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# Room temperature “Optical Nanodiamond Hyperpolarizer”: physics, design and operation

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Dynamic Nuclear Polarization (DNP) is a powerful suite of techniques that deliver multifold signal enhancements in NMR and MRI. The generated athermal spin states can also be exploited for quantum sensing and as probes for many-body physics. Typical DNP methods require the use of cryogenics, large magnetic fields, and high power microwave excitation, which are expensive and unwieldy. Nanodiamond particles, rich in Nitrogen-Vacancy (NV) centers, have attracted attention as alternative DNP agents because they can potentially be optically hyperpolarized at room temperature. Here, unraveling new physics underlying an optical DNP mechanism first introduced in [Ajoy *et al.*, *Sci. Adv.* 4, eaar5492 (2018)], we report the realization of a miniature “optical nanodiamond hyperpolarizer”, where <sup>13</sup>C nuclei within the diamond particles are hyperpolarized via the NV centers. The device occupies a compact footprint and operates at room temperature. Instrumental requirements are very modest: low polarizing fields, low optical and microwave irradiation powers, and convenient frequency ranges that enable miniaturization. We obtain best reported optical <sup>13</sup>C hyperpolarization in diamond particles exceeding 720 times of the thermal 7T value (0.86% bulk polarization), corresponding to a ten-million-fold gain in averaging time to detect them by NMR. In addition the hyperpolarization signal can be background-suppressed by over two-orders of magnitude, retained for multiple-minute long periods at low fields, and deployed efficiently even to <sup>13</sup>C enriched particles. Besides applications in quantum sensing, and bright-contrast MRI imaging, this work opens possibilities for low-cost room-temperature DNP platforms that relay the <sup>13</sup>C polarization to liquids in contact with the high surface-area particles.

## I. INTRODUCTION

Dynamic Nuclear Polarization (DNP)<sup>1</sup>, the process of transferring spin polarization from electrons to surrounding nuclei, *hyperpolarizing* them to levels of large fictitious magnetic fields<sup>2</sup>, has been a burgeoning field with applications across numerous disciplines. For instance the versatile, noninvasive and chemically specific spectroscopic and imaging techniques<sup>3</sup> of NMR and MRI can see their signals enhanced by orders of magnitude through the use of DNP<sup>4</sup>. Moreover hybrid electron-nuclear quantum sensing platforms, for instance gyroscopes<sup>5-7</sup>, can see sensitivity gains through nuclear hyperpolarization. Finally the generated *athermal* spin states provide valuable physical testbeds to study many body quantum dynamics, spin transport and localization in dipolar coupled spin systems<sup>8,9</sup>. That said however, conventional methods of DNP<sup>10-12</sup> involve the use of cryogenic conditions ( $\lesssim 1\text{K}$ ) and high magnetic fields ( $\gtrsim 3\text{T}$ ) in order to first generate the electron polarization. In some applications, this limits hyperpolarization throughput due to several hour-long relaxation times and the necessity to cool down the sample every time. In many respects, this restricts wider real-world deployment given the high cost of setup and maintenance of cryogenic polarizer devices. There is, therefore, a strong desire for inexpensive room-temperature DNP platforms that can potentially retrofit existing NMR/MRI infrastructure, and provide hyperpolarization generation “*at source*”<sup>13</sup>.

In recent years, the development of defect centers in wide bandgap semiconductors has proffered them as interesting candidates for optical room temperature hyperpolarization. This

leverages the fact that electronic spin defects in these systems can be optically initialized<sup>14</sup>. Nanodiamond particles endowed with Nitrogen Vacancy (NV) defect centers have been suggested as one such compelling hyperpolarization platform<sup>15-18</sup>. The NV electrons can be optically polarized with modest resources, the polarization transferred to <sup>13</sup>C nuclei in the lattice, and subsequently relayed to nuclei in a liquid in contact with the high surface-area ( $\gtrsim 10\text{m}^2/\text{g}$ ) particle surfaces<sup>19,20</sup>. Hyperpolarized particulate diamonds portend other applications: powdered samples represent the optimal size configuration to fill a sensor volume and maximize the number of spins available for quantum sensing<sup>7</sup>. They also engender possibilities for quantum sensors constructed from single levitating hyperpolarized diamond particles<sup>21</sup>. Finally, nanodiamonds are fluorescent and non-toxic<sup>22-24</sup>, and hyperpolarization opens pathways for imaging these particles in a dual-modality consisting of optical and MRI imaging simultaneously.

