superconducting magnets[2][3], the maximum operating frequency of high-resolution NMR will likely increase to close to 1500 MHz within the next 5 years[4]. This will create an increasing demand for high power sources and technologies at frequencies up to 1 THz (300 μm) for DNP applications.

II. Experimental Setup

All the applications that will be described here employ quasi-optical 'bridges' in combination with oversized circular corrugated waveguides for low loss transport of the (sub)millimeter radiation from the source to the sample and to the detector. A quasi optical bridge can be configured to be largely frequency independent, and allow the incorporation of low-loss passive

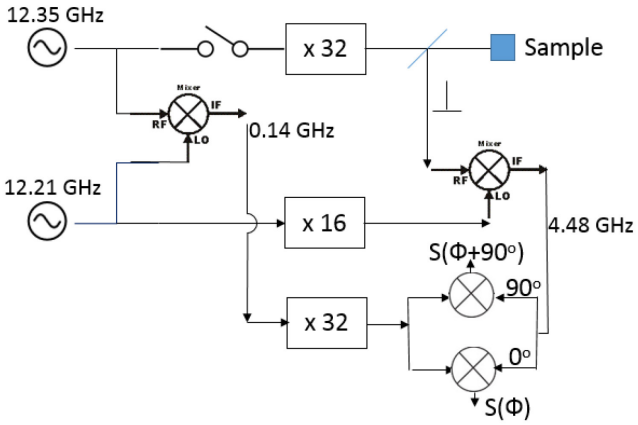

Fig. 1. Schematic setup for pulsed EPR at 395 GHz, with quadrature detection. S(Φ) and S(Φ+90°) are the final signals that allow for simultaneous detection of absorptive and dispersive components in a digital oscilloscope.

elements. It also can provide a convenient way of taking advantage of, and to manipulate the microwave polarization for optical excitation and detection[5][6].

The quasi optical bridge is used in combination with oversized corrugated waveguides witin the space-constrained environment of the high-field magnets. The quasi-optical bridges and elements (flat and off-axis elliptical mirrors, free standing wire grids, Faraday rotators, corrugated horns) have been fabricated by Thomas Keating Ltd.

A. Pulsed EPR

The super-heterodyne schematic setup for pulsed EPR at 395 GHz is shown in Fig 1. The source is a solid state multiplication chain delivering 20 mW over a 390-400 GHz band, with the detection system primary element a 2nd harmonic mixer with its 195 GHz local oscillator (LO) generated by a similar multiplication chain (both Virginia Diodes Inc.). The source is multiplied up (x32) from a 12.35 GHz synthesizer. A PIN diode switch at 12.35 GHz provides the pulsed capability for pulsed EPR. The 20 mW pulses pass through the quasi-optical (QO) table which provides for attenuation, isolation, and polarization control. The linearly polarized millimeter-wave pulses excite the electron spins in the sample, which is either contained in a Fabry-Perot type resonator for small samples or without resonator. With the microwaves propagating along the field direction, the coherent response of the spins is circularly polarized, and can be detected in the polarization perpendicular to the incident millimeter waves. This signal is mixed down to an IF frequency in the 4-5 GHz range with the help of a second multiplier chain and second-harmonic mixer. A phase-stable reference is generated from the 12 GHz synthesizer with the appropriate delays, allowing simultaneous measurement of absorption and dispersion.

In pulsed EPR, the pW-nW response from the spin system is measured directly after excitation with relatively intense pulses from the millimeter-wave source. In order to protect the detector from damage and saturation, the 25-40 dB isolation from the incident pulses is that is achieved by using a linear polarization for the excitation pulses, and detecting in the perpendicular polarization is a crucial for successful implementation in the absence of low-loss high-frequency switches.

In some cases like liquids at room temperature the electron spin relaxation times are too fast to measure with low power sources. For these we use a high power quasi-optical spectrometer operating at 95 GHz [7].

B. DNP

For the enhancement of the NMR signal in either the solid state (typically large bio-molecules in a frozen solution) or in the liquid state (small organic molecules), typically high powers are required. For solid state (magic angle spinning) NMR, forbidden electron-nuclear spin transitions need to be excited, while for liquid state NMR, the excitation power needs to compete with fast spin relaxation at ambient temperatures. The microwave frequencies needed are determined by the NMR magnetic field, and corresponds to 395 GHz for 600 MHz NMR. At the moment these powers are typically generated by gyrotrons, which can deliver 10-50W of power at these frequencies (Bruker Biospin). They are relatively noisy and free running sources, and not well suited for direct EPR measurements. Fig. 2 shows the quasi-optical bridge that conditions and transports the radiation from the gyrotron into the NMR sample space for the solid state magic-angle spinning DNP. The quasi-optical bridge allows for a variation of the power without changing any source settings, for the employment of shutters, and for the purification of the mode. It also allows to alternatively use the low power 395 source and detector combination that is also used for pulsed EPR, in order to perform in situ EPR needed to verify sample quality and resonant frequency.

