

# Spinning-Driven Dynamic Nuclear Polarization with Optical Pumping

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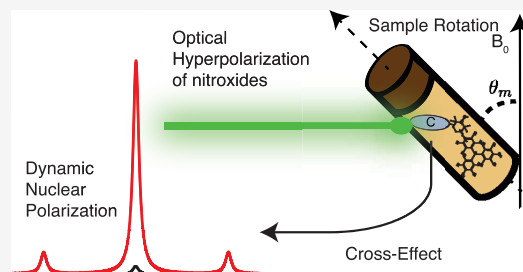


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**ABSTRACT:** We propose a new, more efficient, and potentially cost effective, solid-state nuclear spin hyperpolarization method combining the cross-effect mechanism and electron spin optical hyperpolarization in rotating solids. We first demonstrate optical hyperpolarization in the solid state at low temperatures and low field and then investigate its field dependence to obtain the optimal condition for high-field electron spin hyperpolarization. The results are then incorporated into advanced magic-angle spinning dynamic nuclear polarization (MAS-DNP) numerical simulations that show that optically pumped MAS-DNP could yield breakthrough enhancements at very high magnetic fields. Based on these investigations, enhancements greater than the ratio of electron to nucleus magnetic moments ( $>658$  for  $^1\text{H}$ ) are possible without microwave irradiation. This could solve at once the MAS-DNP performance decrease with increasing field and the high cost of MAS-DNP instruments at very high fields.



## 1. INTRODUCTION

Magic-angle spinning dynamic nuclear polarization (MAS-DNP) is a powerful solid-state nuclear magnetic resonance (ssNMR) method that reduces the duration of ssNMR experiments by orders of magnitude.<sup>1</sup> In short, the high polarization of paramagnetic species stemming from microwave ( $\mu\text{w}$ ) irradiation at the Larmor frequency can be transferred to nuclei to enable molecular-level characterization even when the isotope of interest is in low concentration or has low receptivity.<sup>2–5</sup> Over the past two decades, there has been significant progress in the development of hardware,<sup>6–11</sup> sample preparation methods,<sup>12–16</sup> paramagnetic species used as sources for DNP<sup>17–22</sup> and the theoretical understanding of MAS-DNP.<sup>23–26</sup> MAS-DNP most commonly uses biradicals<sup>27</sup> to generate the nuclear hyperpolarization via the cross-effect (CE) mechanism, which involves fast energy level anticrossing.<sup>23–26,28,29</sup>

As in conventional ssNMR, very high field MAS-DNP ( $>14.1$  T/600 MHz) enables higher resolution but faces multiple challenges, such as reduced efficiency of the CE with the field<sup>30,31</sup> and significant microwave absorption at high frequencies,<sup>11</sup> which reduce the large electron polarization difference and the concomitant nuclear polarization enhancement.<sup>25,30,32,33</sup> Finally, the significant cost of high-field MAS-DNP instrumentation limits widespread availability.

In parallel to DNP developments, optical irradiation has been used to improve NMR sensitivity. For example, nuclear hyperpolarization in ssNMR experiments via photo-CIDNP was observed in certain systems.<sup>34–40</sup> Furthermore, optical electron spin hyperpolarization offers a promising approach for carrying out solid-state and liquid-state Overhauser DNP,<sup>41,42</sup> and the hyperpolarized triplet state has been combined with

the integrated solid effect at low fields to generate nuclear spin hyperpolarization.<sup>43–49</sup>

In this article, we propose a novel method that can provide much higher hyperpolarization than traditional MAS-DNP at high fields, in addition to addressing the issues listed above via the use of optical electron spin hyperpolarization in the solid state. The concept, dubbed optically pumped MAS-DNP (MAS-OPDNP), uses optical irradiation to photophysically generate the electron spin polarization difference required for the CE mechanism and build on the effect of the sample's rotation to hyperpolarize the nuclei. This concept enables nuclear spin hyperpolarization that is not restricted to the ratio of electron to nucleus magnetic moments, while potentially using affordable hardware. Finally, the method is expected to be field-independent, and therefore, it should be easily added to most modern ssNMR spectrometers.