In recent work we had demonstrated the first experimental technique for the generation of optically hyperpolarized diamond particles<sup>20</sup>. We relied on an unconventional DNP regime operational at low fields and exhibited hyperpolarization of the <sup>13</sup>C nuclei irrespective of the orientation of the individual crystallites. In this paper, we refine the experimental conditions for the optimal generation of hyperpolarization, by focusing on the field dependence of the underlying DNP process. We demonstrate that this optical DNP mechanism is fully orientation independent and low-field only, occurring at polarization fields  $B_{\text{pol}}=1-70\text{mT}$ , and low-enough to be generated with the simplicity of a refrigerator magnet. Besides magnetic field, we demonstrate that the DNP mechanism affords benign requirements for optical and microwave (MW) excitation.

Leveraging this new physics, we construct a room temperature “optical nanodiamond hyperpolarizer” device that can

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produce  $^{13}\text{C}$  hyperpolarization in diamond particles with high throughput ( $\approx 20\text{mg}/\text{min}$ ). Fig. 1A shows a photograph and rendered view of the device. Fig. 2 (Multimedia view) shows the construction of the device, and Ref. <sup>25</sup> shows a video it in operation. It has an ultracompact form-factor ( $\sim 10\text{in.}$  edge) that houses all the electronic, MW and optical components required to produce hyperpolarization in diamond particles at room temperature. The device is portable enough to “DNP-retrofit” any magnet system. We have deployed two such devices across 7T and 9.4T (imaging) magnets at UC Berkeley and UC Davis. We emphasize that the ability to construct such a hyperpolarization device is itself somewhat surprising, and due to a confluence of factors unique to the physics of optically pumped quantum defects. In this paper we uncover these features and also highlight engineering design aspects that make possible the miniaturizable device.

## II. HYPERPOLARIZATION RESULTS

We begin in Fig. 1B-E by demonstrating representative results using our device on various types of diamond samples. The  $^{13}\text{C}$  hyperpolarization enhancements  $\varepsilon$  are evaluated with respect to the thermal Boltzmann level at 7T, corresponding to a time acceleration for spectroscopy or imaging  $t_{\text{acc}} \approx \varepsilon^2 \frac{T_1(7T)}{T_1(B_{\text{pol}})}$ . The key advantage of optical hyperpolarization is that the enhancement factor is not theoretically bounded, unlike in conventional methods wherein  $\varepsilon \leq \gamma_e/\gamma_n$ , the ratio of the electronic and nuclear gyromagnetic ratios. For a typical single crystal sample ( $3.24 \times 3.24 \times 0.3\text{mm}$ ) we obtain in Fig. 1B large DNP enhancements  $\varepsilon = 950$  corresponding to a  $^{13}\text{C}$  polarization level  $\sim 1.1\%$  and larger than ten-million fold acceleration ( $t_{\text{acc}} \approx 5.3 \times 10^7$ ) in averaging time. For randomly oriented microcrystalline diamond powder (see Fig. 1B), we obtain the best reported polarization, with  $\varepsilon = 720$ , corresponding to a  $^{13}\text{C}$  polarization level  $\sim 0.86\%$ , and an acceleration factor  $t_{\text{acc}} \approx 9.8 \times 10^6$ . We note that while cryogenic DNP provides larger enhancements, a majority of the obtained hyperpolarization is lost upon sample transfer outside the cryostat<sup>26,27</sup>. The polarization in Fig. 1C is thus ultimately slightly stronger, can be obtained at higher throughput, and is optically replenishable. Moreover, due to the DNP being carried out under ambient conditions, the hyperpolarization enhancements can be maintained even when the particles are immersed in solution: for instance, common solvents like water, DMSO, oil, and biologically relevant liquids such as saline and blood (see Supplementary Information<sup>28</sup>). The microcrystals in Fig. 1C are employed for all the other experiments reported in this manuscript.

Given the high polarization gain (see Fig. 1D), we are also able to detect a *single* hyperpolarized diamond microparticle with a single-shot SNR  $>40$  (see Fig. 1D(ii)). There is substantial room for further signal enhancements because the particle herein occupies a very small part of the detection coil ( $\sim 1\text{cm.}$  cylinder) corresponding to sample filling-factor for NMR detection  $\approx 6 \times 10^{-6}$ . Such high signals portend quantum sensing applications constructed out of hybrid spin-mechanical systems in single microparticles<sup>29,30</sup>. Finally Fig. 1E demonstrates results with the device on a large mass  $\approx 42\text{mg}$  of commercially available 100nm nanodiamond particles in solution (see *Materials*). We ascribe the lower polarization herein to be limited by material properties and finite optical penetration through the col-

