Rapidly enhanced spin polarization injection in an optically pumped spin ratchet

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Rapid injection of spin polarization into an ensemble of nuclear spins is a problem of broad interest, spanning dynamic nuclear polarization (DNP) to quantum information science. We report on a strategy to boost the spin injection rate by exploiting electrons that can be rapidly polarized via high-power optical pumping. We demonstrate this in a model system of Nitrogen Vacancy center electrons injecting polarization into a bath of $^{13}\text{C}$ nuclei in diamond. We innovate an apparatus with thirty lasers to deliver >20W of continuous, nearly isotropic, optical power to the sample with only a minimal temperature increase. This constitutes a substantially higher power than in previous experiments, and through a spin-ratchet polarization transfer mechanism, yields boosts in spin injection rates by over two orders of magnitude. Our experiments also elucidate speed-limits of nuclear spin injection that are individually bottlenecked by rates of electron polarization, polarization transfer to proximal nuclei, and spin diffusion. This work demonstrates opportunities for rapid spin injection employing non-thermally generated electron polarization, and has relevance to a broad class of experimental systems including in DNP, quantum sensing, and spin-based MASERs.

Introduction – The injection of polarization into an ensemble of nuclear spins is a task of central importance in a variety of contexts. Not only is it the basis for dynamic nuclear polarization (DNP) [1,2], but it is also important for the initialization of spin-based quantum information processors [3–6], quantum sensors [7–9], and in emerging applications in spintronics [10–12]. Critical to such applications is the rate at which polarization can be injected, measured, for instance, in terms of total angular momenta injected per unit time. For DNP applications, this rate ultimately determines the possible throughput of hyperpolarized spectroscopy and imaging [13].

The goal of this paper is to demonstrate the potential for enhanced rates of spin injection employing non-thermally generated electron polarization [10,14,15]. We focus on the central spin system as in Fig. 1A, reflective of the scenario encountered in DNP, employing a model system of optically polarizable Nitrogen Vacancy (NV) center electrons (labeled $e$) in diamond and considering polarization transfer to lattice $^{13}\text{C}$ nuclei ($n$) [16,17].

Considering Fig. 1A, the buildup of bulk nuclear polarization proceeds through a relayed process and the rate of spin injection is determined as an interplay between three rates: (i) the rate at which the electron polarization is generated, $k_e$, (ii) the rate of $e\rightarrow n$ polarization transfer to proximal nuclei, $\nu_r$, and (iii) nuclear spin diffusion, $\nu_d$, that serves to transmit polarization over long distances in the lattice [18,19]. In thermal DNP settings, $k_e\approx T_1^{-1}e$ is system specific, cannot be controlled, and can be relatively slow at low temperatures [20–22]; likewise $\nu_r$ is constrained by the available microwave (MW) power at high magnetic fields [23–25]. In contrast, in optical DNP, $k_e$ is set by laser intensity, potentially allowing access to the $k_e\gg T_1^{-1}e$ regime wherein source polarization can be rapidly generated. Simultaneously, optical $e$-polarization permits DNP at low fields where high MW powers are readily accessible. This in turn portends rapidly transmitting the $e$-polarization to nuclei via high power MWs to significantly enhance the hyperpolarization rate.

A key contribution of this paper is an innovation that delivers high optical power continuously to the electrons, allowing us to approach the $\nu_r\gg T_1^{-1}e$ regime. Time-averaged optical power here (>20W) is substantially higher than previous experiments (see [26] for comparison). At low fields, we demonstrate an approach to increase the polarization injection rate through a “lock-step” increase in laser and MW power. We identify hyperpolarization speed-limits by delineating experimental regimes where each of the three rates in Fig. 1A individually bottleneck polarization injection. Ultimately, we show high-power optical DNP can yield significant gains in injection polarization rate, boosted by as much as two orders of magnitude compared to more con-
ventional regimes. Rapid hyperpolarization obtained here opens avenues for quantum sensors (e.g. gyroscopes [27,28] and spin sensors [29]) constructed out of hyperpolarized diamond nuclear spins. The approach here is also readily generalizable to other experimental systems, including optically pumped triplet systems for DNP [30,31] and MASERs [32,33].

System – In these experiments, we employ a $\approx16\text{mm}^3$ single-crystal sample with $\approx1\text{ppm}$ NV concentration and natural abundance $^{13}\text{C}$ (Fig. 1A). The inter-NV spacing is $\approx24\text{nm}$ [34,35], and $^{13}\text{C}$ lattice density is $\approx0.92/\text{nm}^3$. $T_1\approx5\text{min}$ sets the overall polarization memory time for the system [35].

In what follows, we refer to the incident optical and MW power in Watts as $\eta_o$ and $\eta_r$ respectively. These are related to $\{\kappa_e, \kappa_r\}$ in Fig. 1A, but denote experimentally employed parameters. NV centers are optically polarized to the $m_z=0$ state, yielding an $e$-polarization, $P_e(t)=1-\exp(-t\kappa_e)$ (Fig. 1B), assuming a monoeponential rate constant $\kappa_e$. In reality, $\kappa_e=c_e\eta_e$ is approximately proportional to the optical power applied. The absolute $e$-polarization obtained depends on several factors (e.g. interconversion between NV charge states [36,37]) and is difficult to precisely quantify.

Optically generated polarization obviates the need for high magnetic fields for DNP. Lower fields come with significant advantages, such as the availability of high MW powers at low frequencies. DNP is excited at $B_0=36\text{mT}$ through a mechanism involving CW optical and swept MW irradiation (Fig. 1B) for period $T$ [38,39]. Each sweep event injects polarization into $e$-proximal nuclei, akin to a “ratchet” (Fig. 1C). Bulk polarization is interrogated via RF induction at 7T. We employ pulsed spin-lock readout [40–42] that permits long $^{13}\text{C}$ precession lifetimes exceeding 100s, with a decay constant $T_2^\ast>20\text{s}$ [43]. Signal is accumulated for the entire period and sampled every 1ns in windows between the pulses. As a result, we obtain high measurement fidelity, with integrated SNR as high as $10^8$ per shot [43]. This high sensitivity plays an important role in unraveling factors that affect polarization injection rates.

