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Frequency-swept dynamic nuclear polarization

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ABSTRACT

Dynamic nuclear polarization (DNP) improves the sensitivity of NMR spectroscopy by the transfer of electron polarization to nuclei via irradiation of electron-nuclear transitions with microwaves at the appropriate frequency. For fields > 5 T and using g \sim 2 electrons as polarizing agents, this requires the availability of microwave sources operating at >140 GHz. Therefore, microwave sources for DNP have generally been continuous-wave (CW) gyrotrons, and more recently solid state, oscillators operating at a fixed frequency and power. This constraint has limited the DNP mechanisms which can be exploited, and stymied the development of new time domain mechanisms. We report here the incorporation of a microwave source enabling facile modulation of frequency, amplitude, and phase at 9 T (250 GHz microwave frequency), and we have used the source for magic-angle spinning (MAS) NMR experiments. The experiments include investigations of CW DNP mechanisms, the advantage of frequency-chirped irradiation, and a demonstration of an Overhauser enhancement of ~25 with a recently reported water-soluble BDPA radical, highlighting the potential for affordable and compact microwave sources to achieve significant enhancement in aqueous samples, including biological macromolecules. With the development of suitable microwave amplifiers, it should permit exploration of multiple new avenues involving time domain experiments.

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1. Introduction

Dynamic nuclear polarization (DNP) [1–3] has transformed from a niche spin physics experiment to a relatively widespread and commercially available technique [4], and it can trace its modern renaissance to the adoption of the gyrotron as a microwave source [5]. For magic-angle spinning (MAS) NMR, it has achieved sensitivity improvements by orders of magnitude and enabled investigations of materials and biological macromolecules heretofore not feasible [6–9]. These impressive results have been obtained with continuous-wave (CW) microwave sources exploiting CW DNP mechanisms, which rely on the saturation of energy level transitions. The further potential of DNP lies in the realization of pulsed DNP [10] at high fields, which generates and manipulates spin coherences as routinely done in the case of nuclear spin energy levels using radiofrequency (RF) pulses in NMR. Pulsed methods can lead to field-independent enhancements, in contrast

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to CW methods which scale unfavorably with increasing magnetic field.

However, pulsed DNP also imposes stricter requirements on microwave source capabilities. The first requirement is that while CW DNP only requires sufficient microwave fields to saturate electron energy level transitions, i.e. $\omega_{1S} \gg 2\pi/T_{1e}$, pulsed DNP requires that the excitation rate of the coherence induced by microwave irradiation be greater than the rate of spin–spin (T₂) relaxation, i.e. $\omega_{1S} \gg 2\pi/T_{2e}$. For a narrow-line monoradical such as trityl OX063 at 80 K, T_{1e} is on the order of ms while T_{2e} is on the order of μ s, so pulsed DNP will require $\omega_{1S}/2\pi \ge 5$ MHz [10]. The second requirement, and the primary topic of this work, is that the source must be capable of modulating the frequency, amplitude, and phase of microwave radiation. Pulse lengths must be concomitantly short with the higher microwave B_1 , on the order of ns, and modulations of the amplitude and phase must occur even faster.

Frequency-agile gyrotron oscillators have shown that they can alter the microwave frequency by up to 20 MHz per μ s and achieve a pseudo-gating ability by quickly shifting the microwave frequency on- and off-resonance [11,12]. However, pulsed DNP sequences that generate and manipulate electron spin coherences,







such as TOP-DNP [13], TPPM- and XiX-DNP [14], and BEAM-DNP [15], operate on the timescale of ns, too fast for the current generation of gyrotron oscillators, but perhaps within reach with further innovations. Besides gyrotron sources, solid-state microwave sources have recently emerged as attractive options for frequency, amplitude, and phase modulations while also being cost- and space-efficient. They consist of frequency multiplier diodes to take advantage of mixers, amplifiers, and filters readily available at lower frequencies to achieve complete amplitude and phase modulation. Incorporating arbitrary waveform generation leads to the most flexible microwave sources for pulsed DNP applications. An arbitrary waveform-modulated microwave source for EPR and DNP applications was demonstrated at 5 T [16-18] and more recently at 7 T [19-21]. Kuzhelev and Akhmetzyanov et al. showed the advantage of arbitrarily-shaped, broadband pulses for PELDOR measurements in EPR [22]. Sergevev et al. demonstrated a 263 GHz solid-state diode source for MAS DNP application [23], but without arbitrary waveform capabilities.