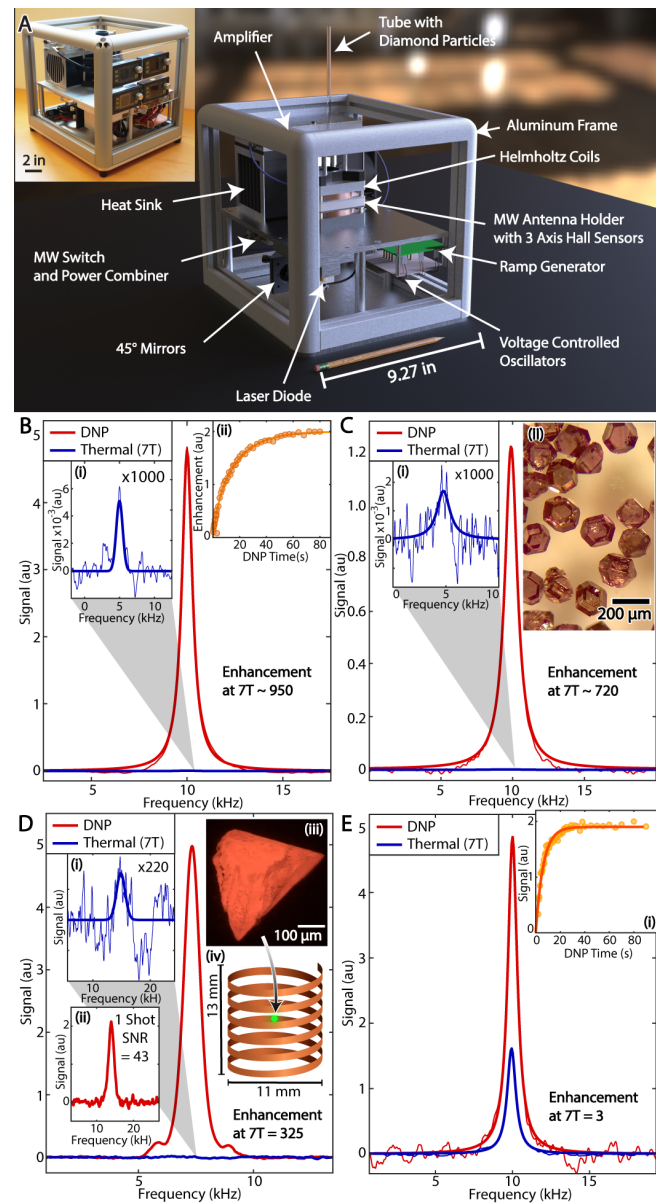


Figure 1. **Nanodiamond hyperpolarizer.** (A) *Rendered model.* Compact device ( $< 10\text{in.}$  cubical edge) containing all optical, microwave (MW), and control components generates hyperpolarized diamond particles at high throughput  $\approx 20\text{mg}/\text{min}$ . *Inset:* Photograph of the constructed device (see Fig. 2). See Ref. <sup>25</sup> for video of operation. (B-D) *Results using hyperpolarizer device at 38mT.*  $^{13}\text{C}$  signals are measured by transfer to a 7T NMR magnet. Red (blue) lines show the DNP signal (7T thermal signal, zoomed in insets). (B) *Single crystal DNP,* demonstrating enhancement  $\varepsilon \approx 950$ . Here DNP and thermal are with 10, 120 averages respectively. Hyperpolarization buildup, typical for most samples, occurs in under 60s. (C) *Microcrystalline diamond powder DNP,* with best reported polarization enhancements  $\varepsilon \approx 720$ . DNP = 1, thermal = 120 averages. *Inset:* Particle micrograph. (D) *Single particle DNP* of a 10%  $^{13}\text{C}$  enriched and  $\sim 400\mu\text{m}$  sized single particle showing  $\varepsilon = 325$  over 7T. Here DNP and thermal are both 512 averages. *Inset (ii):* Single shot DNP signal with SNR  $\approx 43$  in a  $1235\text{mm}^3$  NMR coil. *Inset (iii):* Particle micrograph with fluorescence from NV centers. *Inset (iv):* Schematic of detection coil. We obtain large single shot signals despite poor sample fill-factors  $\sim 10^{-6}$ . (E) *Nanodiamond DNP* with commercial 100nm NDs in solution, showing  $\varepsilon = 3$  over 7T. DNP = 10, thermal = 512 averages. *Inset:* Hyperpolarization buildup curve.