Ratchet driven polarization – To elucidate the hyperpolarization mechanism, consider that the MW sweeps have an instantaneous frequency, $\omega_{MW}(t)=B_0 \omega_0 + f_0 - B/2$ (Fig. 1B), where $B$ is the sweep bandwidth around $f_0$, the electronic spectral center, and $\omega_r$ is the sweep rate. $\omega_r$ plays a key role in determining the ultimate rate of hyperpolarization buildup in the nuclei (Fig. 1E). Every sweep event transfers a finite amount of polarization, and the total number of sweeps, $T_\omega$, is curtailed by the nuclear $T_1\approx5\text{min}$. Ideal ratchet operation involves maximizing $\omega_r$ while maintaining high polarization transfer efficiency $\eta_\omega$ per sweep. Optimal operation occurs when the sweep rate $\omega_r=\omega_{opt}$, and can be derived by elucidating how the polarization buildup rate $P(\omega_r)$ depends on the interplay of rates in Fig. 1A.

Consider that the $e-n$ Hamiltonian for $N$ nuclei (Fig. 1A) in the rotating frame at field $B_0$ has the form [44],

$$H(\omega_{MW})=(\Delta-\gamma_e B_0)S_z^2+\Omega_e S_z+\Omega_n S_x+\sum_{j=1}^{N} (\omega_j^{(0)} P_0 I_{z,j} + \omega_j^{(1)} P_1 I_{z,j}^\dagger)$$

where $S(I)$ refer to electron (nuclear) operators, and $\gamma_{e,n}$ are the respective magnetogyric ratios. The first two terms denote the NV zero-field splitting ($\Delta=2.87\text{GHz}$) and Zeeman field; $\Omega_e$ is the $e$-Rabi frequency ($\Omega_e=c_e \eta_e$) proportional to the MW power applied, and we assume an NV axis aligned with $B_0$ (along $z$). The last term describes nuclear field in either electronic manifold – $P_0$ and $P_1$ are projection operators in the $m_z=0$ and $m_z=1$ manifolds, and the nuclear resonance frequencies herein are $\omega_j^{(0)}$ and $\omega_j^{(1)}$ respectively [44]: $\omega_j^{(0)}=\omega_n+\gamma_n B_0 A_j^\dagger$, and, $\omega_j^{(1)}=[(\omega_n+A_j^\dagger)^2+(A_j^\dagger)^2]^{1/2}$, where $\omega_n=\gamma_n B_0$ and $A_j=J_z^\dagger + J_x^\dagger$ is the hyperfine coupling.
Spin ratchet polarization transfer is simplest to illustrate for a single $e-n$ system [44,45]. Diagonalization leads to four Landau-Zener level anti-crossings (LZ-LACs), with energy gaps, $\varepsilon_1 \approx \varepsilon_{n,\eta_r}$ and $\varepsilon_2 \approx \frac{2\varepsilon_{e,\eta_r} \Delta t}{\omega_{opt} + A_1}$ (see Fig. 1D), such that $\varepsilon_2 < \varepsilon_1$. Swept MWs cause a traversal through this LZ-LAC cascade. Its action can be evaluated under simplifying approximations that capture the experiments [44]: (i) LZ-LACs are assumed to be traversed sequentially, and, (ii) $e$-repolarization is assumed to occur at the start of every sweep event. This entails negligible laser action at the LZ-LACs, and is valid when $B \gg \varepsilon_{1,2}$, as in our experiments. Hyperpolarization buildup occurs because the energy gaps are conditioned on the nuclear state; traversals through the LZ-LACs are differentially adiabatic or diabatic, leading to a population bias towards one nuclear state (here $[\downarrow]$). Indeed, population bifurcation at a LZ-LAC is set by its adiabaticity and captured by respective tunneling probabilities $T_{1,2}(\omega_r) = \exp(-\varepsilon_{1,2}^{2}/\omega_r B)$ (Fig. 1C). Hyperpolarization occurs when sweep rates $\omega_r$ are such that $T_1 \rightarrow 0$ (adiabatic) and $T_2 \neq 0$ (diabatic) [44]. The rate of polarization buildup is then (26)

$$\dot{P}(\omega_r) \approx \omega_r \left[ 1 - \exp \left( -\frac{\varepsilon_{e,\eta_r}}{\omega_r} \right) \right] \left[ 1 - (T_2) \left( 1 - (2T_1 - 1)^2 \right) \right]. \quad (1)$$

The first term in square brackets is the rate of $e$-polarization and the last term captures the $e-n$ polarization transfer efficiency per sweep. We identify an optimal rate $\omega_{opt}$ arising when $d\dot{P}/d\omega_r = 0$. Points in Fig. 1E show a typical measured DNP profile $P(\omega_r)$, from where $\omega_{opt}$ is easily identifiable. Solid line here is a fit to Eq. (1).

It is intuitive to see why an optimal rate $\omega_{opt}$ should exist. More rapid sweeps (high-$\omega_r$) can allow faster ratchet operation, but come at the cost of (i) reduced electron polarization and (ii) lower transfer efficiency per sweep because the differential adiabaticity in Fig. 1D is compromised. Indeed, at very high-$\omega_r$, $T_1 \approx T_2 \approx 1$, and $\dot{P} \rightarrow 0$. Therefore $\omega_{opt}$ reflects an overall speed-limit for $e-n$ polarization transfer, and defines the rate at which the ratchet (Fig. 1C) should be operated. We note connections to recent work concerned with speed-limits of quantum state transfer in qubit networks [46–50]. The physics of direct $e-n$ polarization transfer is essentially unchanged from Eq. (1) even for large $N$ [44, 51]; however, since experiments primarily probe bulk nuclei, there is a non-negligible role from spin diffusion.