Finally, in developing new and improving established DNP methods, it is important to be able to record the Zeeman field profiles to discern and disentangle the dominant DNP mechanism. Historically, this has required a magnet equipped with a sweep coil to vary the main magnetic field B_0 . The sweep process is tedious, requiring that the probe be retuned as the NMR frequency changes, data is usually low resolution for that same reason. This process also increases the rate of helium boiloff, increasingly relevant as helium becomes scarce and expensive. In the worst case, an improperly conducted field sweep can lead to a magnet quench. Using an arbitrary waveform generator (AWG) to independently perform frequency sweeps over any range up to several GHz circumvents these issues: the sweeps require essentially no supervision or retuning of the probe, and pose no danger to the magnet. All told, these reasons provided ample rationale for developing an AWG-based microwave frequency sweep system for DNP at high fields.

We report here the implementation of a frequency-swept AWGequipped solid-state source for DNP experiments at 250 GHz (9 T). We attain a frequency range of \sim 8 GHz centered at 250 GHz with microwave output power of 160 mW, and demonstrate the observation of all contemporary high-field CW DNP mechanisms - the Overhauser effect (OE) [2,24–28], the solid effect (SE) [29–31], the cross effect (CE) [32-37] and the recently discovered mechanism of resonant mixing (RM) [38,39]. With this modest power, the generated Rabi field B_1 is insufficient to fully realize the usefulness of frequency chirps with MAS probes, though we do observe a modest improvement over monochromatic irradiation in a mixed radical system. Among CW DNP mechanisms, we observe the best performance with the Overhauser effect, and have previously used the microwave source to investigate the nuclear polarization transfer pathway in BDPA radicals in ortho-terphenyl matrix [27,28]. Here, we demonstrate the OE with a recently reported watersoluble BDPA as a promising means for DNP studies of biological macromolecules without requiring an expensive high-power gyrotron.

The reported instrumental advances are important steps towards realizing pulsed DNP at magnetic fields of 9 T and above. The AWG enables any conceivable pulsed DNP sequence with a time resolution of <100 ps, including the repeated pulse architecture of TOP-DNP and XiX-DNP. Beyond rectangular pulses, the possibility of shaped pulses achieving desired excitation patterns, becoming increasingly relevant as our ability to manipulate electron spins approaches that of dedicated EPR spectroscopy. The next steps include increasing the generated B_1 by augmenting the arrangement with a microwave amplifier and/or a more efficiently coupled sample chamber.

2. Results and discussion

Our 250 GHz microwave circuit is shown schematically in Fig. 1. and can be divided into two sets of components: one for the generation of arbitrary shaped microwaves at relatively low frequenand the second for amplification and frequency cies multiplication up to 250 GHz. Regarding the capabilities, the circuit can output arbitrarily modulated microwaves of frequency 250 ± 4 GHz at up to 220 mW, but with the directional isolator inserted (protecting the sensitive multiplier diodes from reflections), we achieve an overall output power of up to 160 mW. Modulation of the phase, frequency, or amplitude is performed by appropriately varying the AWG output. The AWG is a Keysight M8190A with two output channels operating at 12 gigasamples/ sec with 12-bit vertical resolution. The nominal bandwidth of the AWG is 5 GHz (slightly under the Nyquist frequency), though we normally operate it around half that frequency, at 2.5 ± 1 GHz. The time resolution of the AWG is ~83 ps, though further investigation is needed to understand the implications of this parameter on the length of our shortest possible well-defined pulse.

Developments in diode technology enabled the two frequencydoubling diodes (depicted as the "×4" block in Fig. 1) to handle the increased input power from the high-power amplifier at 60 GHz while maintaining 8% total conversion efficiency (~32% for the first doubler, ~25% for the second doubler) in the multiplication process. Similar diodes from the same research efforts have been used in commercial instruments, and the trajectory of engineering advances shows promise for 500 mW at 263 GHz and 100 mW at 527 GHz in the future.

