

Rapid scan ESR: A versatile tool for the spin relaxation studies at (sub)THz frequencies

Cite as: Appl. Phys. Lett. **120**, 120502 (2022); doi: [10.1063/5.0083010](https://doi.org/10.1063/5.0083010)

Submitted: 21 December 2021 · Accepted: 24 February 2022 ·

Published Online: 23 March 2022



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Export Citation



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ABSTRACT

The development of pulse electron spin resonance (ESR) spectroscopy at microwave frequencies above 100 GHz is rather challenging and expensive due to the low output power of modern high-frequency solid state electronics. However, there is a number of scientific problems that require spin relaxation measurements at THz frequencies. The rapid scan ESR is an alternative technique that does not require high microwave power and still provides information on the spin relaxation times. The method takes advantage of fast sweeps of the excitation microwave frequency over the ESR line. When the frequency sweep reaches a sufficiently high rate, distinct oscillations (also called *wiggles*) appear in the ESR spectrum. These oscillations bear information about T_2 electron spin relaxation time, which can be extracted via fitting the rapid scan spectrum using the modified Bloch equations. In this Perspective Letter, we introduce the recent advances in this technique and discuss the future steps necessary to make the THz rapid scan ESR a convenient and easy to use tool.

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I. INTRODUCTION

Electron spin resonance (ESR) spectroscopy is an indispensable tool in a researcher's arsenal working in fields of materials science, chemistry, and biology. This technique provides valuable information about the electronic structure and bonding of paramagnetic species in molecules and solids.^{1,2} ESR is also used to monitor chemical reactions with free radical intermediates.³ Another important application of ESR had been found in structural biology: the dipolar interaction between spins located at different parts of a large molecule (naturally abundant or artificially introduced by spin labeling) allows one to measure the distance between these spins at the nanometer scale, e.g., to get information on the molecule's geometry and flexibility.^{4,5} The development of methods for pulse excitation had greatly improved the ESR spectroscopy in terms of sensitivity, control, manipulation of spins, amount of information obtainable, and simplification of recorded spectra due to the possibility to isolate different interactions.^{6–9} Moreover, pulse ESR is essential for electron spin dynamics studies through measuring the longitudinal T_1 and transverse T_2 relaxation times. This extraordinary advance became possible due to progress in microwave technology and high-speed signal acquisition. The efficient spin manipulation requires intense and short microwave pulses in order to flip the magnetization by 90° and 180° . For example,

the most commonly used commercial pulse ESR spectrometer (X-band frequency, ~ 9.5 GHz) uses amplifiers with up to 1 kW output power.

The last two decades in ESR spectroscopy are marked by increased interest in performing the measurements at (sub)THz microwave frequencies, i.e., above 95 GHz. The benefits of high frequencies are threefold: access to high energy transitions in systems with large zero-field splitting, increased spectral resolution owing to higher magnetic fields applied, and, in some cases, improved sensitivity. The majority of high-frequency ESR (HFESR) spectrometers generate the excitation microwaves by frequency multiplication of ~ 10 GHz input with the subsequent power amplification.¹⁰ This approach is particularly useful for broadband continuous wave, which does not demand high microwave power. However, for pulse applications, some tricks are required. First, the resonant cavities are used to effectively increase the microwave B_1 field at the sample position and to improve the overall sensitivity. The disadvantage of this approach is that the cavity operates only at one given frequency, and therefore, a set of different resonators is necessary if one desires multi-frequency studies.^{11–15} Additionally, specially shaped pulses generated by an arbitrary waveform generator can increase the excitation bandwidth and improve the efficiency of spin magnetization manipulation.^{16,17} Another possibility is to use high power microwave sources such as

backward wave oscillators, gyrotrons, orotrons, free-electron lasers, synchrotrons, far-infrared lasers, and klystrons.^{18,19} However, some of them are dedicated to large research infrastructures and require specially trained specialists. Moreover, these devices mostly operate in the continuous wave mode, and slicing the microwaves into short pulses with steep edges is a very challenging task. Finally, the tunability is rather narrow and is limited to a few GHz. All these restrictions lead to immensely large investments required for broad frequency pulse HFESR operation, making it a slowly emerging field.¹⁸

Among many scientific topics that can benefit from pulse HFESR, the dynamic nuclear polarization (DNP) clearly stands out. DNP is used for a substantial increase in the sensitivity in the nuclear magnetic resonance (NMR) and imaging (MRI) by transferring a much higher spin polarization of electrons to nuclear spins.²⁰ Usually, the source of electron spins is a molecule with one or more unpaired electrons, a so-called polarizing agent (PA), which is added to the sample-containing solution. DNP has already shown some remarkable results for ¹H-NMR with enhancement factors of 700 for a frozen solution²¹ and just under 100 for liquid samples at room temperature.^{22–24} Such prominent progress in DNP-NMR seems to be phenomenal since the method's development mostly follows the path of trial and error, especially in the part of PA design and synthesis. Depending on the exact transfer mechanism, PAs with different properties are required: monoradicals with a narrow ESR line best perform under the solid and Overhauser effects, whereas biradicals are suitable for the cross effect.²⁰ One of the factors governing the overall DNP enhancement is the saturation factor, which reflects how easily the ESR transition can be saturated by the microwaves. The electron spin relaxation times T_1 and T_2 play a crucial role in the saturation factor. Usually, their studies are performed by pulse ESR where one can access and separate contributions from various relaxation processes by applying different microwave pulse sequences.⁶ It should be emphasized that the electron spin relaxation changes with the magnetic field (and, consequently, with microwave frequency), and therefore, the data obtained with the conventional low-field/low-frequency pulse ESR contain less DNP relevant information. In this regard, it is crucial to perform relaxation studies at fields/frequencies used in DNP-NMR (Table I).