Importantly, Eq. (1) suggests that the rate of polarization transfer, encoded in $\omega_{opt}$, can be enhanced through a simultaneous increase in laser and MW power – higher-$\eta_r$ allows faster $e$-repolarization, and higher-$\eta_r$ permits faster sweeps while maintaining differential adiabaticity. This is the key insight we exploit in this paper. In the ultimate limit, ratchet performance (encoded by $\omega_{opt}$) is just limited by spin diffusion.

Enhanced optical excitation – Spin injection rates can potentially exceed that of conventional DNP because optically polarizable electrons can be polarized faster than $T^{-1}_e$ and rapidly transferred to proximal nuclei at low field. Achieving sufficient optical power to access this regime, however, is a technical challenge. Previous experiments with NV centers, both for DNP and quantum sensing, were predominantly in the $\eta_{opt} < 5$W regime (see SI [26]) and limited by sample heating [52–55]. In this work, we develop a novel laser delivery system that enables continuous sample irradiation at $\eta_{opt} > 20$W. To our knowledge, this constitutes the highest time-averaged power employed for $e$-polarization (see comparison in SI [26]). There have been several reports of DNP with pulsed lasers [56,57]. While possessing higher peak power, they entail long dead times ($\gg T_{1e}$), where electrons are not being polarized (see [26]). In contrast, the CW optical excitation here yields continuous $e$-repolarization, and is advantageous for DNP with electrons with broad ESR spectra [39]. Furthermore, lower peak power injection here allows more efficient heat diffusion and time-averaged power before sample damage thresholds are reached.

The apparatus (shown in Fig. 2A) consists of a 3D printed carbon fiber dome-shaped structure (“laser dome”) that houses 30 diode lasers ($\approx 0.8$W each) delivered via multimode fibers (beam diameter $\approx 4$mm). We exploit relaxed requirements on optical mode quality, polarization, and stability necessary for $e$-polarization. This enables using an array of low-cost diode lasers to generate a high total optical power. The fibers are pressure fit into grooves that geometrically align towards the dome center (Fig. 2C). The almost isotropic excitation pattern uniformly illuminates each of the sample facets and the exact beam arrangement is staggered for minimal overlap with the MW excitation coil (zoomed in Fig. 2D). It also allows a significantly larger sample volume to be irradiated compared to previous ap-
Fig. 4. Enhancing rate of polarization transfer at high laser and MW power. (A) DNP sweep rate profiles $P(\omega_r)$ (see Fig. 1E) for different regimes of MW power (I-IV) $\eta_r=0.1\text{W-53W}$, in each of which laser power is varied $\eta_e=0.4\text{W}$ (an attenuated laser) - 20.8W (26 lasers) (see colorbar). Here polarization time is 20s. Plots are shown against $\omega_r^{1/2}$ (upper axes denote $\omega_r$). Solid lines are fits to ratchet model (Eq. (1)). Corresponding values of maximum signal and $\omega_{\text{opt}}$ are shown in Fig. 5. (B) Normalized curves in (A) focusing on $\eta_e=0.4\text{W}$ and 20.8W. Dashed lines elucidate optimal rates $\omega_{\text{opt}}$ (extended to (A)). Shifts are denoted by arrows. **(I-II)** At low MW powers, clustering of curves in (A) show that $\omega_{\text{opt}}$ changes slowly with $\eta_r$, and yield little signal gain (see Fig. 5B-C). **(III-IV)** At high MW powers, increasing $\eta_r$ shifts $\omega_{\text{opt}}$ to higher frequencies. Profiles in panels (B)(iii-iv) are almost identical, indicating that beyond a threshold, increasing MW power does not result in increasing $\omega_{\text{opt}}$ (see Fig. 5C).

Large optical powers require the ability to mitigate sample heating. We designed an in-situ heat exchanger that efficiently ejects heat while keeping the sample free from motion. Fig. 3A describes its operation. The sample is held in a test tube surrounded by $\approx$4mL water. Thermal energy injected into the diamond is rapidly dissipated to the water, which serves as a heat sink. The water is kept at a stable temperature by flowing cool nitrogen gas ($\approx$20$^\circ$C at inlet) across the test tube. The gas is delivered from slits built into the neck region of the laser dome (blue arrows in Fig. 3A). Nitrogen flow rate is calibrated so the water temperature is $\approx$9$^\circ$C when lasers are off. Heat exchange exploits the excellent thermal conductivity of diamond (2200Wm$^{-1}$K$^{-1}$) and the large heat capacity of water for efficient thermal dissipation (red arrows in Fig. 3A). The benefit of this relayed heat transfer strategy is that the cold gas does not contact the sample directly, and the sample volume can be enclosed – an advantage for shuttling to high field for detection [61].

Heat exchanger performance is found to be highly effective. Fig. 3B-C depicts measured temperature buildup in the sample and surrounding fluid under 120s continuous irradiation at different optical powers. After 120s, the lasers are turned off, and the temperature dissipation is again monitored. Even at sustained 24W optical power (an intensity of $\approx$0.19kW/cm$^2$) employing thirty lasers, the (asymptotic) steady-state temperature is less than 30$^\circ$C and no sample damage is observed. Fig. 3D plots the steady-state temperatures for different powers. From the buildup rate, we estimate that $\approx$50W power can be applied before system limits (related to water boiling) are reached.