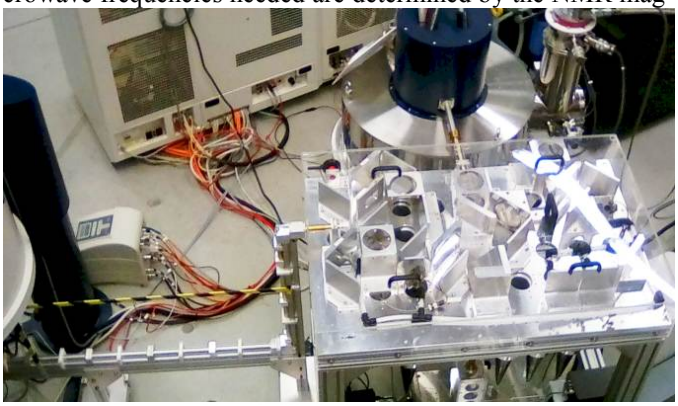

Fig. 2. Quasi-optical table for DNP, with the gyrotron source in the upper right and the NMR magnet on the left.

III. Results and Discussion

For the efficacy of the DNP process one of the important parameters is the electron spin relaxation time. In fact two relaxation times can be distinguished: the T_2 relaxation time is also referred to as the coherence time, or phase coherence time. It is a measure of the changes in the spin environment that change the resonance frequency of the individual spins in the system. In most cases related to DNP it does not have a strong frequency or field dependence, except when the temperature is low with respect to energy of the millimeter wave photon[8], which is currently of importance for dissolution DNP[9], but which will also become important for solid state DNP at higher frequencies. However here we focus on the T_1 relaxation time, which is the time with which the spin system returns to thermal equilibrium via energy exchange with its surroundings, and which is referred to as the spin lattice relaxation time.

At lower frequencies the spin lattice relaxation is typically dominated by two phonon processes, which have a strong temperature dependence, but a weak frequency dependence. At high frequencies, because of a larger phonon density of states

at the operating frequency, single phonon direct processes become more important. Experiments directly in the time domain at these high frequencies will help understand the frequency dependence of the DNP processes. As an example Fig. 3 shows some preliminary measurements of the T_1 relaxation times of Cr^{3+}, V^{2+}, and Mn^{2+} impurities in a single crystal of MgO at 240 and 336 GHz. All these impurities show a significant frequency dependence with the relaxation becoming faster by a factor of 2-4 over a large temperature range by increasing the frequency by a factor of 1.4. Similar effects have been observed in organic radicals that are used in many DNP experiments.

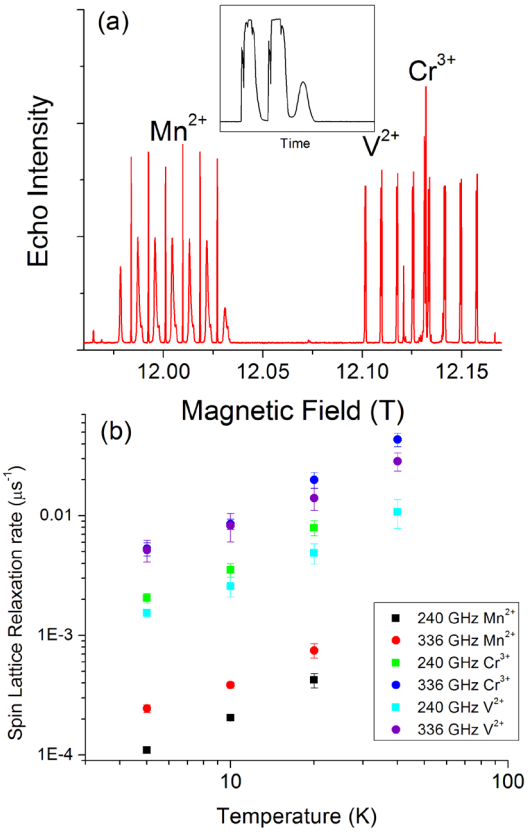

Fig. 3. (a) 336 GHz echo detected EPR spectrum of impurities in a MgO substrate at 20 K. The inset shows a 2-pulse Hahn echo sequence followed by the response from the sin system (echo). (b) Spin-lattice relaxation rates for impurities in MgO at 240 and 336 GHz.

IV. Future Requirements

Currently the highest NMR frequency where DNP is applied is 800 MHz, which corresponds to 527 GHz (570µm)[10]. The expected development of NMR to frequencies of the order of 1500 MHz requires reliable high power sources for DNP up to 1000 GHz. This will be somewhat mitigated by a reduction in sample size, so that less total power is needed for identical power density. For pulsed EPR, an additional requirement is phase stable sources. While there has been a lot of development of solid state sources, the power tends to go down fast above 400-500 GHz. For the spectroscopists the development of a high-frequency gyro amplifier, which would combine both high power and stability would also greatly increase the sensitivity for EPR.

It will also be increasingly important to avoid electric dipole absorption by water in air, and in the windows and sample-holder materials. However, because of the gain in the sensitivity and resolution of DNP and NMR at higher frequencies, the rewards in terms of knowledge of protein structure, function, and properties will enable targeted development of new medications and therapies.

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