A promising alternative to the pulse HFESR is the rapid scan ESR (RS-ESR). This technique finds itself in the middle between the pulse and continuous wave ESR, combining the advantages of both: it

TABLE I. Commonly used magnetic fields and frequencies in ¹H-NMR spectroscopy and the corresponding ESR frequencies for $g \approx 2$.

Magnetic field (T)	NMR (MHz)	ESR (GHz)
9.385	400	263 ^a
11.740	500	329
14.095	600	395
16.444	700	461
18.805	800	527
21.160	900	593
23.490	1000	661

^aThe only commercially available pulse HFESR spectrometer.

grants access to the spin relaxation studies and, on the other hand, does not require high microwave power.²⁵ Consequently, the use of resonant cavities is not necessary, and the multi-frequency measurements can be performed in one spectrometer. Information about the spin-spin relaxation time T_2 is extracted from the specific distortions in the ESR spectrum appearing under the fast changing microwave frequency or magnetic field.^{26,27} The lowest measurable T_2 time in pulse ESR is limited by the spectrometer dead time (about 50 ns in common spectrometers)—a delay between the excitation pulse and start of the signal acquisition. Rapid scan ESR, however, does not have this flaw, and the access to short relaxation times is just a question of high enough sweep and acquisition rates (see Fig. 1). A general relation between the relaxation time and the sweep rate necessary to achieve the rapid scan regime is

$$\gamma \left| \frac{dB}{dt} \right| \geq \frac{1}{T_2^2} \quad \text{or} \quad \left| \frac{d\omega}{dt} \right| \geq \frac{1}{T_2^2}, \quad (1)$$

where γ is the gyromagnetic ratio, B is the applied magnetic field, and ω is the microwave angular frequency. Accordingly, systems with long spin relaxation require moderate scan rates, which can be produced either by the magnetic field or microwave frequency. However, as the relaxation time becomes shorter, faster and faster scan rates are necessary, and it becomes impossible to perform RS-ESR with the magnetic field sweeps. That is why we develop and perform RS-ESR in the frequency domain, i.e., scanning the microwave frequency at a constant magnetic field.^{28,29} With this approach, we can create extremely fast scans (10^5 THz/s), which allows us to measure T_2 times down to nano-seconds scale.³⁰ If one were about to repeat this experiment in the field domain, it would require to sweep the magnetic field at the unachievable rate of 10^7 T/s. Another advantage of the frequency domain is the possibility to generate broad scans to cover broad ESR spectra in one measurement.

In this Perspective, we will show the recent advances, challenges, and prospects of the RS-ESR at THz frequencies. We will discuss experimental and theoretical aspects, with the latter being mostly

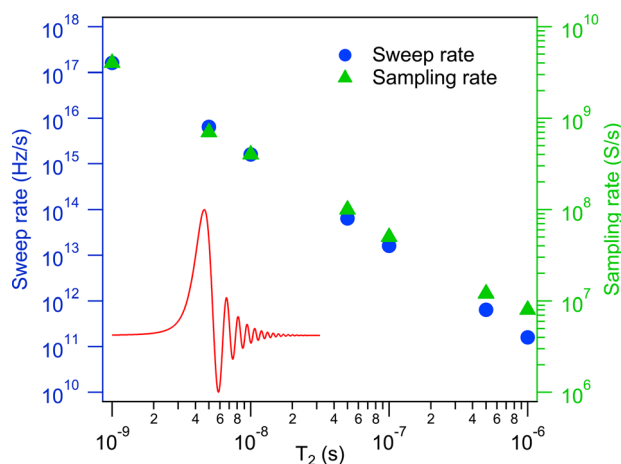


FIG. 1. T_2 relaxation time dependence of the sweep rate and the minimal data acquisition rate necessary to acquire rapid scan signals under the $df/dt = 1/2\pi T_2^2$ condition. The inset shows a rapid scan spectrum corresponding to this condition.

focused on the relaxation processes affected by the molecular motion in liquids.

II. RAPID SCAN ESR AT THZ FREQUENCIES IN INHOMOGENEOUSLY BROADENED SYSTEMS

When the sweep rate (magnetic field or microwave frequency) reaches condition (1), i.e., becomes comparable or faster than the spin-spin dynamics, the ESR spectrum undergoes specific distortions in the form of transient oscillations (also known as *wiggles*), as it is shown in the insert of Figs. 1 and 2. These oscillations resemble the free induction decay (FID) signal but with the progressively decreasing period of oscillations. The effect of a fast sweep on a spin system can be described by the convolution operator

$$r(t) = (s * d)(t) = \int_{-\infty}^{+\infty} s(\tau)d(t - \tau)d\tau, \quad (2)$$

or by simple multiplication in the Fourier space

$$R(\omega) = S(\omega)D(\omega), \quad (3)$$

where $r(t)$ is the rapid scan signal, $s(t)$ is the free induction decay signal, and $d(t)$ is the drive function, which describes the rapid scan excitation profile. Therefore, the problem of restoring the undistorted (slow-scan) ESR spectrum $S(\omega)$ is a matter of post-processing, though the experimental and numerical noise can cause artifacts in the reconstructed spectrum, and its details can be found elsewhere.^{30,31}

In the case of a homogeneously broadened resonance line (e.g., phase-coherent spins), the RS-ESR spectrum can be simulated by the modified Bloch equations expressed in the rotating with B_1 field coordinate system $\{\mathbf{u}, \mathbf{v}, \mathbf{z}\}$:

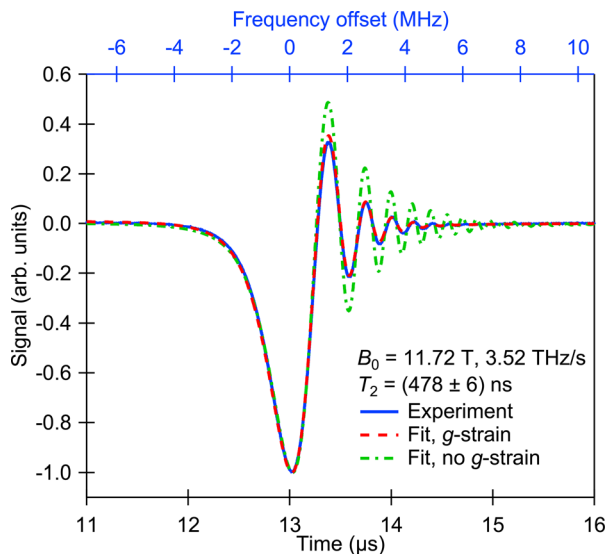


FIG. 2. An example of rapid scan ESR acquired on a single micro-crystal of LiPc (blue) and its fit with homogeneous (green) and inhomogeneous (red) broadening models. Incident microwave power is 1 mW, 10^4 averages, and the total acquisition time is 5 s.

$$\begin{aligned} \frac{dM_u}{dt} &= -\frac{M_u}{T_2} - [\Delta\Omega + \omega(t)]M_v, \\ \frac{dM_v}{dt} &= [\Delta\Omega + \omega(t)]M_u - \frac{M_v}{T_2} - \gamma B_1 M_z, \\ \frac{dM_z}{dt} &= \frac{M_0}{T_1} + \gamma B_1 M_v - \frac{M_z}{T_1}, \end{aligned} \quad (4)$$

where M_u , M_v , and M_z are projections of the total magnetization M_0 , $\Delta\Omega$ is the offset of the resonance line from the center of the sweep $\omega(t)$, and B_1 is the magnitude of the magnetic component of the microwaves. The sweep profile $\omega(t)$ can be arbitrary, but usually, it is either linear, $\omega(t) = bt$, or harmonic, $\omega(t) = A_{mod} \cos(\omega_{mod}t)$. The numerical solution of these equations followed by fitting to the measured spectrum allows extraction of T_2 time.

Things are somewhat different when an ESR spectrum contains inhomogeneously broadened line(s) due to unresolved (hyper)fine structure, g -factor anisotropy, and strains or a non-uniform magnetic field distribution over the sample. First, this leads to necessity of faster sweep rates as condition (1) becomes $|d\omega/dt| \geq \Delta\omega^2$, where $\Delta\omega$ is the half width at half maximum of the slow scan ESR spectrum, which can be characterized by a new relaxation time $T_2^* = 1/\Delta\omega < T_2$. Second, the Bloch equations of form (4) cannot be used to simulate the RS-ESR spectrum anymore. The first complication is of a purely technical nature, and ESR lines with $\Delta\omega$ up to 100 MHz can be recorded in the rapid scan mode with the modern fast microwave sources.³⁰ Dealing with the second complication has two possible paths. Generally speaking, it is possible to further modify the Bloch equations incorporating the inhomogeneous broadening as an additional fictitious relaxation mechanism. For example, the effect of magnetic field non-uniformity can be accounted for by substituting the relaxation terms $1/T_2$ by $1/(T_2 + T_2^*)$ as Erwin Hahn had suggested in his classic paper on the nuclear FID.³² However, in the presence of several broadening sources (as it usually happens), the modification of equations (4) becomes too complicated. For this reason, we follow another approach. Regardless of the origin of inhomogeneous broadening, the resulted slow scan ESR spectrum is a sum of contributions from individual spin packets. According to Eq. (2), the same holds for the rapid scan regime: the individual rapid scan responses form the overall RS-ESR signal, e.g., $r(t) = (\sum s_i * d)(t) = \sum (s_i * d)(t) = \sum r_i(t)$. Consequently, the rapid scan spectrum of a complex system can be obtained as a weighted sum of solutions of the Bloch equations (4) with the corresponding $\Delta\Omega$ and T_2 .

To demonstrate this approach, we have performed a set of measurements on a crystalline needle (0.7 mm long and 0.01 mm thick) of Lithium Phthalocyanine (LiPc) in broad frequency and field ranges. This is a well-known organic semiconductor with unpaired electrons used in the ESR oximetry.^{33–35} It is characterized by extremely small ESR linewidth due to the exchange narrowing: at the microwave frequency of ~ 9.5 GHz (magnetic field of 340 mT), the linewidth $\Delta\omega \simeq 50$ kHz.³⁶ However, at higher magnetic fields, the resonance line becomes broader due to the shortening of the spin-spin relaxation time T_2 and the appearance of inhomogeneous contributions from g -factor strain and, perhaps, unresolved hyperfine splitting from Li and N nuclei. In Fig. 2, we present an example where the inhomogeneous broadening prohibits the use of the Bloch equations in form (4). Oscillations in the experimentally recorded signal (blue trace) fade out much faster than it is predicted by a single homogeneously broadened

line model (green trace). In the second model, we had introduced inhomogeneous broadening as the g -strain. We calculated 30 rapid scan spectra with normally distributed g -factors and summed them up with the corresponding weights. As it can be seen from Fig. 2, this simple model gives an excellent agreement with the experiment.