Lockstep polarization increase – In the ratchet model without spin diffusion, $\omega_{\text{opt}}$ plays a key role as a proxy for the rate of nuclear spin injection. We now demonstrate that high power optical delivery via the apparatus in Fig. 2, allied with simultaneous high MW power, can yield significant enhancements to $\omega_{\text{opt}}$, and thereby, spin injection rates. In parallel, we quantify the speed-limits for bulk polarization buildup as an interplay of
Fig. 5. Speed limits for polarization transfer. (A-B) Maximum signal in Fig. 4 plotted on a (A) linear and (B) logarithmic scale. Curves correspond to $\eta_e$-regimes studied. Combined optical-MW $\eta_e$-$\eta_r$ power increase yields a $>200$-fold boost in hyperpolarization level. (C) Optimal sweep rates $\omega_{\text{opt}}$ extracted from Fig. 4 for increasing $\eta_e$, at different MW power regimes (I-IV). Points are extracted $\omega_{\text{opt}}$ values, while lines are linear fits. (I) At low MW power $\eta_r=0.1W$, increasing $\eta_e$ yields an almost flat response due to slow polarization transfer away from NV centers. (II-III) Increasing MW power relieves this bottleneck, reflected in the increased slope. (IV) Increasing MW power further yields no marked change in $\omega_{\text{opt}}$ slopes, indicating a speed-limit due to spin diffusion. (D) Spin ratchet simulations similar to (C) assuming a maximal 10% e-polarization polarization. slopes continually increase with $\eta_e$ due to absence of spin diffusion. (E) Speed up of ratchet $d\omega_{\text{opt}}/d\eta_e$ obtained from slopes in (C). Plateau at high MW power indicates a spin diffusion bottleneck. (F) Signal increase with MW power. Vertical slice of data in (A) at $\eta_e=20.8W$. We observe the signal beginning to plateau with increasing MW power.

the rates discussed in Fig. 1A. As such, this is complementary to recent work studying polarization transfer rates in conventional DNP [62-64]. Consider first power in Fig. 4A. We measure sweep rate dependent DNP profiles $P(\omega_r)$ with $T=20s$ similar to Fig. 1E, but at several regimes of optical $\eta_e$ and MW $\eta_r$ power. In particular, we consider four regimes of MW power between $\eta_r=0.1-53W$, and for each, measure $P(\omega_r)$ profiles for different effective optical powers $\eta_e=0.4W$ (an attenuated laser) - 20.8W (26 lasers). This is estimated here by measuring the effect of each laser individually on the $^{13}$C hyperpolarization signals [26]. Upper and lower axes in Fig. 4A denote $\omega_r$ and $\omega_r/2$ respectively. Solid lines are fit to Eq. (1). Optimal sweep rates $\omega_{\text{opt}}$ (dashed lines) are determined from maxima of the fitted curves. To improve clarity, lower panels (Fig. 4B) focus on normalized profiles at $\eta_e=0.4W$ and 20.8W. Increasing optical power $\eta_e$ leads to a rightward shift in $\omega_{\text{opt}}$ (arrows), and the magnitude of the shift apparently increases at higher MW powers.

We also briefly introduce Fig. 5 which will aid the discussion that follows. Fig. 5A-B show obtained maximal polarizations against $\eta_e$ for the MW power regimes (colorbar) considered, plotted on a linear (Fig. 5A) and logarithmic (Fig. 5B) scale. Signal here is measured at $\omega_{\text{opt}}$. Solid lines are guides to the eye. In a complementary manner, points in Fig. 5C display the extracted optimal rates $\omega_{\text{opt}}(\eta_e)$ for different MW powers. Solid lines are linear fits. Fig. 5E, in turn, plots the slope of these lines, $\sim d\omega_{\text{opt}}(\eta_e)/d\eta_e$, while Fig. 5F plots the polarization for different MW powers at $\eta_e=20.8W$ (vertical slice in Fig. 5A). A combined view Fig. 4-Fig. 5 allows the ability to correlate $\omega_{\text{opt}}$ to the absolute spin injection rates into the nuclei.

We now systematically consider factors setting $\omega_{\text{opt}}$ from left-to-right in Fig. 4, starting from the low-MW power regime I ($\eta_e=0.1W$). This regime relates to the situation in high-field DNP where MW power is low due to technological constraints. In Fig. 4A(i), we observe the DNP profiles clustered at $\omega_r=50$-120Hz. Increasing optical power only weakly increases $\omega_{\text{opt}}$ (see Fig. 4B(i) and Fig. 5C), and there is little increase in hyperpolarization signal. This indicates a $k_e$ induced speed-limit set by adiabaticity constraints – in the ratchet picture in Fig. 1D, the energy gaps are small and sweep rates $\omega_r$ required to satisfy adiabaticity are slow. Increasing optical power therefore yields no significant increase in nuclear polarization levels (see Fig. 4A(i)). We observe in fact, a slight decrease in signal at high $\eta_e$ (see also Fig. 5B), associated with the rightward shift in $\omega_{\text{opt}}$ in Fig. 4B(i). This signal drop is beyond the scope of Eq. (1) and challenging to model. We hypothesize it arises because the electrons are depolarized multiple times during each MW sweep event, including
at the LZ-LACs, making polarization transfer less efficient. Simultaneously, we observe oscillations in the $P(\omega_e)$ profiles in the high $\eta_e-\eta_r$ regime.