With the goal of providing some helpful insights for those interested in constructing similar systems, we show in Fig. 2 an alternative design of the microwave circuit, which we ended up rejecting, detailing the undesired results and the changes we made to our current design. An off-the-shelf amplifier-multiplier-chain (AMC) for our frequency would take an input signal of just over 10 GHz and, through a series of multiplication and amplification steps, multiply it N = 24 times to yield 250 GHz microwaves. Accordingly, we used a 10 GHz local oscillator (LO) and mixed it with signals from an AWG, outputting only a few tens of MHz. However, the resultant DNP frequency profiles for a BDPA/OTP sample were abnormal (Fig. S1). This prompted us to investigate the signals provided to the circuit at 10 GHz and those exiting at 250 GHz. We found that despite a relatively clean input signal, where undesired frequencies were suppressed by \sim 30 dB relative to the desired one (Fig. 2(A)), the output signal was a comb of frequencies (sidebands) centered about the desired frequency, almost equal to the desired frequency in amplitude and spaced by the AWG frequency (Fig. 2 (C)). We then saw that the sidebands were related to the multiplication process, with an intermediate density of sidebands observed after the first tripler stage (Fig. 2(B)). The result is understood by considering that the multipliers also act as mixers when multiple tones are present in the input signal. Thus, the amplitude of an undesired sideband relative to the primary frequency is increased by a factor of $20 \cdot \log N$ dB during a multiplication step with multiplication factor *N*, the same as the fundamental increase in phase noise with frequency multiplication. As such, even though our sidebands were well-suppressed at 10 GHz, they became prominent following multiplication by N = 24. In our revised circuit design (Fig. 1), we use a much higher AWG frequency to ensure that any sidebands are far away, and we use a bandpass filter to remove those sidebands and provide the multipliers with as clean an input as possible. Additionally, we perform the mixing at a higher frequency so that the multiplication factor after mixing is as low as possible; a high-frequency IQ mixer operating around 60 GHz was available off-the-shelf and easily incorporated into



Fig. 1. The circuit used to generate microwaves at 250 GHz. A 10 GHz signal from an oscillator is fed into a series of passive components, starting with a set of three frequency doublers, and the output at 60 GHz is mixed at an IQ Mixer with a signal from an arbitrary waveform generator operating between 1.5 and 3.5 GHz. The upper sideband of the mixer between 61.5 and 63.5 GHz is filtered before being amplified (active component), and further multiplied using frequency doublers to achieve an output frequency between 246 and 254 GHz at an output power of 220 mW. To protect the multipliers from reflected power, we utilize an isolator with an insertion loss of -1.4 dB, attenuating the power to 160 mW.



Fig. 2. Block diagram of the initial frequency multiplier design which was rejected. Illustrated are representative frequency measurements made at points (A), (B), and (C) as shown in the circuit diagram in (D), with the LO set to 10.4 GHz and the AWG outputting + 10 MHz, for a nominal final frequency of 249.84 GHz. Plotted spectra are approximate reconstructions of the spectrum analyzer output onto the absolute frequency domain, and powers can be assessed within a plot but not between plots as the downconversion schemes for each frequency differ significantly. (A): output from the IQ mixer shows the desired signal at 10.41 MHz and the suppressed opposite sideband and leakage of the LO. (B): output following a single tripler step. (C): dense comb of sidebands at the final output. (D): schematic of source configuration for these measurements.

our system. These changes appeared to resolve our issues, as subsequent measurements of the output frequency now yield only a single tone, as illustrated in Fig. 3, where we see a line of ~0.5 MHz width. Finally, we note that the diode array runs at an elevated temperature, and therefore we added cooling fans and thermoelectric Peltier devices to reduce the operating temperature and prolong the device lifetime.

We also compared the frequency stability of the new system's output to that of our 250 GHz gyrotron (Fig. 3). The AMC output frequency had a standard deviation of about 60 kHz, while that of the gyrotron was about 1.6 MHz, an order of magnitude larger.

This result is expected: ultimately, the AMC frequency stability is primarily tied to the stability of our 10 GHz phase-locked loop local oscillator, while the gyrotron output frequency is tied to fluctuations in the beam voltage and current, among other factors [40,41]. For most applications, the slight fluctuations of the gyrotron frequency are not critical, but for precise DNP and EPR measurements, the additional stability of the AMC is essential.