A great advantage of rapid scan HFESR is its multi-frequency capability. Since there are no resonant microwave cavities, the rapid scan measurements can be performed at any frequency within the operation range of the microwave source/detector. This is especially useful for low temperature experiments as no time is wasted on reloading and re-cooling the sample. Figure 3 shows the spin relaxation rate of LiPc as a function of the applied magnetic field in the range of 3–15 T accompanied by X- and Q-band pulse measurements from Ref. 36 for the sake of completeness. The relaxation time T_2^* was derived from the linewidth of the deconvoluted spectra. The relaxation rate $1/T_2^*$ increases linearly with the magnetic field. This perfectly falls within the g -strain broadening mechanism in which $1/T_2^* = \Delta g \mu_B B$, where Δg is the g -strain magnitude and μ_B is the Bohr's magneton. Spin-spin relaxation time T_2 shortens with the magnetic field as well, though not as steep as T_2^* . Above 6 T, the contribution from g -factor strain is sufficient for unequivocal separation of the relaxation times.

III. RAPID SCAN ESR SIMULATION BASED ON SPIN DYNAMICS AFFECTED BY MOLECULAR MOTION

As it was shown above, the rapid scan technique has the potential to reveal detailed characteristics of the spin relaxation processes at high magnetic fields and frequencies. Usage of this technique to study spin dynamics and molecular motion of liquid dissolved organic radicals can become a very useful tool in the optimization of DNP at high magnetic fields, which are typical for NMR spectrometers (Table I). However, utilization of the rapid scan requires the development of a systematic approach to simulate rapid scan ESR spectra taking into

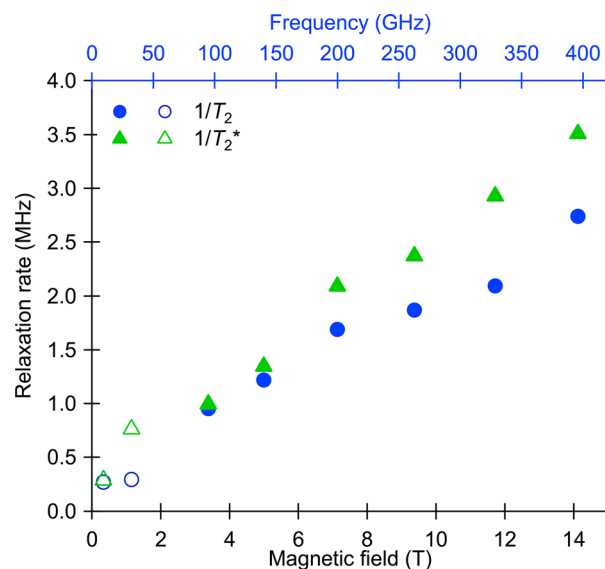


FIG. 3. Magnetic field dependence of the electron spin relaxation times T_2 and T_2^* in LiPc at room temperature. Low field values (open markers) are taken from Ref. 36.

account the physical nature of the underlying relaxation processes and employing the least possible number of fitting parameters. In other words, we need to find a procedure to express feature-rich rapid scan ESR spectra through the spin dynamics affected by molecular motion. In this way, we can validate models describing the molecular motion of spin carrying systems and verify the assumptions made in the computation of the spin magnetization. Furthermore, the information extracted by fitting rapid scan ESR spectra can be used to predict signals that are recorded in other magnetic resonance experiments, such as, for example, DNP enhanced NMR measurements. In this context, we have developed a computer program for the simulation of ESR spectra with rapidly varying frequency of the irradiating microwaves. In this program, the simulations are performed employing Direct Solution of Liouville/von Neumann Equation (DiSoLiNE), which was described in our recent publication.³⁷ DiSoLiNE allows us to determine the density matrix of the spin system subject to relaxation processes, which are modeled by stochastic methods, and under the action of the microwaves with an arbitrary magnitude, phase and frequency time dependence. The information about the transverse electronic spin magnetization, which is observed in experiments, is contained in the density matrix of the spin system.

As an example, we showcase a DiSoLiNE application to nitroxide radicals, which play a very important role in ESR spectroscopy and DNP. Figure 4 demonstrates a prediction of a rapid frequency scan ESR experiment on ^{14}N -TEMPOL nitroxide radicals dissolved in liquids at the high magnetic field of 9.2 T, which corresponds to the microwave frequencies close to 260 GHz. In addition to the specification of magnetic fields B_0 and B_1 , which was $10 \mu\text{T}$ here, the DiSoLiNE simulation program requires values of magnetic tensors (g -tensor, hyperfine, A , and nitrogen nuclear quadrupole, Q , interaction tensors)

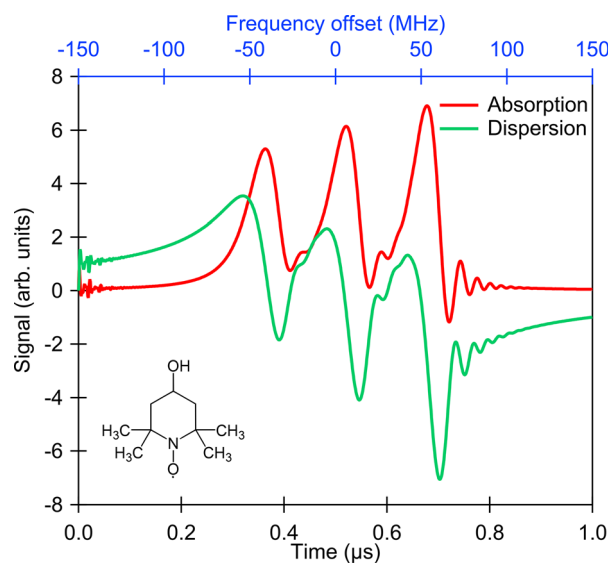


FIG. 4. Simulated dynamics of the transverse electron spin magnetization in the rapid frequency scan ESR experiment performed on liquid dissolved ^{14}N -TEMPOL at 9.2 T and the sweep rate of 300 THz/s. The simulations were performed in the fast motion regime with nitroxide rotational correlation time, $\tau_c = 20$ ps and with the following magnetic tensor principle values [g] = [2.0088, 2.006, 2.002], [A] = [18, 18, 105] MHz, and [Q] = [0.1, 1.6, -1.7] MHz.