The present work first demonstrates experimentally, in the solid state and X-band (low field), that optically driven electron spin hyperpolarization is possible for nitroxides commonly used for MAS-DNP.<sup>27,50,51</sup> We subsequently investigate the field dependence of optical electron spin hyperpolarization and its characteristic time scales. Based on these results, we propose a chromophore-radical-radical polarizing agent and present simulations that were conducted

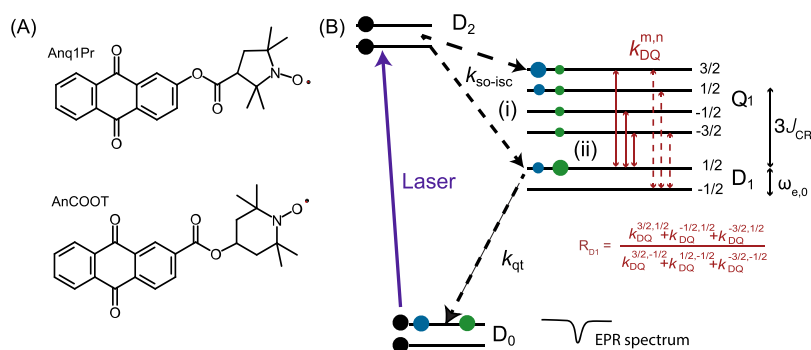
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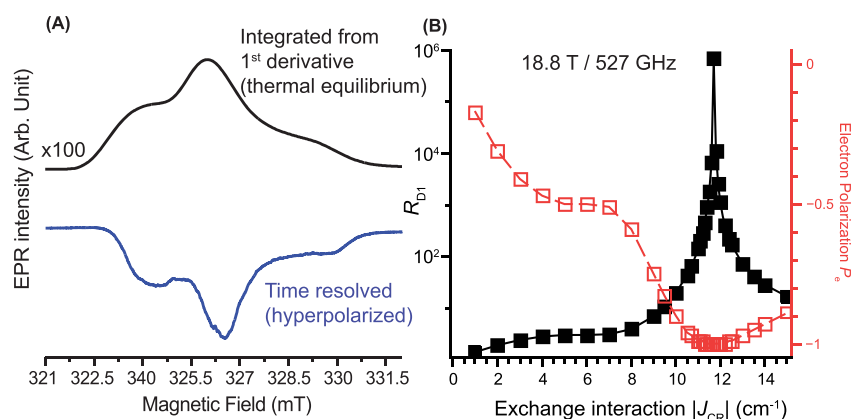
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**Scheme 1.** (A) Structures and Acronyms of the Molecules Examined in This Study and (B) Key Processes Involved in Electron Spin Hyperpolarization in a Chromophore-Radical Adduct at Low Magnetic Field ( $\sim 0.3$  T)



The laser pulse excites the molecule from the  $D_0$  to the  $D_2$  state (termed sing doublet),<sup>62,70</sup> which then decays from  $D_2$  to  $Q_1/D_1$  (mixing of the triplet and the doublet) via SO-ISC, followed by the quenching of the  $D_1$  state (termed trip-doublet) to  $D_0$  at a rate of  $k_{qt}$ . Two mechanisms lead to hyperpolarization in the  $D_0$  state: (i) the selective transition of the SO-ISC and (ii) the reversible transitions between  $D_1$  and  $Q_1$  states (RQM). Black dots represent the initial photoexcited populations, and the blue and green dots denote the population redistributions after processes (i) and (ii), respectively. For process (ii), after decay via SO-ISC, the populations in the  $Q_1$  state are equilibrated via longitudinal relaxation and driven by the RQM pathway via the  $D_1 \rightarrow Q_1$  transitions, thanks to cross-relaxation, with rates defined by the  $k_{DQ}^{m,n}$  between  $Q_1^m$  and  $D_1^n$  (red arrows) to generate hyperpolarization in the  $D_0$  state. The ratio of rates  $R_{D1} = \frac{\sum k_{DQ}^{m,1/2}}{\sum k_{DQ}^{m,-1/2}}$  (red solid and red dashed arrows) quantifies the selective polarization in the  $D_1$  states.  $\omega_{e,0}$  represents the Zeeman Larmor frequency, and  $3J_{CR}$  ( $< 0$ ) represents the magnitude of the exchange splitting between the  $Q_1$  and  $D_1$  states.



**Figure 1.** (A) Experimental EPR spectrum (integrated from the first derivative) of ANCOOT in toluene at 100 K (black line) and its hyperpolarized EPR spectrum recorded for  $2.5 \mu\text{s}$  after a 355 nm laser pulse (blue line) and integrated using a boxcar averager over  $0.3 \mu\text{s}$  (see SI for experimental details). The gain factor of  $-100$  for the Boltzmann signal represents the ESP enhancement obtained from time-resolved experiments (TREPR), see Appendix 4. (B) Plot of the RQM selectivity factor,  $R_{D1}$  (black squares), and the corresponding values of  $P_e$  (red squares) as a function of the exchange parameter,  $|J_{CR}|$  ( $J_{CR} < 0$ ), for the case of pure RQM, that is, process (ii) (Scheme 1). N.B. solid black and dashed red interpolating lines are provided as a guide to the eye.

with a high-performance MAS-DNP numerical tool<sup>25,52</sup> to explore the potential of the CE MAS-DNP mechanism at a high magnetic field using optical electron spin hyperpolarization. The results are then discussed in light of experimental considerations.