Now upon increasing MW power seven-fold (Fig. 4A(ii)) to regime II with $\eta_r=0.7W$, there is a larger increase in $\omega_{\text{opt}}(\eta_r)$ with optical power. This rightward shift in Fig. 4A(ii) manifests as an increased slope in Fig. 5C(II). Intuitively, higher $\eta_r$ yields larger energy gaps in Fig. 1D and affords faster sweep rates. When the optical powers are low, electron polarization is not produced rapidly enough at the NV source. Increasing $\eta_r$ therefore relieves this $\kappa_\nu$ bottleneck. From Fig. 5E, $\omega_{\text{opt}}$ in regime II increases 2-fold with respect to regime I, and there is a simultaneous ~10x increase in polarization (Fig. 5B). However, clustering of $P(\omega_r)$ profiles in Fig. 4A(ii), and slow growth in Fig. 5C(II), still suggests that $\kappa_r$ limits the rate of polarization transfer.

Fig. 4B(iii) considers a further 10-fold increase in MW power (regime III). Here a rightward shift in $\omega_{\text{opt}}$ is clearly evident with increasing optical power, and spin-ratchet operation is rapid, evidenced by the increased slope in Fig. 5C(III). Higher $\eta_r$ allows faster sweeps due to weaker adiabaticity constraints, and $\eta_r$ can be simultaneously boosted to increase the rate of source $e$-polarization, yielding a lockstep $\kappa_\nu-\kappa_r$ increase in hyperpolarization rate. The concomitant signal increase is evident in Fig. 5A-B. We also note that the resulting maximal rates $\omega_{\text{opt}}$~0.65kHz approach, and potentially exceed, the thermal rate $T_{1e}^{-1}$~0.2kHz expected in this sample.

One might expect that a further increase in MW power will continue to yield such gains. This is shown in simulations in Fig. 5D where we model direct $e\rightarrow n$ polarization transfer without spin diffusion. Interestingly, however, we experimentally observe that a subsequent increase in MW power to $\eta_r=53W$ (regime IV) provides no significant increase in $\omega_{\text{opt}}$ (see Fig. 4A-B(iv)). This is also reflected in Fig. 5C, where $\omega_{\text{opt}}(\eta_r)$ manifests as a series of overlapping lines beyond $\eta_r=7W$. This plateauing of rates is also evident in Fig. 5E. Correspondingly, the relative signal increase in Fig. 5A-B begins to slow down (see Fig. 5F). Overall this points to the presence of a third speed-limit, which we ascribe to be due to spin diffusion $\kappa_{dl}$. Here polarization is rapidly transferred from the NV center to proximal $^{13}C$ nuclei, but is limited in its ability to reach the bulk nuclei. Indeed, Fig. 5B-C demonstrates that while e-polarization rates increase with $\eta_r$, nuclear spin injection is ultimately limited by spin diffusion. As such, spin injection can be considered optimally rapid in this regime.

Finally, let us quantify spin injection gains from our strategy with respect to more conventional approaches. We attempt to make two comparisons: first, gains with respect to typical optical DNP experiments (see SI [26]), and second, gains with respect to the regime typically employed in high-field DNP. For the first case, consider spin injection with two optical powers, $\eta_e=0.4W$ and 20.8W in regime IV. The former is representative of powers employed previously for optical DNP [56,57] (see [26]), and the latter corresponds to the use of a 26 laser array here. Fig. 6A shows the respective polarization buildup curves. The steeper polarization growth in the latter is evident. Fig. 6B shows the corresponding $^{13}C$ NMR spectra at $T=90$s, wherein an $\approx$13-fold increase in signal is observed. Narrow spectral linewidths $\approx 16mHz$ here are due to slow spin-lock decays [43]. To focus on e-proximal polarization injection separately from strong effects from spin diffusion, Fig. 6C instead considers the small-time regime ($T<0.6s$). Polarization buildup is approximately linear in this regime; colorbar shows different optical powers employed. Corresponding slopes (Fig. 6D) permit quantification of absolute polarization injection rates ($%/s$) by comparing against the thermal polarization at $T=7T$ ($10^{-5}$). Fig. 6D demonstrates that spin injection rate scales approximately linearly with optical power, arising from the increased rate of source e-polarization $\kappa_r$ at the NV center sites. Indeed, the sustained high-power optical delivery possible via Fig. 2, yields a $\approx$179-fold increase in polarization injection with higher power pumping. In this case, measure a linearized bulk injection rate of $\approx 0.016%/s$ averaged over the sample.

For the second comparison with respect to conventional DNP, consider two MW powers, $\eta_r=100mW$ and $\eta_r=53W$ (regimes I and IV respectively) at $\eta_e=20.8W$. The former is representative of typical MW powers in high-field DNP (without gyrotrons). From the peaks of the corresponding traces in Fig. 4A, we observe an $\approx$168-fold increase in polarization in the latter case (see Fig. 5F). Overall, while a precise comparison between disparate experimental systems is difficult, data in Fig. 4 and Fig. 6 indicate that harnessing non-thermal $e$ polarization can yield spin injection gains by more than two orders of magnitude over conventional approaches.

**Outlook** – One can imagine extending the work here in a number of promising directions. First, the experiments here illustrate the strengths of non-thermally polarized electrons for DNP. $e$-polarization can be replenished at a rate $\kappa_r>T_{1e}^{-1}$, and does not require cryogenic high-field conditions (unlike Boltzmann-based DNP). This allows access to low-field regimes where MW power can be plentiful. Simultaneously applied high optical and MW power can yield bulk spin injection rates ultimately limited by only spin diffusion. Similar arguments can be extended to other non-thermally generated DNP approaches, including with parahydrogen [13,66,67]. The speed limits of spin injection elucidated here are relevant for applications in quantum information transfer and memories.

Second, the strategy for high-power optical illumination and thermal management developed here is extensible to other systems, including organic triplet molecular systems, and UV generated non-persistent radicals [57,68]. We envision applications to $e$-spin MASERs [32,33], and quantum sensors with $e$-spin ensembles [58,69], where reaching higher optical powers is the primary factor limiting magnetometer sensitivity [55]. Finally, the rapidly injected spin polarization here projects onto applications that exploit hyperpolarized $^{13}C$ spins as quantum sensors [29], leveraging their long lifetimes in the laboratory [35,70] and rotating frames [42,43]. This includes magnetometers [29,51], gyroscopes [27,65,71], sensors for dark-matter searches [72,73], and as RF imaging agents [74].