and specification of radical random rotational motion in a solvent, characterized by the rotational correlation time τ_c . These parameters are used to construct the Hamiltonian of the nitroxide spin system and the relaxation operator, which enter the Liouville von Neumann equation in the fast motion regime.^{38–41} Here, we assumed that the relaxation of the nitroxide spin system to its thermal equilibrium state is caused by the modulation of the electronic Zeeman, electron nuclear hyperfine, and nitrogen nuclear quadruple interactions by thermal random rotational motion of nitroxide radical molecules in liquid, whereas such processes as diffusion in an inhomogeneous magnetic field and Heisenberg spin exchange were neglected.^{42–47} For our simulations, shown in Fig. 4, we have chosen the values of magnetic tensors and τ_c corresponding to low concentrated TEMPOL radicals in water at room temperature. It is important to mention that in our previous work, we have performed the simulation of the experimental slow scan CW-EPR spectrum with the same program and simulation parameters except for the scan rate, which was there 20 times slower to avoid line wiggling. Having achieved a good agreement of the simulated and experimental slow scan EPR spectra of water solved TEMPOL, we made a theoretical prediction of the rapid scan spectrum shown in Fig. 4. In comparison to low field slow scan nitroxide spectra, which consist of three sharp lines, the signal shown in Fig. 4 exhibits significant broadening at high fields ($B_0 = 9.2$ T) and clear rapid scan effects manifested by the transient oscillations. According to the data in Fig. 4, these wiggles appear at the frequency sweep rate, $d\omega/dt$, of about $2\pi \times 300$ THz/s. This result gives us a hint for an optimal value of the sweep rate in experimental studies. If this sweep rate is utilized to roughly estimate the value of the electronic transverse relaxation time, T_2 , via the formula (1), we obtain T_2 about 20 ns, which is in good agreement with the values obtained from the line widths of the experimental slow scan spectrum of water solved TEMPOL.^{37,48} Furthermore, we observe different intensities of the oscillations for all three nitroxide spectral lines shown in Fig. 4. Such behavior of electron spin magnetization indicates T_2 dependence on spectral position and is a result of an interplay between spin dynamics and relaxation processes. The result, shown in Fig. 4, is only one example, which can be obtained employing DiSoLiNE adapted in this work. Simulation of frequency rapid scan EPR spectra for arbitrary values of B_0 and shapes of $B_1(t)$ can be easily implemented without introducing additional undefined parameters. Remarkably, such prediction of rapid scan EPR spectra would be impossible based on Bloch equations without assuming values of relaxation times T_1 and T_2 for each spectral line and each B_0 value. Hence, fitting measured spectra with the simulated signals, which are obtained as a solution of Liouville/von Neumann equation describing spin dynamics in detail, gives us an instrument to verify dynamic models of spin carrying molecules and use them in further applications.

IV. CONCLUSIONS AND NEAR FUTURE

Rapid scan ESR, and especially its frequency domain implementation, shows great potential in the electron spin dynamics studies at (sub)THz frequencies. Alongside the non-resonant induction mode design of modern HFESR spectrometers, it offers a number of favorable features. Frequency sweeps are sufficiently fast for granting access to the nanosecond scale relaxation times, and, on the other hand, they can span over tens of GHz, covering the whole ESR spectrum of systems with more than one unpaired electron and (hyper)fine splitting.

The microwave non-resonant sample holder facilitates multi-frequency measurements. As we have shown above, this approach brings spin relaxation measurements to an unprecedentedly broad range of magnetic fields using only one ESR spectrometer. The fine tunability of the magnetic field and microwave frequency can be particularly useful for investigations of the clock and zero-field splitting transitions observed, for instance, in single molecule magnets – qubit candidates for quantum computation.^{49–51} Another important advantage of the non-resonant holder is its possibility to accommodate samples of different forms and sizes: powders, single crystals, liquids, and thin films. The synergy of the presented here experimental and simulation tools defines the near future of the rapid scan HFESR—relaxation studies of DNP polarizing agents in liquid and frozen solutions.

Another promising approach to rapid scan ESR is the utilization of the ESR-on-a-chip technology.⁵² Though the rapid scan mode (sweep rate of 400 THz/s) was demonstrated only at X-band frequencies so far, the concept is expected to support high frequencies as well.^{53,54} In this method, a submillimeter size coil of a voltage controlled oscillator (VCO) is used for microwave generation and ESR detection. The small sample volume, limited by the coil's size, can be partially mitigated by the use of an array of injection-locked VCOs.

A particular advantage of the rapid scan ESR is fast acquisition. Depending on the sweep time, the measurement with averaging takes from tens of microseconds to a few seconds. Consequently, the implementation of rapid scan ESR to studies of time dependent phenomena looks exciting. For example in a recent Bruker webinar, the time resolution of 10 ms was demonstrated in spin trapping in photoinduced reactions and 1.25 ms in an experiment with free falling BDPA.⁵⁵ The main directions may include the monitoring of fast chemical reactions with ESR active intermediates, performing ESR in excited states (transient ESR) and observing the switching processes in molecular spin switches.

Despite these advances, rapid scan HFESR is still at its early development stage, and there are certain obstacles to deal with before the method becomes routinely usable by a general scientific community. These obstacles are of two origins: technical and fundamental.