Fig. 4 shows the DNP frequency profiles obtained with the instrument configuration in Fig. 1 on DNP test samples exhibiting different CW DNP mechanisms: the cross effect with AMUPol [42], the solid effect and Overhauser effect with BDPA [26,28],



Fig. 3. Frequency stability measurements of the two sources near 250 GHz. Measurements were made using a harmonic downconversion scheme and the FFT function of a digital oscilloscope. The scope's sampling rate was 5.0 GSa/s and each trace contains 50 kSa (10 μ s acquisition time); each plotted point corresponds to the frequency of maximum intensity for a particular trace, and two traces acquired per second.



Fig. 4. ¹H DNP (A-C) and ¹³C DNP (D) frequency profiles obtained with the setup on polarizing agents (A) AMUPol in 6:3:1 glycerol- $d_8:D_2O:H_2O$ exhibiting CE DNP, (B) h_{21} -BDPA and Phe- d_5 -BDPA in OTP matrix exhibiting OE and SE DNP, (C) Trityl-OX063 in 6:3:1 DMSO- $d_6:D_2O:H_2O$ exhibiting SE and arguably resonant mixing (RM), and (D) diamond powder containing P1 centers primarily exhibiting CE DNP (to natural abundance ¹³C nuclei). Profiles in (A-C) were collected under MAS (5–7 kHz) at 90–100 K, and (D) under static conditions at room temperature. Specific experimental details are available in the SI.

the resonant mixing effect [38] (or debatably thermal mixing effect [43]) with trityl, and the ¹³C enhancement profile of diamond powder containing P1 centers, which has been reported to include several overlapping mechanisms [44]. The enhancement of the static diamond powder was ~200 and will be discussed in more detail in a future publication. One unexpected result was the emergence of fine, ripple-like features in the AMUPol profile (Fig. 4(A)). A previous study with a solid-state diode source also showed some fine features when compared to a field profile with a gyrotron source [23], and we likely have somewhat lower power than that study, exacerbating the effect. One might also suspect that the effect is an instrumental artifact, e.g. standing waves on the waveguide. We believe this not to be the case as no such ripples are observed in any of the other profiles in Fig. 4. We are currently investigating these ripples using other samples and instruments, and will discuss the results including their physical origin in a forthcoming publication.

At 9 T, the frequency range needed to explore all these mechanisms spans ~1.5 GHz while maintaining a constant output power. With a conventional gyrotron, one would fix the frequency and power of the gyrotron and sweep the NMR magnetic field, which is a tedious process, expensive both in time and excess helium boil-off. A gyrotron can be designed to be tunable over several GHz [45], but the frequency and power must be constantly monitored to guarantee an accurate profile. With the AWG, frequency adjustment is instantaneous and repeatable, allowing entire profiles to collect largely unattended. As a result, while the absolute enhancements with only 160 mW of microwave power are modest compared to those with several watts from a gyrotron, the ease of collecting these profiles has made it practical to investigate these CW mechanisms in detail.

To take advantage of our ability to modulate the microwave output, we compared the single-frequency enhancements in Fig. 4 to those using a frequency chirp. In most cases, our limited output power made the chirp no better than the single frequency. However, we did observe a slight improvement in cross effect enhancement for a mixed radical system [46] of 30 mM 4-amino TEMPO and 15 mM Trityl-OX063 as Han and colleagues reported previously [21]. This system is favorable for observing the benefit of chirped irradiation: the narrow-line trityl is more efficiently saturated by chirping the microwave frequency across the EPR line at a rate faster than the MAS frequency.

The resultant cross effect enhancement, which depends on the polarization difference between the narrow-line trityl and wide-line nitroxide, concomitantly increases. In Fig. 5 we report a max-



Fig. 5. Relative performance of repeated 1 microsecond chirps of varying chirp widths for a sample of 15 mM trityl OX063 and 30 mM 4-amino TEMPO in 6:3:1 glycerol- d_8 :D₂O:H₂O. For all experiments, the MAS frequency was 5 kHz and the sample temperature 100 K.