**Conclusions** – In conclusion, we have demonstrated the ability to rapidly inject spin polarization into a lattice of nuclear spins via optically polarized electrons under simultaneously applied high-power optical and MW irradiation. In the process, we elucidated speed-limits that bottleneck bulk polarization transfer in various regimes, and showed that high power excitation can yield gains in spin-injection rate that exceed two orders of magnitude. Our work informs on interesting new opportunities afforded by non-thermally polarized electrons for DNP and quantum sensing.

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Supplementary Information

Rapidly enhanced spin polarization injection in an optically pumped spin ratchet

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Fig. S1. Single-spin ratchet. (A) Landau-Zener level anti-crossings (LZ-LACs) for a system of an NV coupled to a single \(^{13}\)C nucleus (shown in inset) with A\(_{||}>0\). Two pairs of energy gaps are visible, the large gaps being set by the electronic Rabi frequency. The two electronic manifolds are marked. Optical pumping resets the system polarization to the \(m_s=0\) manifolds, and initially the system is unpolarized, yielding equal populations in either of the \(|0,\downarrow\rangle,|0,\uparrow\rangle\) states. Hyperpolarization can be excited under a MW sweep from low-to-high frequency; optimal rate of the sweep \(\omega_{\text{opt}}\) is determined by conditional traversals through the four LZ-LACs. (B) LZ-LAC locations extracted from (A), and arranged in a checkerboard ("Galton board" [51]) of energy and frequency. Population bifurcation as the LZ-LACs are encountered under the MW sweep is captured by the tunneling probabilities \(\tau_{1,2}\). Starting (red) and ending (green) nuclear states are marked.

I. DERIVATION OF POLARIZATION TRANSFER RATE FOR SINGLE-SPIN RATCHET (EQ. (1))

We present here a derivation of the spin ratchet polarization rate (Eq. (1) in the main paper). For more details on the theory, assumptions and generalizations to large \(N\), we refer the reader to Ref. [44]. Consider Fig. S1, we show a single spin ratchet (\(N=1\)) with four Landau-Zener level anti-crossings (LZ-LACs) in the rotating frame of the MWs, here between states of the \(m_s=0\) and \(m_s=1\) manifolds. Upon a MW sweep, there is a traversal of this cascaded LZ-LAC structure from left-to-right. We make the following assumptions that help simplify the theoretical evaluation of traversals, but which are reasonable under the regime of the experiments: (i) the LZ-LACs are assumed to be hit sequentially so that their effects can be evaluated individually, (ii) the nuclear populations are assumed to start in the \(m_s=0\) manifold and bifurcate “down” or “right” upon encountering the LZ-LACs, and (iii) NV electronic (re)polarization is assumed to happen far away from the exact LZ-LAC points.

Consider a single traversal from left-right through the \(N=1\) LACs in Fig. S1, starting from populations restricted to the \(m_s=0\) manifold and ending with NV repolarization. The probabilities of the possible population evolutions are then,

\[
\mathcal{P}(|\downarrow\rightarrow\downarrow|) = (1-\tau_2) + \tau_0 T_1
\]

\[
\mathcal{P}(|\downarrow\rightarrow\uparrow|) = \tau_0 (1-\tau_1)
\]

\[
\mathcal{P}(|\uparrow\rightarrow\downarrow|) = \tau_2 (1-\tau_1) + 2\tau_1 (1-\tau_1) (1-\tau_2)
\]

\[
\mathcal{P}(|\uparrow\rightarrow\uparrow|) = \tau_1 \tau_2 + \tau_1 (1-\tau_2) + (1-\tau_1)^2 (1-\tau_2),
\]

where \(\tau_{1,2}\) here refer to the tunneling probabilities (Fig. S1B), and depend on the adiabaticity of the traversal through the respective LZ-LAC: for example, \(\tau_{1,2} = \exp(e^{\eta_{1,2}}/\omega_r B)\). Indeed, each term in the expressions above can be thought of as referring to a different trajectory through the LZ-LAC structure (schematically shown in Fig. S1B). For instance, there are two paths that constitute the term, \(\mathcal{P}(|\downarrow\rightarrow\downarrow|)\), corresponding to the probabilities of \(|0,\downarrow\rangle\rightarrow|0,\downarrow\rangle\) and \(|0,\downarrow\rangle\rightarrow|+1,\downarrow\rangle\) respectively. Now, in order to determine the nuclear hyperpolarization, we evaluate the difference in populations between the nuclear states at the end of the sweep,

\[
P = [\mathcal{P}(|\downarrow\rightarrow\downarrow|) + \mathcal{P}(|\uparrow\rightarrow\downarrow|)] - [\mathcal{P}(|\downarrow\rightarrow\uparrow|) + \mathcal{P}(|\uparrow\rightarrow\uparrow|)]
\]

\[
= (1-\tau_2) \left[1 - (2\tau_1 - 1)^2\right].
\]

Finally, Eq. (2) illustrates that hyperpolarization develops as a result of the differential adiabaticity of the traversals through the pairs of LZ-LAC conditioned on the nuclear state. The net hyperpolarization developed in time \(T\) has the form,

\[
P = \left[1 - \exp\left(-\frac{e\eta_i}{\omega_r}\right)\right] \cdot T \omega_r \cdot \left[1 - (2\tau_1 - 1)^2\right].
\]

where the first term encapsulates the starting electron polarization, the second term gives the total sweeps in time \(T\), and the last term is Eq. (2). We therefore refer to the mechanism as being a “spin-ratchet”, since each MW sweep event can be thought of as performing work to transfer a finite amount of polarization from the electronic spin to the directly coupled nuclei. While Eq. (1) is derived from the \(N=1\) case displayed in Fig. S1, it acts as a good approximation even at large \(N\) such as in the system in Fig. 1A. This generalization to large \(N\) is further detailed in Ref. [44]. Here, one can show that the system comprises a cascaded structure of \(2^N\) LZ-LACs, and evolution through them can be theoretically evaluated by mapping the dynamics to the operation of a “Galton-board” [44].