## 2. METHOD

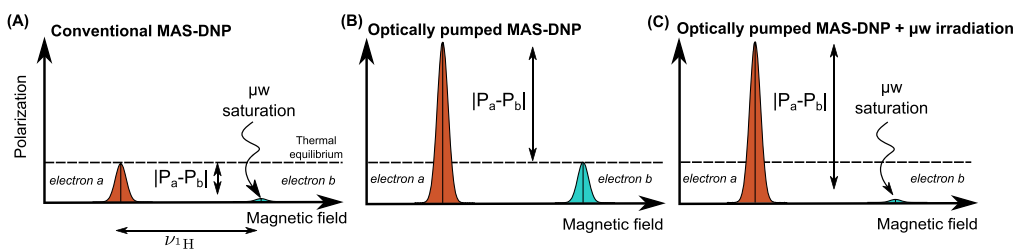
**2.1. Experimental Details.** Steady-state and time-resolved EPR spectra were recorded in a laboratory-built X-band electroparamagnetic resonance (EPR) spectrometer.<sup>53</sup> For the time-resolved EPR, the exciting source was the third harmonic of an Nd:YAG laser (Quantel Model: YG-981C, wavelength: 355 nm, repetition rate: 15 Hz, and energy at the sample: 1–4 mJ/pulse). Because of the extremely strong spin-polarized EPR signals, the laser energy was reduced to its lowest output value. The absorbance of all the solutions at the exciting wavelength was less than 1. The samples, ANCOOT and Anq1Pr, were

dissolved in toluene and placed in a quartz tube (O.D.: 4 mm, I.D.:  $\sim 3$  mm, Wilmad Glass, USA) and then degassed by three cycles of freeze-pump-thaw under a vacuum of 105 mbar. The low-temperature experiments were performed by passing cold  $\text{N}_2$  gas through a Dewar that contained the sample tube. The temperature at the sample tube was calibrated by inserting a thermocouple inside the cavity. Additional experimental details are available in the Supporting Information.

**2.2. Numerical Simulations.** The simulation models of the reverse quartet mechanism at high field is based on previously published results,<sup>54</sup> and the input parameters are detailed in the Supporting Information.

The MAS-OPDNP simulations are based on a previously published MAS-DNP simulations method.<sup>25,52</sup> The model simulates biradicals in a box to account for the inter-biradical interactions, thus accounting for the biradical concentration. The model was modified to account for optical electron spin

**Scheme 2. Schematics of the Proton CE MAS-DNP Mechanism in the Ideal Case of a Biradical with Two Nonoverlapping EPR Spectra Separated by the Proton Larmor Frequency<sup>a</sup>**



<sup>a</sup>(A) Conventional MAS-DNP where the spins of electron *b* are saturated, while the spins of the electron *a* are at thermal equilibrium. The proposed optically pumped hyperpolarization method in which the polarization of electron spin *a* is increased while the electron *b* is at thermal equilibrium (B) or saturated by microwave irradiation (C).

hyperpolarization. Details about the modifications and the parameters used can be found in the [Supporting Information](#).

### 3. RESULTS

#### 3.1. Photophysical Electron Spin Hyperpolarization.

Optically pumped electron spin hyperpolarization can be generated in chromophore-radical (CR) systems during photophysical quenching processes.<sup>55–63</sup> The electron hyperpolarization generation in CR systems is well understood in the liquid state.<sup>64–68</sup> Two mechanisms contribute to the electron hyperpolarization (see energy diagram in [Scheme 1](#)): (i) the spin-orbit-induced inter-system-crossing (SO-ISC)<sup>68,69</sup> and (ii) the  $D_1-Q_1$  conversion via the reverse quartet mechanism (RQM).<sup>54</sup> The first mechanism is due to the spin-orbit coupling, while the second involves the large zero-field splitting (ZFS),  $D_{ZFS}$ , both in the excited triplet state of the chromophore.

Recently, ANCOOT and Anq1PR ([Scheme 1A](#)), two efficient CR-systems, were reported to generate a large electron hyperpolarization in solution.<sup>66,71</sup> We examined their hyperpolarization efficiency in the solid state as a preliminary assessment for MAS-DNP applications. [Figure 1A](#) shows the EPR spectra of ANCOOT in toluene at 100 K in thermal equilibrium (black curve) and hyperpolarized (blue curve) states. The hyperpolarized EPR spectrum is emissive and a near-mirror image of the thermal equilibrium one, without any signature of the quartet EPR spectrum. From the signal intensity ratio, we estimated the electron polarization enhancement to be about  $-100$  times the thermal spin polarization (30% polarization, see the [SI](#) for details on the evaluation of experimental hyperpolarization). The hyperpolarization is generated on a very fast time scale  $<100$  ns (the instrument response time is 100 ns), which is important for applications in MAS-DNP.