Fig. 6. Results using the AWG driven solid state source in conjunction with water-soluble NMe₃-BDPA. (A): Bulk ¹H enhancement for 45 mM NMe₃-BDPA in 6:3:1 glycerol- d_8 : D₂O:H₂O at 95 K and spinning at 6 kHz, demonstrating the effect of freeze-pump-thaw degassing. (B): ¹³C CP spectra of uniformly labeled GNNQQNY microcrystals wet with a small volume of the same 45 mM NMe₃-BDPA at 95 K and spinning at 7 kHz.

imum relative increase of about 13%, resulting in an absolute enhancement of 9.0, using a chirp width of 30 MHz and a chirp time of 1 μ s. We expect that with a higher available ω_{1s} , from increased microwave power and/or improved coupling efficiency, chirped DNP will outperform single-frequency irradiation under a broader range of conditions. We justify this expectation with the theoretical understanding of the cross effect under MAS as distinct events during a rotor period [47]. The microwave irradiation is involved in electron-microwave events, which are avoided level crossings when the microwave frequency matches the electron Larmor frequency that result in saturation of the electron spin. The efficiency of saturation during the event, which leads to polarization difference between electrons and eventually nuclear enhancement, is governed by the adiabaticity probability,

$$P_{EM} \approx \pi \omega_1^2 / \left(2 \frac{\partial |\omega_e|}{\partial t} \right), \tag{1}$$

suggesting the importance of high ω_1 , especially as the chirp rate and thus the effective $\partial |\omega_e| / \partial t$ increases.

With the current instrumentation, we looked to Overhauser effect (OE) DNP as an application which does not require high microwave power. We have previously reported large OE enhancements ($\epsilon ~\sim 70)$ with our AMC microwave source, but these employed BDPA in the organic matrix ortho-terphenyl (OTP) [27,28]. A water-soluble BDPA is desirable for OE DNP in aqueous samples, including biological systems. A recently reported watersoluble derivative of BDPA [48] aimed to mitigate stability issues of previous water-soluble BDPAs [49,50]. With this NMe₃-BDPA, we observed bulk enhancements of ~ 25 in a degassed sample (Fig. 6(A)). We subsequently prepared a sample of microcrystals of the fibril-forming peptide fragment GNNQQNY doped with NMe₃-BDPA and observed a relayed enhancement [51] of 4.2 (Fig. 6(B)). Further optimizations may make NMe₃-BDPA an appealing polarizing agent considering the favorable scaling of the OE with increasing magnetic field [26] and the low required microwave power.

3. Conclusions and Outlook

In this work, we document a solid-state 250 GHz microwave source capable of arbitrary phase, frequency, and amplitude waveform modulation that will be essential for high-field pulsed DNP. We have highlighted some of our considerations in constructing the system, hopefully benefiting DNP spectroscopists planning to assemble similar instruments. We also report a selection of results which remain notable despite the low $\omega_{\rm 1s}$ available. In particular, we showed a facile recording of CW frequency profiles for investigation of DNP mechanisms, an early indication of the potential benefits of frequency-chirped irradiation, and the prospect of using these lower power sources in conjunction with water-soluble OE polarizing agents for high-field investigations of biological systems.

At present, this system is suboptimal for achieving enhancements comparable to a gyrotron, but one can achieve increased ω_{15} while maintaining the arbitrary modulation capability in two ways: a secondary amplification step and improved efficiency of Rabi field generation in MAS stators. For amplifiers, both gyroamplifiers, and at low frequencies (\leq 250 GHz) more compact slowwave devices such as TWT's and klystrons, offer the potential of 100-1000 W output pulses amplified from our 160 mW input source. Ongoing research in the field will soon make these amplifiers available at frequencies relevant to high-field DNP. Regarding stator efficiency, the model of pulsed EPR spectrometers is a relevant waypoint for the potential of resonant cavities: a TE₀₁₁ resonator can achieve efficiencies of ~ 35 MHz/ \sqrt{W} [52], so only 20 mW incident microwave power would achieve $\omega_{1S}/2\pi = 5$ MHz for pulsed DNP, and our system could be used as-is for pulsed DNP in such a static resonator. As for MAS, typical 3.2 mm MAS stators are estimated to achieve a microwave efficiency of ~0.56 MHz/ \sqrt{W} [23], requiring 80 W for the same electron B_1 , but a smaller rotor size and optimized design achieved 1.8 MHz/ \sqrt{W} [23], requiring only 8 W for pulsed DNP. It seems inevitable that a combination of microwave amplifiers and improved microwave coupling will lead to high-field pulsed DNP during MAS.

Data availability

No data was used for the research described in the article.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

Supplementary material to this article can be found online at https://doi.org/10.1016/j.jmr.2023.107511.