The majority of the technical issues come from imperfections in the microwave propagation system of a spectrometer. The unwanted reflections from the quasi-optical elements and the probe's window create standing waves, which cause the phase modulation of a rapid scan signal and a leakage of the excitation power to the detection system. The phase modulation is particularly significant in the case of broad spectra where it results in continuous changes of absorption/dispersion (M_v/M_u) ratio within the spectrum. The excitation power leakage manifests itself as a baseline in the spectrum (also referred to as a background signal) and can be an order or two more intense than the rapid scan signal itself. In principle, these effects could be characterized during calibration of the spectrometer and removed later from the spectrum in the data post-processing. However, the pattern of the modulation and baseline is not constant, and it changes with the probe's temperature and after every sample load. Consequently, the spectrometer has to be recalibrated before each measurement. This approach is feasible for the phase correction since it does not require high precision, and deviations of $\pm 5^\circ$ are acceptable. The background correction though is much more sensitive to the fluctuations, and better methods have to be developed. The procedure that we usually exploit is the so-called on-/off resonance subtraction, originally proposed by Hyde *et al.*²⁸ In this method, the off resonance data set is

recorded at a different magnetic field, so that the ESR line is moved outside the frequency sweep. This provides a clean baseline that is then subtracted from the on-resonance data. This technique works particularly well for narrow ESR lines because the magnetic fields required for shifting the lines are fairly low and can be achieved by a small solenoid coil built in the sample holder. Also, this allows for rather fast on/off cycling, which provides further averaging of the rapid scan signal useful for low concentrated samples. In the case of broad spectra though, the off resonance data can be obtained only by ramping the superconductive magnet. The slow ramping speed and large hysteresis of the superconductive solenoid nullify the benefits of on/off cycling. When the background is a slowly varying signal, a possible way of dealing with it is the Fourier Transform analysis. In the simplest approach, the straightforward high pass filtering is capable of removing the baseline at the cost of relatively small distortions in the rapid scan signal. A more complex procedure would be to find frequencies of the standing waves, build the baseline as a Fourier sum of these frequencies with unknown amplitudes, and subtract it from the on-resonance data.⁵⁶ Unfortunately, none of these baseline subtraction techniques is universal; they either require considerable efforts from a user or are limited to specific experimental conditions. Therefore, a universal and reliable strategy for the background removal is yet to be established.

At the present state, rapid scan ESR is limited to T_2 measurements. According to the Bloch equations (4), the relaxation time T_1 directly influences only the longitudinal magnetization M_z , and the contribution to the transverse magnetization $M_{u,v}$ occurs via the term γB_1 . As a result, the only possible way to measure T_1 is to apply microwaves strong enough to produce a noticeable deviation of the magnetization from its equilibrium. Then, the intensity of a rapid scan signal will decrease with the sweep rate increase due to the lack of time for the spin system to relax. Perhaps excitation frequency sweeps of more sophisticated shapes, rather than linear or sinusoidal, can facilitate such experiments with currently available low-power microwave sources. Another important field for theoretical research is the development (if possible) of phase refocusing experiments, similarly to spin-echo measurements in the pulse ESR. This would bring a completely new horizon for the rapid scan ESR applications. To characterize spin dynamics at high magnetic fields and to describe relaxation processes based on the information encoded in rapid frequency scan spectra even more precisely, incorporation of the spin exchange and the interactions with the solvent nuclei should be implemented.

ACKNOWLEDGMENTS

O.L., A.S and A.M. acknowledge funding from the ERC under the European Union's Horizon 2020 research and innovation program (GA No. 714850); P.N. acknowledges funding from the Grant Agency of the Czech Republic (Grant No. GACR EXPRO 21-20716X). We also acknowledge Mark Tseytlin (West Virginia University) for fruitful discussion and providing us with the LiPc sample.

AUTHOR DECLARATIONS

Author Contributions

All authors contributed equally to this work.

Conflict of Interest

The authors declare no conflicts of interest.

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding authors upon reasonable request.