II. COMPARISON TO LITERATURE

The table in Fig. S2 compares laser parameters of our work with other recent experimental studies on DNP [17, 56, 57, 75] and \(e\)-spin MASERS [32]. Previous literature has explored both pulsed and CW light sources at a variety of different wavelengths. We see from this table that there are several advantages to our approach. First, we employ low-cost diode 520nm diode lasers that can be arrayed together to create a large continuous optical excitation power, as opposed to a singular, more expensive laser.
This also exploits the very relaxed requirements on laser mode quality required for $e$-polarization. We are able to apply significantly higher time-averaged optical power than most previous experiments. Our data (Fig. 3B) indicates that scaling up to even higher power can be relatively easily accomplished. Pulsed laser systems can deliver larger peak power but are limited by slow repetition rates. They also make the sample more susceptible to damage from intense high power pulses [32].

### III. HYPERPOLARIZATION SETUP

Fig. S3 shows the overall hyperpolarization setup, containing the lasers employed for DNP, along with thermal management systems and a Helmholtz coil for application of the polarization field. The setup consists of a three-sided panel design, each with total edge length 18in. and constructed in a compact manner for positioning under a 7T magnet. The laser diodes were mounted on the interior panels, and driver modules on the exterior panels as shown in Fig. S3A-B. This allows the use of short 0.5m fibers while preventing tight bends.

The panels were designed in a manner that allows the laser diodes and drivers to be easily accessible. Each exterior panel holds up to 12 driver modules (Lasertack PD-01289), and each interior panel holds the corresponding Lasertack 520nm laser diodes. The structure can mount laser diodes and modules on up to four sides (allowing a total of 32 lasers). These panels are fastened onto 8020 aluminum frames and can easily screw on or off without having to remove any other parts of the structure. The laser diodes are electrically connected to the driver modules by snap-on connectors. For our experiments we mounted a total of 30 lasers ($\approx$0.8W each) onto three panels.

An Arduino Leonardo microcontroller mounted on each panel, controls the laser diodes. Each microcontroller connects to a central computer via USB serial communication. This permits the ability to turn on or off any combination of lasers with individually set times and duty cycles that can be dynamically reprogrammed.

A large 12in. Helmholtz coil surrounds the dome at the center of the setup. The dome and coil require precise vertical positioning relative to the 7T magnet that is difficult to calibrate ex-situ. To ease in-situ calibration we constructed a multilevel mount connected to a plexiglass plate cover by bolts that can be adjusted to change the vertical positions of the coil and dome simultaneously. This structure is designed such that all of the components could be fabricated in-house using an entry level laser-cutter or 3D printer.

We took a multi-tiered approach to thermal management. There is a need to cool both the sample and the laser diodes themselves to ensure optimal performance. We focus our discussion here to the laser diode cooling, while details of the sample cooling (heat exchanger) is presented in V. A Peltier cooler (TE Inc. TE-63-1.0-1.3) is attached to the base of each diode to maintain a temperature at or below 25°C inside the laser (Fig. S3D). This maintains excitation wavelength and power at 520nm and $\approx$0.8W respectively, even under continuous operation. To prevent overheating at the laser panel interface, a cooling block fed with -20°C nitrogen gas is attached to the base of the device. The slightly heated gas at the exit port of the cooling block is then sent to a copper tube running through each of the laser heads for additional cooling.
We subjected the hyperpolarization device to a series of stress tests to ensure that it could meet the desired operating conditions. One such regimen was running 28 lasers at full power (≈0.8 W optical output each) for one minute on and three minutes off for 6 hours, by which point we assume that the system would have reached thermal equilibrium with its surroundings. While conducting this test we closely monitored temperature across the device via infrared cameras. The laser temperature was found to be under 30°C even during sustained operation.

IV. "LASER DOME": DESIGN AND CONSTRUCTION

The design of the laser dome (Fig. 2) sought to achieve two complementary objectives: (i) mount the maximum number of laser fibers and hence deliver the maximum power to the sample, and (ii) arrange the lasers so that the beams excite the NV centers approximately isotropically (Fig. 2C). To accomplish this, we designed a polyhedral structure of four stacked, coaxial rings, with the top portion of the dome occupied by a cooling column (see Fig. S4). The sample is placed in a test tube in the central cavity of the dome and the fibers are mounted into the dome 4 mm from the sample center.

The absence of a collimator greatly reduces the real estate required for each laser, and ensures optimal divergence to illuminate the sample. We are therefore able to fit 8-14 lasers on each 3D printed ring. Fig. S5B shows one such ring with an added slot for the microwave coil. The 3D printed cavities for fibers are designed in a manner that the unit normal vector of all the fibers points towards the dome centroid where the sample is positioned. Each adjacent fiber tip has ≤1.5 mm separation from its neighbor. The dome was 3D printed in carbon fiber composite material, which was chosen for its high melting point. During fabrication, the layer thickness was varied to achieve the required smoothness of the structure, ensuring tight fits for the fibers.

The MW coil is tightly fit into the laser dome without touching the test tube or inner walls of the dome. It is designed in a manner that minimizes obstruction with the laser beam paths.