References

- [1] A. Abragam, The Principles of Nuclear Magnetism, Clarendon, Oxford, England, 1961.
- [2] A.W. Overhauser, Polarization of nuclei in metals, Phys. Rev. 92 (1953) 411.
- [3] C.P. Slichter, Principles of Magnetic Resonance, 3rd ed., Springer-Verlag, 1989.
- [4] A.S. Lilly Thankamony, J.J. Wittmann, M. Kaushik, B. Corzilius, Dynamic nuclear polarization for sensitivity enhancement in modern solid-state NMR, Progr, Nucl. Magn. Reson. Spectrosc. 102–103 (2017) 120–195.
- [5] L.R. Becerra, G.J. Gerfen, R.J. Temkin, D.J. Singel, R.G. Griffin, Dynamic nuclear polarization with a cyclotron resonance maser at 5 T, Phys. Rev. Lett. 71 (1993) 3561–3564.
- [6] S. Bahri, R. Silvers, B. Michael, K. Jaudzems, D. Lalli, G. Casano, O. Ouari, A. Lesage, G. Pintacuda, S. Linse, 1H detection and dynamic nuclear polarizationenhanced NMR of Aβ1-42 fibrils, Proc. Natl. Acad. Sci. 119 (2022).
- [7] T. Biedenbänder, V. Aladin, S. Saeidpour, B.R. Corzilius, Dynamic nuclear polarization for sensitivity enhancement in biomolecular solid-state NMR, Chem. Rev. (2022).
- [8] E.J. Koers, E.A. van der Cruijsen, M. Rosay, M. Weingarth, A. Prokofyev, C. Sauvée, O. Ouari, J. van der Zwan, O. Pongs, P. Tordo, NMR-based structural biology enhanced by dynamic nuclear polarization at high magnetic field, J. Biomol. NMR 60 (2014) 157–168.
- [9] A.G. Rankin, J. Trébosc, F. Pourpoint, J.-P. Amoureux, O. Lafon, Recent developments in MAS DNP-NMR of materials, Solid State Nucl. Magn. Reson. 101 (2019) 116–143.
- [10] K.O. Tan, S. Jawla, R.J. Temkin, R.G. Griffin, Pulsed Dynamic Nuclear Polarization, eMagRes (2019) 339–352.
- [11] F.J. Scott, E.P. Saliba, B.J. Albert, N. Alaniva, E.L. Sesti, C. Gao, N.C. Golota, E.J. Choi, A.P. Jagtap, J.J. Wittmann, M. Eckardt, W. Harneit, B. Corzilius, S.T. Sigurdsson, A.B. Barnes, Frequency-agile gyrotron for electron decoupling and pulsed dynamic nuclear polarization, J. Magn. Reson. 289 (2018) 45–54.
- [12] C. Gao, N. Alaniva, E.P. Saliba, E.L. Sesti, P.T. Judge, F.J. Scott, T. Halbritter, S.T. Sigurdsson, A.B. Barnes, Frequency-chirped dynamic nuclear polarization with magic angle spinning using a frequency-agile gyrotron, J. Magn. Reson. 308 (2019).
- [13] K.O. Tan, C. Yang, R.T. Weber, G. Mathies, R.G. Griffin, Time-optimized pulsed dynamic nuclear polarization, Sci. Adv. 5 (2019) eaav6909.
- [14] V.S. Redrouthu, G. Mathies, Efficient pulsed dynamic nuclear polarization with the X-inverse-X sequence, J. Am. Chem. Soc. 144 (2022) 1513–1516.
- [15] N. Wili, A.B. Nielsen, L.A. Völker, L. Schreder, N.C. Nielsen, G. Jeschke, K.O. Tan, Designing broadband pulsed dynamic nuclear polarization sequences in static solids, Sci. Adv. 8 (2022) eabq0536.
- [16] A.A. Smith, B. Corzilius, A.B. Barnes, T. Maly, R.G. Griffin, Solid effect dynamic nuclear polarization and polarization pathways, J. Chem. Phys. 136 (2012).
- [17] A.A. Smith, B. Corzilius, J.A. Bryant, R. DeRocher, P.P. Woskov, R.J. Temkin, R.G. Griffin, A 140 GHz pulsed EPR/212 MHz NMR spectrometer for DNP studies, J. Magn. Reson. 223 (2012) 170–179.
- [18] A.A. Smith, B. Corzilius, O. Haze, T.M. Swager, R.G. Griffin, Observation of strongly forbidden solid effect dynamic nuclear polarization transitions via electron-electron double resonance detected NMR, J. Chem. Phys. 139 (2013).
- [19] I. Kaminker, R. Barnes, S. Han, Arbitrary waveform modulated pulse EPR at 200GHz, J. Magn. Reson. 279 (2017) 81–90.
- [20] I. Kaminker, S. Han, Amplification of dynamic nuclear polarization at 200 GHz by arbitrary pulse shaping of the electron spin saturation profile, J. Phys. Chem. Lett. 9 (2018) 3110–3115.
- [21] A. Equbal, K. Tagami, S. Han, Pulse-shaped dynamic nuclear polarization under magic-angle spinning, J. Phys. Chem. Lett. 10 (2019) 7781–7788.
- [22] A. Kuzhelev, D. Akhmetzyanov, V. Denysenkov, G. Shevelev, O. Krumkacheva, E. Bagryanskaya, T. Prisner, High-frequency pulsed electron–electron double resonance spectroscopy on DNA duplexes using trityl tags and shaped microwave pulses, PCCP 20 (2018) 26140–26144.
- [23] I.V. Sergeyev, F. Aussenac, A. Purea, C. Reiter, E. Bryerton, S. Retzloff, J. Hesler, L. Tometich, M. Rosay, Efficient 263 GHz magic angle spinning DNP at 100 K using solid-state diode sources, Solid State Nucl. Magn. Reson. 100 (2019) 63–69.