REFERENCES

- ¹A. Abragam and B. Bleaney, *Electron Paramagnetic Resonance of Transition Ions* (Oxford University Press, 2012).
- ²J. A. Weil and J. R. Bolton, *Electron Paramagnetic Resonance* (John Wiley & Sons, 2006).
- ³S. A. Bonke, T. Risse, A. Schnegg, and A. Brückner, "In situ electron paramagnetic resonance spectroscopy for catalysis," *Nat. Rev. Methods Primers* **1**, 33 (2021).
- ⁴G. Jeschke, "DEER distance measurements on proteins," *Ann. Phys. Chem.* **63**, 419–446 (2012).
- ⁵A. Marko, V. Denysenkov, D. Margraf, P. Cekan, O. Schiemann, S. T. Sigurdsson, and T. Prisner, "Conformational flexibility of DNA," *J. Am. Chem. Soc.* **133**, 13375–13379 (2011).
- ⁶A. Schweiger and G. Jeschke, *Principles of Pulse Electron Paramagnetic Resonance* (Oxford University Press, 2001).
- ⁷O. Schiemann, C. A. Heubach, D. Abdullin, K. Ackermann, M. Azarkh, E. G. Bagryanskaya, M. Drescher, B. Endeward, J. H. Freed, L. Galazzo, D. Goldfarb, T. Hett, L. E. Hofer, L. F. Ibáñez, E. J. Hustedt, S. Kucher, I. Kuprov, J. E. Lovett, A. Meyer, S. Ruthstein, S. Saxena, S. Stoll, C. R. Timmel, M. D. Valentin, H. S. Mchaourab, T. F. Prisner, B. E. Bode, E. Bordignon, M. Bennati, and G. Jeschke, "Benchmark test and guidelines for DEER/PELDOR experiments on nitroxide-labeled biomolecules," *J. Am. Chem. Soc.* **143**, 17875–17890 (2021).
- ⁸A. Marko, V. Denysenkov, and T. Prisner, "Out-of-phase PELDOR," *Mol. Phys.* **111**, 2834–2844 (2013).
- ⁹P. Schöps, J. Plackmeyer, and A. Marko, "Separation of intra- and intermolecular contributions to the PELDOR signal," *J. Magn. Reson.* **269**, 70–77 (2016).
- ¹⁰P. Neugebauer, D. Bloos, R. Marx, P. Lutz, M. Kern, D. Aguilà, J. Vaverka, O. Laguta, C. Dietrich, R. Clérac, and J. van Slageren, "Ultra-broadband EPR spectroscopy in field and frequency domains," *Phys. Chem. Chem. Phys.* **20**, 15528–15534 (2018).
- ¹¹M. Rohrer, O. Brüggemann, B. Kinzer, and T. F. Prisner, "High-field/high-frequency EPR spectrometer operating in pulsed and continuous-wave mode at 180 GHz," *Appl. Magn. Reson.* **21**, 257–274 (2001).
- ¹²J. van Tol, L.-C. Brunel, and R. J. Wylde, "A quasioptical transient electron spin resonance spectrometer operating at 120 and 240 GHz," *Rev. Sci. Instrum.* **76**, 074101 (2005).
- ¹³K. Möbius, A. Savitsky, A. Schnegg, M. Plato, and M. Fuchs, "High-field EPR spectroscopy applied to biological systems: Characterization of molecular switches for electron and ion transfer," *Phys. Chem. Chem. Phys.* **7**, 19–42 (2005).
- ¹⁴G. W. Morley, L.-C. Brunel, and J. van Tol, "A multifrequency high-field pulsed electron paramagnetic resonance/electron-nuclear double resonance spectrometer," *Rev. Sci. Instrum.* **79**, 064703 (2008).
- ¹⁵I. Tkach, I. Bejenke, F. Hecker, A. Kehl, M. Kasanmascheff, I. Gromov, I. Prisecaru, P. Höfer, M. Hiller, and M. Bennati, "1H high field electron-nuclear double resonance spectroscopy at 263 GHz/9.4T," *J. Magn. Reson.* **303**, 17–27 (2019).
- ¹⁶I. Kaminker, R. Barnes, and S. Han, "Arbitrary waveform modulated pulse EPR at 200 GHz," *J. Magn. Reson.* **279**, 81–90 (2017).
- ¹⁷T. F. Prisner, "Shaping EPR: Phase and amplitude modulated microwave pulses," *J. Magn. Reson.* **306**, 98–101 (2019).
- ¹⁸K. Möbius, W. Lubitz, N. Cox, and A. Savitsky, "Biomolecular EPR meets NMR at high magnetic fields," *Magnetochemistry* **4**, 50 (2018).
- ¹⁹E. J. Reijerse, "High-frequency EPR instrumentation," *Appl. Magn. Reson.* **37**, 795–818 (2010).
- ²⁰A. S. L. Thankamony, J. J. Wittmann, M. Kaushik, and B. Corzilius, "Dynamic nuclear polarization for sensitivity enhancement in modern solid-state NMR," *Prog. Nucl. Magn. Reson. Spectrosc.* **102–103**, 120–195 (2017).
- ²¹D. Lee, E. Bouleau, P. Saint-Bonnet, S. Hediger, and G. D. Paëpe, "Ultra-low temperature MAS-DNP," *J. Magn. Reson.* **264**, 116–124 (2016).