The solid-state hyperpolarized EPR spectrum and its time dependence for the anthraquinone nitroxides are determined by the SO-ISC and RQM mechanisms. Their relative contributions at X-band frequencies are beyond the scope of the current work and will be described in a future publication.

At high magnetic fields the SO-ISC mechanism may become less efficient as the net (rotationally invariant) component of the polarization generated during the ISC has an inverse field dependence (see [eq S16](#)).<sup>58,72</sup> It is therefore suspected that the SO-ISC-induced hyperpolarization would likely decrease by orders of magnitude at a high magnetic field (18.8 T). Thus, at a high field and low temperature ( $\sim 100$  K), the RQM is likely the only mechanism that can generate the electron hyperpolarization needed to observed OPDNP.

The polarization generated by the RQM is determined by the rates  $k_{DQ}^{m,n}$  (see [eq 1](#), [Scheme 1](#) and [Appendix 2](#), [eq \(S11\)](#)), which depends on the ZFS and exchange interaction ( $J_{CR}$ ) between the chromophore and radical in the excited  $D_1-Q_1$  state.<sup>65,73</sup> Because of the solid-state nature of the sample,  $k_{DQ}^{m,n}$  would also depend on the orientation of the ZFS tensor with respect to the magnetic field. However, the ZFS ( $\sim 0.3$   $\text{cm}^{-1}$ ) is relatively small compared to the electron Zeeman term at high fields ( $>5$   $\text{cm}^{-1}$ ), and the exchange interaction. Thus, the manifestation of anisotropy in  $k_{dq}$  is expected to be weak. Furthermore, because the CR is dissolved in a glass matrix, all crystal orientations are present in the matrix; we thus used average RQM rates, as it is done in the liquid state:<sup>54</sup>

$$k_{DQ}^{mn} \propto \frac{\langle Q_1^m | H_{ZFS} | D_1^n \rangle^2}{\Delta E(Q_1^m, D_1^n)^2} \quad (1)$$

where  $m \in \left[-\frac{3}{2}, -\frac{1}{2}, \frac{1}{2}, \frac{3}{2}\right]$ ,  $n \in \left[-\frac{1}{2}, \frac{1}{2}\right]$ , and  $\Delta E(Q_1^m, D_1^n)$  is the energy difference between states  $Q_1^m$  and  $D_1^n$ . An estimate of  $k_{DQ}^{mn}$  at a low temperature was obtained by numerical fitting of the time-resolved EPR time profile of ANCOOT recorded at 100 K (see [eq S7](#)).

At high fields,  $k_{DQ}^{mn}$  can be tuned by adjusting  $\Delta E(Q_1^m, D_1^n) \approx 3J_{CR} + (m-n)\omega_{e,0}$  which is dominated by  $J_{CR}$  and the Larmor frequency of the electron  $\omega_{e,0}$ . The optimal value of  $J_{CR}$  to maximize the efficiency of the RQM can be determined through the selectivity factor,  $R_{D1}$ , which is the ratio of the sum of all the rates from  $Q_1$  levels to the  $D_1^{1/2}$  and the  $D_1^{-1/2}$  energy levels, which is written as follows:

$$R_{D1} = \frac{k_{DQ}^{Q_1^{+3/2}D_1^{+1/2}} + k_{DQ}^{Q_1^{-1/2}D_1^{+1/2}} + k_{DQ}^{Q_1^{-3/2}D_1^{+1/2}}}{k_{DQ}^{Q_1^{+3/2}D_1^{-1/2}} + k_{DQ}^{Q_1^{+1/2}D_1^{-1/2}} + k_{DQ}^{Q_1^{-3/2}D_1^{-1/2}}} \quad (2)$$

$R_{D1}$  quantifies how the spin populations redistribute itself within the  $D_1$  states, which ultimately dictate nitroxide hyperpolarization (see [Appendix 3](#) in the [SI](#)).  $R_{D1}$  was calculated at 18.8 T (a typical high field for MAS-DNP), and the resulting plot ([Figure 1B](#)) reveals a large RQM efficiency for  $|J_{CR}|$  in the range of 9–14  $\text{cm}^{-1}$ . It is maximum at  $\sim 12$   $\text{cm}^{-1}$  where  $\Delta E(Q_1^{-3/2}, D_1^{1/2}) = 0$ . In this case, the  $D_1^{1/2} \leftrightarrow Q_1^{-3/2}$  transition becomes the dominant RQM pathway, as the mixing rate constants originating from the other  $D_1-Q_1$  transitions are too small to have an effect (see [Figure S3](#)). This special case enables a selective enhancement of the population of  $D_1^{1/2}$  state and the generation of a very large electron hyperpolarization in the  $D_0$  state via the  $D_1 \rightarrow D_0$  pathway.