- [24] T.R. Carver, C.P. Slichter, Polarization of Nuclear Spins in Metals, Phys. Rev. 92 (1953) 212–213.
- [25] T.R. Carver, C.P. Slichter, Experimental verification of the overhauser nuclear polarization effect, Phys. Rev. 102 (1956) 975–980.
- [26] T.V. Can, M.A. Caporini, F. Mentink-Vigier, B. Corzilius, J.J. Walish, M. Rosay, W. E. Maas, M. Baldus, S. Vega, T.M. Swager, Overhauser effects in insulating solids, J. Chem. Phys. 141 (2014).
- [27] L. Delage-Laurin, R.S. Palani, N. Golota, M. Mardini, Y. Ouyang, K.O. Tan, T.M. Swager, R.G. Griffin, Overhauser dynamic nuclear polarization with selectively deuterated BDPA radicals, J. Am. Chem. Soc. 143 (2021) 20281–20290.
- [28] R.S. Palani, M. Mardini, L. Delage-Laurin, D. Banks, Y. Ouyang, E. Bryerton, J.G. Kempf, T.M. Swager, R.G. Griffin, Amplified overhauser DNP with selective deuteration: attenuation of double-quantum cross-relaxation, J. Phys. Chem. Lett. 14 (2022) 95–100.
- [29] C.D. Jefferies, Polarization of nuclei by resonance saturation in paramagnetic crystals, Phys. Rev. 106 (1957) 164–165.
- [30] C.D. Jefferies, Dynamic orientation of nuclei by forbidden transitions in paramagnetic resonance, Phys. Rev. 117 (1960) 1056–1069.
- [31] B. Corzilius, A.A. Smith, R.G. Griffin, Solid effect in magic angle spinning dynamic nuclear polarization, J Chem Phys 137 (2012).
- [32] A.V. Kessenikh, V.L. Luschikov, A.A. Manenkov, Y.V. Taran, Proton polarization in irradiated polyethylenes, Soviet Phys. Solid State 5 (1963) 321–329.
- [33] A.V. Kessenikh, A.A. Manenkov, Dynamic polarization of nuclei during saturation of nonuniformly broadened electron paramagnetic resonance lines, Soviet Phys.-Solid State 5 (1963) 835–837.
- [34] K.N. Hu, H.H. Yu, T.M. Swager, R.G. Griffin, Dynamic nuclear polarization with biradicals, J. Am. Chem. Soc. 126 (2004) 10844–10845.
- [35] K.-N. Hu, V.S. Bajaj, M.M. Rosay, R.G. Griffin, High frequency dynamic nuclear polarization using mixtures of TEMPO and trityl radicals, J. Chem. Phys. 126 (2007).
- [36] K.N. Hu, G.T. Debelouchina, A.A. Smith, R.G. Griffin, Quantum mechanical theory of dynamic nuclear polarization in solid dielectrics, J. Chem. Phys. 134 (2011).
- [37] K.N. Hu, C. Song, H.H. Yu, T.M. Swager, R.G. Griffin, High-frequency dynamic nuclear polarization using biradicals: A multifrequency EPR lineshape analysis, J. Chem. Phys. 128 (2008).
- [38] R.S. Palani, M. Mardini, Y. Quan, R.G. Griffin, Dynamic nuclear polarization with trityl radicals, J. Magn. Reson. 107411 (2023).