- ²²P. Neugebauer, J. G. Krumpal, V. P. Denysenkov, G. Parigi, C. Luchinat, and T. F. Prisner, "Liquid state DNP of water at 9.2 T: An experimental access to saturation," *Phys. Chem. Chem. Phys.* **15**, 6049 (2013).
- ²³P. Neugebauer, J. G. Krumpal, V. P. Denysenkov, C. Helmling, C. Luchinat, G. Parigi, and T. F. Prisner, "High-field liquid state NMR hyperpolarization: A combined DNP/NMRD approach," *Phys. Chem. Chem. Phys.* **16**, 18781–18787 (2014).
- ²⁴T. Dubroca, S. Wi, J. van Tol, L. Frydman, and S. Hill, "Large volume liquid state scalar Overhauser dynamic nuclear polarization at high magnetic field," *Phys. Chem. Chem. Phys.* **21**, 21200–21204 (2019).
- ²⁵G. R. Eaton and S. S. Eaton, "Rapid-scan electron paramagnetic resonance," in *eMagRes* (American Cancer Society, 2016), pp. 1529–1542.
- ²⁶J. W. Stoner, D. Szymanski, S. S. Eaton, R. W. Quine, G. A. Rinard, and G. R. Eaton, "Direct-detected rapid-scan EPR at 250 MHz," *J. Magn. Reson.* **170**, 127–135 (2004).
- ²⁷D. G. Mitchell, R. W. Quine, M. Tseitlin, R. T. Weber, V. Meyer, A. Avery, S. S. Eaton, and G. R. Eaton, "Electron spin relaxation and heterogeneity of the 1:1 α,γ -bis(diphenylene- β -phenylallyl) (BDPA)/benzene complex," *J. Phys. Chem. B* **115**, 7986–7990 (2011).
- ²⁸J. S. Hyde, R. A. Strangeway, T. G. Camenisch, J. J. Ratke, and W. Froncisz, "W-band frequency-swept EPR," *J. Magn. Reson.* **205**, 93–101 (2010).
- ²⁹M. Tseitlin, G. A. Rinard, R. W. Quine, S. S. Eaton, and G. R. Eaton, "Rapid frequency scan EPR," *J. Magn. Reson.* **211**, 156–161 (2011).
- ³⁰O. Laguta, M. Tuček, J. van Slageren, and P. Neugebauer, "Multi-frequency rapid-scan HFEPR," *J. Magn. Reson.* **296**, 138–142 (2018).
- ³¹M. Tseitlin, "General solution for rapid scan EPR deconvolution problem," *J. Magn. Reson.* **318**, 106801 (2020).
- ³²E. L. Hahn, "Nuclear induction due to free Larmor precession," *Phys. Rev.* **77**, 297–298 (1950).
- ³³P. Turek, J.-J. André, A. Giraudeau, and J. Simon, "Preparation and study of a lithium phthalocyanine radical: Optical and magnetic properties," *Chem. Phys. Lett.* **134**, 471–476 (1987).
- ³⁴K. J. Liu, P. Gast, M. Moussavi, S. W. Norby, N. Vahidi, T. Walczak, M. Wu, and H. M. Swartz, "Lithium phthalocyanine: A probe for electron paramagnetic resonance oximetry in viable biological systems," *Proc. Natl. Acad. Sci. U. S. A.* **90**, 5438–5442 (1993).
- ³⁵M. Afeworki, N. R. Miller, N. Devasahayam, J. Cook, J. B. Mitchell, S. Subramanian, and M. C. Krishna, "Preparation and EPR studies of lithium phthalocyanine radical as an oxymetric probe," *Free Radical Biol. Med.* **25**, 72–78 (1998).
- ³⁶H. Sato, L. A. Dalton, D. Ha, R. W. Quine, S. S. Eaton, and G. R. Eaton, "Electron spin relaxation in x-lithium phthalocyanine," *J. Phys. Chem. B* **111**, 7972–7977 (2007).
- ³⁷A. Marko, A. Sojka, O. Laguta, and P. Neugebauer, "Simulation of nitrogen nuclear spin magnetization of liquid solvated nitroxides," *Phys. Chem. Chem. Phys.* **23**, 17310–17322 (2021).
- ³⁸F. Bloch, "Generalized theory of relaxation," *Phys. Rev.* **105**, 1206–1222 (1957).
- ³⁹R. K. Wangsness and F. Bloch, "The dynamical theory of nuclear induction," *Phys. Rev.* **89**, 728–739 (1953).
- ⁴⁰A. Redfield, "The theory of relaxation processes," in *Advances in Magnetic and Optical Resonance* (Wiley-VCH, 1965), pp. 1–32.
- ⁴¹J. H. Freed and G. K. Fraenkel, "Theory of linewidths in electron spin resonance spectra," *J. Chem. Phys.* **39**, 326–348 (1963).
- ⁴²A. Abragam, *Principles of Nuclear Magnetism* (Oxford University Press, Oxford, 2011).
- ⁴³A. Marko, B. Wolter, and W. Arnold, "Magnetization density calculation for diffusing spins," *Phys. Rev. B* **69**, 184424 (2004).
- ⁴⁴A. Marko, B. Wolter, and W. Arnold, "Application of a portable nuclear magnetic resonance surface probe to porous media," *J. Magn. Reson.* **185**, 19–27 (2007).
- ⁴⁵R. D. Bates, "Use of nitroxide spin labels in studies of solvent–solute interactions," *J. Chem. Phys.* **67**, 4038–4044 (1999).
- ⁴⁶Y. Molin, K. Salikhov, and K. Zamarayev, *Spin Exchange*, Springer Series Vol. 8 (Springer, 1980).
- ⁴⁷B. D. Armstrong and S. Han, "A new model for overhauser enhanced nuclear magnetic resonance using nitroxide radicals," *J. Chem. Phys.* **127**, 104508 (2007).
- ⁴⁸D. Sezer, M. Gafurov, M. J. Prandolini, V. P. Denysenkov, and T. F. Prisner, "Dynamic nuclear polarization of water by a nitroxide radical: Rigorous treatment of the electron spin saturation and comparison with experiments at 9.2 Tesla," *Phys. Chem. Chem. Phys.* **11**, 6638 (2009).
- ⁴⁹M. Affronte, F. Troiani, A. Ghirri, A. Candini, M. Evangelisti, V. Corradini, S. Carretta, P. Santini, G. Amoretti, F. Tuna, G. Timco, and R. E. P. Winpenny, "Single molecule magnets for quantum computation," *J. Phys. D* **40**, 2999–3004 (2007).
- ⁵⁰C. Schlegel, J. van Slageren, M. Manoli, E. K. Brechin, and M. Dressel, "Direct observation of quantum coherence in single-molecule magnets," *Phys. Rev. Lett.* **101**, 147203 (2008).
- ⁵¹D. Aravena and E. Ruiz, "Spin dynamics in single-molecule magnets and molecular qubits," *Dalton Trans.* **49**, 9916–9928 (2020).
- ⁵²S. Künstner, A. Chu, K.-P. Dinse, A. Schnegg, J. E. McPeak, B. Naydenov, J. Anders, and K. Lips, "Rapid scan electron paramagnetic resonance using an EPR-on-a-chip sensor," *Magn. Reson.* **2**, 673–687 (2021).
- ⁵³A. V. Matheoud, G. Gualco, M. Jeong, I. Zivkovic, J. Brugger, H. M. Ronnow, J. Anders, and G. Boero, "Single-chip electron spin resonance detectors operating at 50 GHz, 92 GHz, and 146 GHz," *J. Magn. Reson.* **278**, 113–121 (2017).
- ⁵⁴Personal communication with Prof. Dr. Jens Anders (University of Stuttgart) on January 31, 2022.
- ⁵⁵See <https://www.bruker.com/de/news-and-events/webinars/2021/Bruker-EPR-RapidScan-Info-Day.html> for "Bruker EPR: Rapid Scan Info Day."
- ⁵⁶M. Tseitlin, T. Czechowski, R. W. Quine, S. S. Eaton, and G. R. Eaton, "Background removal procedure for rapid scan EPR," *J. Magn. Reson.* **196**, 48–53 (2009).