The model predicts an electron hyperpolarization level after laser irradiation,  $P_e$  (red curve, Figure 1B, see the SI for derivation), that can reach  $-1$  at the optimal  $J_{CR}$ ; however, it also shows that smaller exchange interactions (i.e.,  $4\text{--}8\text{ cm}^{-1}$ ) already yield significant hyperpolarization  $P_e \approx -0.5$ . Such exchange interactions can be attained in existing CR systems, given that earlier studies on the chromophore TEMPO showed  $J_{CR}$  values in the range of  $1\text{--}5\text{ cm}^{-1}$ .<sup>54</sup>

Hence, we conclude that solid-state optical electron spin hyperpolarization is possible at X-band frequencies (Figure 1). In addition, at high fields, strong electron hyperpolarization in the solid state can be obtained via an “RQM-only” mechanism, provided that the  $J_{CR}$  falls within a favorable range. In turn, this allows us to explore the potential of MAS-DNP using optically pumped hyperpolarized nitroxides.

**3.2. Optically Pumped CE for MAS-DNP.** From the mechanistic analysis of the photophysical hyperpolarization, it is now possible to assess how optical pumping could benefit CE under MAS-DNP. CE MAS-DNP requires the use of biradicals, that is, molecules with two coupled unpaired electrons in their ground state.

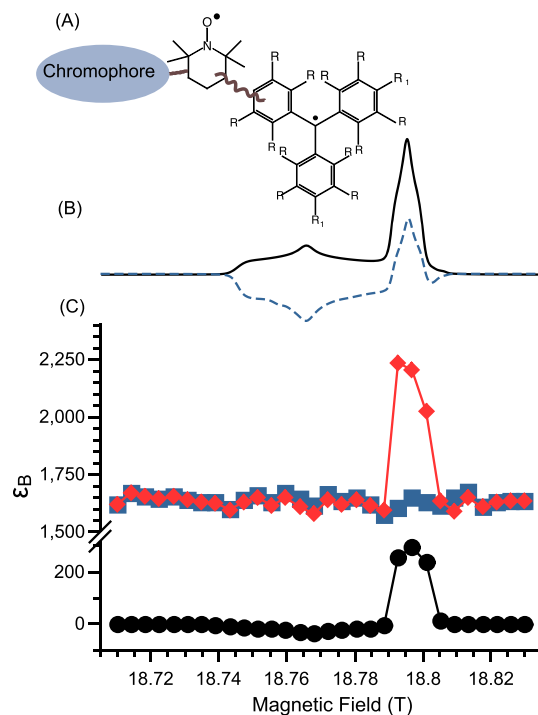
Scheme 2 shows an ideal CE biradical model with two interacting moieties ( $a$ ) and ( $b$ ) with electron Larmor frequencies,  $\nu_{a(b)}$ , and difference matching the Larmor frequency of the proximate nuclear spins,<sup>33,74,75</sup>  $\nu_n$ , such that  $|\nu_a - \nu_b| \sim |\nu_n|$ . When an electron spin polarization difference,  $|P_{e,a} - P_{e,b}|$ , is generated, this results in nuclear hyperpolarization.<sup>32,33</sup> Under DNP, it is the  $\mu w$  irradiation that generates  $|P_{e,a} - P_{e,b}|$  (Scheme 2A). The nuclear polarization,  $|P_n|$ , in a steady state, is related to  $|P_{e,a} - P_{e,b}|$  by<sup>32</sup>

$$|P_{e,a} - P_{e,b}| \geq |P_n| \quad (3)$$

If instead  $a$  is hyperpolarized via optical means, two other cases can be envisioned: (i)  $a$  is hyperpolarized, and  $b$  is at thermal equilibrium (Scheme 2B); or (ii)  $a$  is hyperpolarized, and  $b$  is saturated with a microwave irradiation (Scheme 2C).

To realize the concept presented in Scheme 2B, C, we need a molecule composed of a chromophore and biradical  $CR_a-R_b$ , where C and  $R_a$  are much closer to each other than C and  $R_b$ , such that in the excited state,  $|J_{CR_a}| \sim 5\text{--}14\text{ cm}^{-1}$  and  $J_{CR_b} \sim 0\text{ cm}^{-1}$ . In addition, in the ground state, the biradical,  $R_a-R_b$ , should have similar properties to typical biradicals that are used as MAS-DNP polarizing agents. For example, biradicals composed of trityl and nitroxide moieties are known to be efficient for MAS-DNP.<sup>21,74,76</sup> The three cases in Scheme 2 were simulated using a fictitious “ $CR_a-R_b$  = chromophore-TEMPO-trityl” molecule represented at the top of Figure 2 (herein, electron “ $a$ ” stands for the nitroxide and “ $b$ ” for trityl, unless otherwise specified).

