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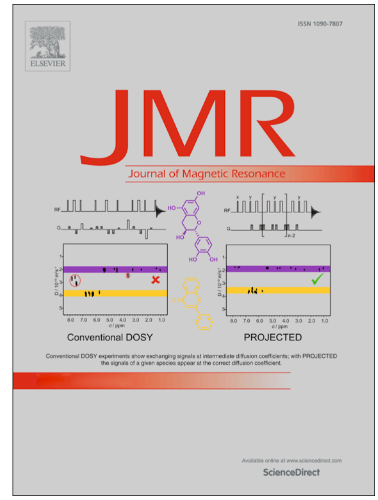


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# Multi-frequency rapid-scan HFEPR

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**Abstract**

Gaining access to electron spin dynamics at (sub-)THz frequencies is highly challenging. However, this information is highly relevant for the understanding and development of spin polarization agents in dynamic nuclear polarization methods and single-molecule magnets for quantum computation. Here we demonstrate the first rapid-scan EPR experiment in 200 GHz frequency region. A voltage controlled oscillator (VCO) generated fast sinusoidal frequency sweeps with scan rates up to $3 \times 10^5$ THz/s after the frequency multiplication, which is equal to $10^7$ T/s in field representation. Such high scan rates provide access to extremely short relaxation times $T_2 = (2\pi \times sweep\ rate)^{-0.5} \approx 1$ ns. The absence of a microwave cavity allowed us to perform multi-frequency experiments in the 170 – 250 GHz range. A further advantage of a cavity-less approach is the possibility to use vast sweeps, which in turn, allows the deconvolution using a linear sweep function. The deconvoluted spectra obtained with this method are identical to the slow-rate spectrum. We find spin-spin relaxation times of several nanoseconds for pure LiPc samples in this frequency range. These values cannot be obtained by means of conventional pulsed EPR methods.

*Keywords:* Rapid scan HFEPR, frequency domain, spin dynamics, THz frequencies

## 1. Introduction

The recent development of solid-state instrumentation for THz frequency range, namely microwave sources, allows performing broadband continuous wave (CW) EPR spectroscopy at very high fields and frequencies [1]. The implementation of HFEPR is very advantageous since it *(a)* increases the spectral resolution of measurements, (*b*) provides access to the high zero-field splitting energies, and (*c*) in principle may possess higher sensitivity (compared to X-or Q-band spectrometers), due to the Boltzmann distribution factor. Although CW HFEPR is a powerful method, which has already contributed to solving many scientific problems [2, 3, 4], it is not amenable to the investigation of spin dynamics, i.e., spin relaxation processes. However, relaxation processes play a very important role in such fields as dynamic nuclear polarization (DNP) [5, 6, 7], quantum computation [8, 9]. In general, one can extract the spin relaxation time $T_2$ from a CW spectrum if the following conditions are fulfilled:

- the resonance line is homogeneously broadened,
- the amplitude $A_{mod}$ and frequency $f_{mod}$ of the field modulation are small compared to the line width $\Delta H$: $A_{mod}$, $2\pi f_{mod}/\gamma \ll \Delta H$
- the sweep rate of the external magnetic field $H_0$ is much lower than the relaxation rates: $\left|\gamma \frac{dH_0}{dt}\right| \ll 1/(T_1 T_2)$
- the microwave power is low so that saturation does not occur: $\gamma^2 H_1^2 T_1 T_2 \ll 1$
- the time constant of the phase sensitive detection is short enough so as not to distort the line.

Only in this case, the EPR line is not affected by passage effects and the line width at half maximum $\Delta f$ is defined by the relaxation time: $\Delta f = (\pi T_2)^{-1}$ [10]. Unfortunately, it is rarely possible to fulfill all the conditions completely. For this reason, pulse methods have become the preferred technique to study the spin dynamics. Nowadays, a large number of pulse sequences exists, which make it possible to investigate in details the relaxation processes and mechanisms in different spin systems. However, pulse EPR requires high quality and thus very expensive microwave components. At THz frequencies, the sufficient power can be achieved only with (*a*) highly optimized spectrometers based on the solid-state sources (e.g., the Bruker ELEXYS II 263 GHz system) or (*b*) high power klystrons and gyrotrons (usually used in DNP-NMR systems). The essential shortcoming of these systems is a very narrow tuning range, usually less than 2 GHz. Consequently, a set of such systems is required to cover the whole millimeter and submillimeter ranges. An alternative method is rapid scan EPR [11, 12, 13]. In this method the frequency or more commonly, the magnetic field is swept at rates that are fast compared to the spin dynamics times. The fast sweep rate influences the line shape, creating ”wiggles” that allows determination of the spin dynamics rate.

Strictly speaking, the rapid-scan EPR is a CW technique since the microwave frequency or magnetic field is swept continuously over the resonance line. However, in contrast to the

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