V. SAMPLE THERMAL MANAGEMENT

Here we describe more technical details of the sample cooling heat exchanger design. Large optical powers make handling sample heating a necessity and an important technical challenge. The 3D printed laser dome encapsulates a cooling column at its top portion to enable efficient sample cooling. This cooling system exploits three key features: (i) excellent thermal conductivity of diamond that transmits the injected heat to the surrounding water, (ii) high heat capacity of the water, and (iii) cold air flow that works to eject heat from the water. Overall, this creates an efficient and hyperpolarization compatible heatsink around the diamond. Importantly, the sample test tube itself has no liquids flowing into it, and hence it can be mechanically shuttled for NMR measurements [61].

The sample cooling column (Fig. S3C) consists of two concentric slotted cylindrical shells. Cooled nitrogen (at -20°C) is fed into ports from the top of the cylindrical column at 48 cfm to chill the water surrounding the diamond. Similar to the operation of a Dyson bladeless fan, the slots in the cylindrical shells create vortex currents which increase the characteristic length of heat transfer. Additionally, this design increases turbulence within the chamber, which better dissipates heat within the gaseous medium. The top of the column has an orifice for warmer gases to escape; this is also from where the sample test tube is shuttled for 13C NMR [61].

Our experimental observations of the heat exchanger performance are presented in Fig. 3 of the main paper. In experiments, a K-type thermocouple is used to record system temperature un-
The penetration depth of 0.0787 mm; this regime overcomes some of the absorption in the sample. Diamond has a high absorption coefficient of 12.7 mm indicating a concentration of light at the center of the diamond.

The simulation (Fig. 2E) shows an overlapping pattern of ray traces from the laser fiber tip positions in the dome, passing through air (refractive index \( n = 1 \)), glass (\( n = 1.6 \)), water (\( n = 1.33 \)) and ultimately the diamond (\( n = 2.54 \)) (Fig. 2E). We included effects of refraction, and the intrinsic 6° laser beam divergence. Attenuation was not included; attenuation in air, glass (absorption coefficient \( k = 0.34 \text{m}^{-1} \)), and water (\( k = 0.045 \text{m}^{-1} \)) is negligible. The optical simulation (Fig. 2E) shows an overlapping pattern of ray traces indicating a concentration of light at the center of the diamond.

Diamond has a high absorption coefficient of 12.7 mm and penetration depth of 0.0787 mm; this regime overcomes some of the potential attenuation losses due to the overlapping rays produced by the lasers.

**VI. OPTICAL SIMULATION**

Our experiments are carried out on a 4x4x1 mm diamond sample. Using the exact position of the fibers, we employed COMSOL to carry out a simple optical simulation based on laser ray tracing from the laser fiber tip positions in the dome, passing through air (refractive index \( n = 1 \)), glass (\( n = 1.6 \)), water (\( n = 1.33 \)) and ultimately the diamond (\( n = 2.54 \)) (Fig. 2E). We included effects of refraction, and the intrinsic 6° laser beam divergence. Attenuation was not included; attenuation in air, glass (absorption coefficient \( k = 0.34 \text{m}^{-1} \)), and water (\( k = 0.045 \text{m}^{-1} \)) is negligible. The optical simulation (Fig. 2E) shows an overlapping pattern of ray traces indicating a concentration of light at the center of the diamond.

Diamond has a high absorption coefficient of 12.7 mm and penetration depth of 0.0787 mm; this regime overcomes some of the potential attenuation losses due to the overlapping rays produced by the lasers.

**VII. CHARACTERIZATION OF LASER HOMOGENEITY**

In this section, we describe experiments to characterize and optimize the homogeneity of the laser excitation on the diamond sample. Our goals are to maximize the uniformity of the optical illumination in order to ensure that every part of the sample sees approximately the same laser excitation intensity (here \( \approx 0.8 \text{W per laser} \)). These measurements will be employed in order to normalize the effective laser intensities in the experiments performed in Fig. 4 of the main paper. Optical inhomogeneity itself can arise from factors including:

1. Misplacement of the laser. From the vantage point of a few lasers excitation slots, the MW coil casts a shadow on the sample. Lasers mounted on these positions therefore strike the sample with their intensity greatly suppressed. The exact positions depends on...
Fig. S6. Characterization of the hyperpolarization signal from each laser. (A) Panel shows the signal obtained from each laser operated individually. Lasers are numbered from top-to-bottom and clockwise. We find an approximately homogeneous generation of hyperpolarization with slight variations stemming from geometric effects in the manner in which the laser beam strikes the sample. Two laser diodes (number 11 and 12) show worse performance because they have degraded with time and have a lower power output.

The exact MW coil employed in the experiment. We find that for

a typical split coil design, 30 lasers can easily be accommodated with minimal loss.

ii. Off-center MW coil. The 3D printed slots in the laser dome ensures that fibers that are placed into them are naturally aligned to the exact geometric center of the dome structure. This assumes, however, that the MW coil itself is centrally located in the dome cavity in order to minimize overlap with the laser beams.

iii. Total internal reflection. Depending on the size, shape and orientation of the sample, some of the lasers are more effective because optical beams from them undergo total internal reflection within the diamond.

Hyperpolarization levels obtained from each laser applied individually to the sample provides the best means to characterize the homogeneity of the optical excitation. We carry out such DNP experiments with each laser illuminated for 20s, and measure the $^{13}$C hyperpolarized NMR signal under pulsed spin lock for 20s. The resulting integrated signals are then correlated with position on the dome. Any inhomogeneities due to coil or laser misplacement can then be easily identified. It is evident from Fig. 2E that hyperpolarization can be arranged to be homogenous to a good degree even for the 28 applied lasers. Two lasers in Fig. S6 had degraded in performance and were at reduced intensity. The experiments also reveal that the maximum hyperpolarization intensity arises, somewhat counterintuitively, for lasers striking the sample at the diagonal top positions.