Under MAS, this spin system undergoes fast energy-level anticrossings (or rotor events)<sup>32</sup> because the EPR spectra of trityl and TEMPO are anisotropic and therefore overlap with one another. This means that the nuclear hyperpolarization results from CE rotor events that transfer the polarization from the electron pair to the nuclei. These rotor events are active because of MAS, and it is important to note that they can perturb the nuclear spin polarization even in the absence of  $\mu w$  irradiation.<sup>77,78</sup> In addition, because the EPR spectra overlap, the dipolar/exchange rotor events are active. This type of rotor event is key for maintaining the electron polarization difference and ensures that the transfer of polarization to the nuclei has a constant sign, allowing for large polarization buildups.<sup>32,33</sup>



**Figure 2.** (A) Fictitious “Chromophore-TEMPO-Trityl”  $CR_a-R_b$  molecule. The wavy line represents unspecified bonds. (B) Simulated EPR spectra of  $CR_a-R_b$  in thermal equilibrium (solid black line) with laser irradiation assuming  $P_{e,a} = -0.25$  (dashed blue line). (C) Simulations of the MAS-DNP field profiles using the modified Box model for conventional MAS-DNP (black dots), optically hyperpolarized MAS-DNP (blue squares), and combined  $\mu w$  and optical irradiated hyperpolarization (red diamonds). In all simulations, the optical hyperpolarization leads to  $P_{e,a} \rightarrow -0.75$ , and for clarity, we plot  $\epsilon_B = -f(B_0)$  for the optical hyperpolarization case. Details about the spin system are given in the SI.

The complexity of this mechanism and its dependence on relaxation properties requires treatment with numerical simulations. Therefore, we used the “Box model,” which accounts for multiple three-spin systems {2 electron spins + 1 proton spin} distributed in a bounded space that has been extensively tested and validated.<sup>25,52,79</sup> This model treats the inter-biradical interactions to mimic those of a 10 mM biradical solution (see the SI), which faithfully represents the spin dynamics of the electrons.<sup>25</sup> The model is modified to account for optical hyperpolarization by assuming that under continuous (or pulsed) laser irradiation, nitroxide hyperpolarization is generated on a time scale faster than the MAS period, as determined by the RQM analysis (see the SI for details).

Figure 2C displays the nuclear spin polarization gain as function of the magnetic field (see the SI for calculation details) for conventional MAS-DNP (black dots), optical hyperpolarization (blue squares), and optical hyperpolarization combined with  $\mu w$  irradiation (red diamonds). The field profile calculated for conventional MAS-DNP spans the entire EPR spectra of the trityl-TEMPO (shown in Figure 2B) and has a sharp feature at the trityl Larmor resonant frequency.<sup>21,74,76</sup> In this case, the maximum polarization gain is  $\epsilon_B \approx 295$ , with the chosen simulation parameters (see the SI). On the other hand, the field profile in the presence of both optical and  $\mu w$  irradiation is very similar in shape but present now a staggering maximum value,  $|\epsilon_B| \approx 2200$ .

While this result is outstanding, the curve with blue squares, which reports  $\epsilon_B$  in the case of optical hyperpolarization (only) is also very encouraging: it predicts  $|\epsilon_B| \approx 1700$ . This is seven times higher than that in the conventional MAS-DNP case and also corresponds to the baseline of the optical and  $\mu w$  irradiation cases. This enhancement is the result of the CE mechanism being always active under MAS.<sup>23,33</sup> In the absence of  $\mu w$  irradiation, this can give rise to nuclear depolarization<sup>77,78</sup> for bis-nitroxides as  $|P_{e,a} - P_{e,b}|_{\mu w, \text{off}} \leq |P_{n, \text{eq}}|$ , while trityl-nitroxides do not depolarize significantly, that is,  $|P_{e,a} - P_{e,b}|_{\mu w, \text{off}} \approx |P_{n, \text{eq}}|$ . The centers of mass for the trityl and nitroxide EPR spectra are separated by the proton Larmor frequency, leading to little depolarization ( $\epsilon_B \approx 1$ ), as seen outside of the EPR resonant field (Figure 2C, black dots).<sup>21</sup> For CR<sub>a</sub>-R<sub>b</sub>, this separation of the centers of mass of the EPR spectra is key for efficient DNP with optical hyperpolarization, enabling the existence of an electron spin polarization difference. At  $B_0 = 18.8$  T and 100 K, the thermal equilibrium polarization of the trityl is  $P_{e,b}^{\text{eq}} \approx 0.12$ ; thus, with electron hyperpolarization of the nitroxide (Figure 2, blue square and red diamonds), we have the following relation:

$$|P_{e,a} - P_{e,b}^{\text{eq}}| \gg |P_{n, \text{eq}}| \quad (4)$$

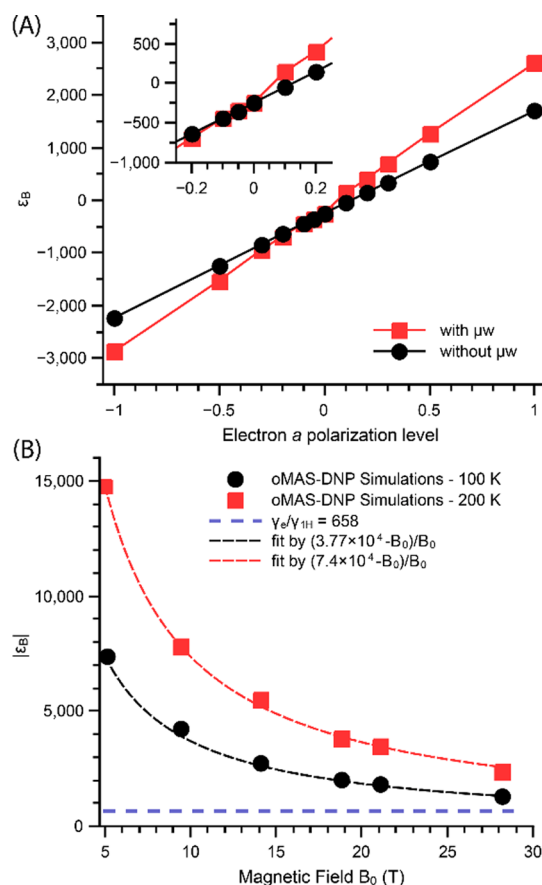
which explains the large  $|\epsilon_B|$ .

A broad range of scenarios were explored, which report  $\epsilon_B$  as a function of the nitroxide hyperpolarization level with and without  $\mu w$  (Figure 3A). Both sets of simulations display linear trends, with a steeper slope when biradicals are under  $\mu w$  irradiation (because of the larger  $|P_{e,a} - P_{e,b}|$ ). Enhancements  $|\epsilon_B|$  larger than the ratio of electron to proton magnetic moments ( $\sim 658$ ) can be achieved for  $P_{e,a} \rightarrow 0$  or  $P_{e,a} \rightarrow 2P_{e,b}^{\text{eq}} = 0.24$ . However, with the chosen parameters, nitroxide electron hyperpolarization must be lower than  $-0.3$  or higher than  $0.4$ , as shown in Figure 3A. These values are larger than the ideal case because  $|P_{e,a} - P_{e,b}|$  is affected by the interbiradical interactions. Under MAS, they tend to equilibrate polarization among all the trityls and the nitroxides contained in the Box,<sup>25,77</sup> thereby affecting the average electron spin polarization difference. This effect is spin-system dependent; therefore, different slopes (Figure 3A) are obtained for different electron relaxation times, magnetic fields, radical concentrations, and/or temperatures (see examples in the SI). The enhancement can also be calculated as a function of the magnetic field. For a given  $P_{e, \omega}$  using (see the SI for full derivation):

$$\epsilon_B = \frac{B_{\text{eff}} - B_0}{B_0} \quad (5)$$

where  $B_{\text{eff}}$  is an effective magnetic field.

Figure 3B displays  $|\epsilon_B|$  as function of the field with  $P_{e,a} \rightarrow -0.75$  and without  $\mu w$  irradiation, which confirms  $|\epsilon_B| > 658$ . The simulations carried out at 100 and 200 K perfectly fit with eq 5. At higher temperatures, the significantly larger  $|\epsilon_B|$  is the result of the lower equilibrium polarizations for both trityl electrons and the protons. This illustrates yet another potential benefit of MAS-OPDNP: better efficiency at higher temperature. Of course, this would depend on the relaxation times at higher temperature, where the CE mechanism may not be as efficient in terms of total nuclear polarization. Finally, the MAS-OPDNP simulations of a bis-nitroxide with a structure equivalent to "AMUPol"<sup>52</sup> are reported in the SI. While the EPR spectra of R<sub>a</sub> and R<sub>b</sub> have the same centers of mass, the



**Figure 3.** (A) Calculated MAS-DNP polarization gain,  $\epsilon_B$ , for a trityl-nitroxide biradical using the modified Box model, with  $\mu w$  irradiation (red squares), and without (black dots) as a function of nitroxide hyperpolarization. (B) Calculated  $|\epsilon_B|$  as a function of magnetic field without  $\mu w$  irradiation, assuming nitroxide hyperpolarization of  $P_{e,a} \rightarrow -0.75$  at 100 K (black dots) and 200 K (red squares). All other simulation parameters were kept constant. Dashed lines: best fits using eq 5.