- [39] Y. Quan, Y. Ouyang, M. Mardini, R.S. Palani, D. Banks, J. Kempf, W.T. Wenckebach, R.G. Griffin, Resonant mixing dynamic nuclear polarization, J. Phys. Chem. Lett. (2023) (submitted for publication).
- [40] A. Fokin, M. Glyavin, G. Golubiatnikov, L. Lubyako, M. Morozkin, B. Movschevich, A. Tsvetkov, G. Denisov, High-power sub-terahertz source with a record frequency stability at up to 1 Hz, Sci. Rep. 8 (2018) 4317.
- [41] S.-T. Han, R.G. Griffin, K.-N. Hu, C.-G. Joo, C.D. Joye, J.R. Sirigiri, R.J. Temkin, A.C. Torrezan, P.P. Woskov, Spectral characteristics of a 140-GHz long-pulsed gyrotron, IEEE Trans. Plasma Sci. 35 (2007) 559–564.
- [42] C. Sauvée, M. Rosay, G. Casano, F. Aussenac, R.T. Weber, O. Ouari, P. Tordo, Highly efficient, water-soluble polarizing agents for dynamic nuclear polarization at high frequency, Angew. Chem. Int. Ed. 52 (2013) 10858–10861.
- [43] A. Equbal, Y. Li, T. Tabassum, S. Han, Crossover from a solid effect to thermal mixing 1H dynamic nuclear polarization with trityl-OX063, J. Phys. Chem. Lett. 11 (2020) 3718–3723.
- [44] D. Shimon, K.A. Cantwell, L. Joseph, E.Q. Williams, Z. Peng, S. Takahashi, C. Ramanathan, Large room temperature bulk DNP of 13C via P1 centers in diamond, J. Phys. Chem. C 126 (2022) 17777–17787.
- [45] A.B. Barnes, E.A. Nanni, J. Herzfeld, R.G. Griffin, R.J. Temkin, A 250GHz gyrotron with a 3GHz tuning bandwidth for dynamic nuclear polarization, J. Magn. Reson. 221 (2012) 147–153.
- [46] K.-N. Hu, V.S. Bajaj, M. Rosay, R.G. Griffin, High-frequency dynamic nuclear polarization using mixtures of TEMPO and trityl radicals, J. Chem. Phys. 126 (2007).
- [47] K.R. Thurber, R. Tycko, Theory for cross effect dynamic nuclear polarization under magic-angle spinning in solid state nuclear magnetic resonance: the importance of level crossings, J. Chem. Phys. 137 (2012).
- [48] S. Mandal, S.T. Sigurdsson, Water-soluble BDPA radicals with improved persistence, Chem. Commun. 56 (2020) 13121–13124.
- [49] E.L. Dane, T.M. Swager, Synthesis of a Water-Soluble 1,3-Bis(diphenylene)-2phenylallyl Radical, J. Org. Chem. 75 (2010) 3533–3536.
- [50] O. Haze, B.R. Corzilius, A.A. Smith, R.G. Griffin, T.M. Swager, Water-soluble narrow-line radicals for dynamic nuclear polarization, J. Am. Chem. Soc. 134 (2012) 14287–14290.
- [51] P.C.A. van der Wel, K.-N. Hu, J. Lewandowski, R.G. Griffin, Dynamic nuclear polarization of amyloidogenic peptide nanocrystals: GNNQQNY, a core segment of the yeast prion protein Sup35p, J. Am. Chem. Soc. 128 (2006) 10840–10846.
- [52] D. Schmalbein, G.G. Maresch, A. Kamlowski, P. Höfer, The Bruker highfrequency-EPR system, Appl. Magn. Reson. 16 (1999) 185–205.