resulting  $|\epsilon_B|$  is on the order of 200 at 14.1 T, which is very similar to the conventional MAS-DNP for AMUPol.<sup>52</sup>

#### 4. DISCUSSION

The low field (0.3 T) EPR experiments showed that significant electron spin hyperpolarization is achievable at 100 K with a chromophore covalently bonded to a nitroxide molecule and dissolved in a glass-forming matrix (toluene). The analysis of the hyperpolarization mechanism indicates that a very large exchange interaction between the chromophore and the nitroxide is needed to yield high electron spin hyperpolarization at a very high field, as the SO-ISC mechanism becomes weaker with field.<sup>58,72</sup> The strength of the interaction between C and R<sub>a</sub> must be of the order of the electron Larmor frequency to favor the RQM mechanism, that is,  $\sim 10$ – $12$   $\text{cm}^{-1}$ , which favors the selective transition  $D_1^{1/2} \leftrightarrow Q_1^{-3/2}$  at 18.8 T. In addition, the analysis of the hyperpolarization transfer mechanism and the numerical simulations of the MAS-OPDNP reveals that the success of this proposed concept requires the synthesis of new CR<sub>a</sub>-R<sub>b</sub> molecules possessing the appropriate exchange interactions in the excited state and in the ground state. For successful MAS-OPDNP experiment, the design of such a molecule must enable both a very strong C-R<sub>a</sub> ( $|J_{\text{CR}_a}| \sim 4$ – $12$   $\text{cm}^{-1}$ ) and a weak C-R<sub>b</sub> interaction ( $|J_{\text{CR}_b}| < 1$

$\text{cm}^{-1}$ ) in the excited state, while leading to significant  $R_a$ - $R_b$ , (i.e., a dipolar coupling  $D_{a,b} \sim 30$  MHz and an exchange interaction  $|J_{a,b}| \sim 10$ s MHz). This design remains possible. A large C- $R_a$  interaction in the excited state can be achieved by tuning the bridge between the chromophore and the nitroxide, that is, reducing the number of bonds and favoring resonant structures.<sup>59,80</sup> The coupling in between the nitroxide and the trityl (used in the simulations as an example) must be longer, typically of the order of 5–6 bonds.<sup>76</sup> For a successful MAS-OPDNP, the  $R_a$ - $R_b$  bridge should avoid conjugated bonds in order to prevent large C- $R_b$  couplings in the excited state. Current bridges used in MAS-DNP with trityl-Nitroxides<sup>20,76,81</sup> already possess the right properties, which illustrates the viability of the approach.

The chromophore used to hyperpolarize the nitroxide in the solid-state is only compatible with organic solvents and requires samples that are transparent in the near-UV region (355 nm). In the first development stages of the method, toluene could be used to prove the viability of the approach. The application to aqueous samples may be a challenge, but recent progress indicates that chromophore modifications could make it possible.<sup>44</sup> In addition, water-soluble anthraquinones can also be examined for the hyperpolarization generation.

Lastly, the sample irradiation could be achieved with a pulsed or a CW laser source. Setup using irradiation under MAS has been demonstrated experimentally in CIDNP experiments, using continuous wave UV sources and (UV transparent) sapphire rotors.<sup>38,39</sup> The approach could be adopted to carry out MAS-OPDNP at cryogenic temperatures using a commercial MAS-DNP probe to enable good temperature control.<sup>82</sup> A decay of chromophore (bleaching) could occur under CW UV irradiation, and thus, a pulsed laser should avoid both the decay of the chromophore yield high average electron spin hyperpolarization. The ANCOOT and Anq1pr have demonstrated experimentally a significant stability in toluene and pulsed laser irradiation, with very little decay over time which may make them good molecules to begin exploring MAS-OPDNP as a mixture with trityl molecules.

## 5. CONCLUSIONS

In conclusion, the MAS-OPDNP simulations demonstrate that even moderate nitroxide hyperpolarization could theoretically lead to  $|e_B| > 658$ . This new concept might also work at higher temperatures, which may be beneficial for samples that require higher peak resolutions.

Importantly, this innovative approach removes the need for expensive high power  $\mu\text{W}$  sources and “sweepable” high-field NMR magnets. Instead, MAS-OPDNP would rely on much more affordable high-power lasers that are currently commercially available and sample spinning. Finally, the MAS-OPDNP concept has the potential to be a paradigm shift for high-field MAS-DNP, which will have broad impacts on the characterization of numerous materials and biological molecules.

## ■ ASSOCIATED CONTENT

### SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpca.2c01559>.

RQM numerical simulations, the experimental details of the low field optical hyperpolarization, and the numerical model of the MAS-DNP simulations (PDF)

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### Notes

The authors declare no competing financial interest.

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