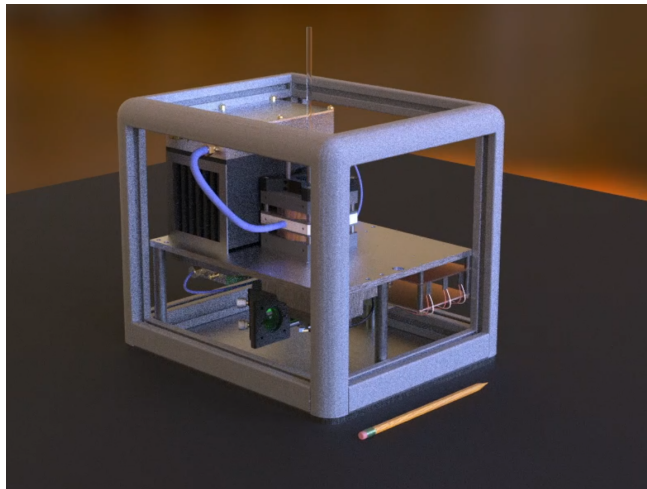


Figure 2. **Video** showing rendered construction of the hyperpolarizer device and all its component parts (Multimedia view).

loidal suspension. In Ref.<sup>31</sup>, we study these material conditions affecting hyperpolarization and demonstrate methods by which the diamond particles can be rendered more suitable for optical DNP.

### III. TECHNOLOGY ENABLING MINIATURIZATION

Hyperpolarization is achieved by the continuous application of laser and frequency swept MW irradiation at low background fields  $\mathbf{B}_{\text{pol}}$ <sup>20</sup> (see Fig. 3B). The laser polarizes NV centers (we estimate to  $>10\%$ ) to the  $m_s=0$  sublevel, and the MWs transfer the polarization to the  $^{13}\text{C}$  nuclei. In practice we use a combination of three cascaded MW sweepers for greater signal enhancement<sup>32</sup>. Refining and expanding on the work in Ref.<sup>20</sup>, we begin by first summarizing the key results of this paper. Miniaturized hyperpolarization devices are possible because of a confluence of four factors stemming from the underlying DNP mechanism:

(i) *Field*: – We observe that hyperpolarization is optimum at a low polarizing field  $\mathbf{B}_{\text{pol}} \approx 38\text{mT}$ . Such low fields are simple to produce in a the miniature footprint either through a permanent magnet or a simple magnetic coil. There are no requirements on field alignment. Given that we are dealing with powders with inherently broadened electronic spectra, there are very little constraints on field homogeneity. In principle we expect that DNP can proceed even in inhomogeneous settings with  $\Delta B_{\text{pol}} \sim B_{\text{pol}}$ , while in our experimental demonstrations  $\Delta B_{\text{pol}}/B_p \approx 0.1$ . Moreover, due to spin reorientation during sample shuttling, the polarization field does not need to be aligned with the detection NMR field. This allows installation and retrofits of the device anywhere in the vicinity of detection magnets.

(ii) *Optics*: – the laser excitation required is of very low power since the NVs need to be polarized only once every  $T_{1e}$  relaxation cycle. We estimate the optical power  $\approx 30\text{--}400\text{mW/mm}^3$  depending on number of laser sources employed. We contrast this with higher optical powers  $\sim 1\text{mW}/(\mu\text{m})^2$  typically required for quantum sensing experiments employing optical NV center readout. There are no requirements on excitation wavelength ( $510\text{nm} \lesssim \lambda \lesssim 575\text{nm}$ ), linewidth, or mode

quality. Indeed diffuse irradiation through multimode optical fibers are sufficient. The optical excitation is in completely *cw*-mode, requiring no synchronization or pulsing infrastructure (eg. AOMs). This facilitates the use of (one or multiple) inexpensive miniaturizable laser diode excitation sources.

(iii) *Microwaves*: – the MW power required is exceedingly low ( $\approx 2\text{mW/mm}^3$ ). There is a relatively weak dependence of the DNP enhancement on MW power<sup>20</sup>, making the hyperpolarization robust to MW inhomogeneity. We estimate the electron Rabi frequency  $\Omega_e \lesssim 100\text{kHz}$  and a MW inhomogeneity of  $\approx 12\%$  from the 4mm loop antenna in our device<sup>28</sup>. Moreover, since the MWs are chirped, they are inherently robust against carrier phase noise, especially when compared to more conventionally pulse-based DNP approaches<sup>16</sup>. Our MW excitation linewidth, for instance, is rather broad  $\approx 10\text{MHz}$ . The frequency sweep band ( $\mathcal{B} \sim 3.64\text{--}4\text{GHz}$ ) at  $B_{\text{pol}}=38\text{mT}$  lies in the commercial WiMAX regime, and the use of commercial chip scale voltage controlled oscillator (VCO) sources ubiquitously available in this band simplify miniaturization. Broadband antennas can deliver the MWs, with no requirement for a MW cavity or sophisticated transmission infrastructure. MW chirp repetition rates are slow  $\omega_r \approx 147\text{Hz}$ , robust  $\Delta\omega_r \approx 53\text{Hz}$ , and to a good approximation independent of polarizing magnetic field. This allows simple frequency sweep infrastructure and the cascading of multiple MW sources to boost DNP efficiency<sup>32</sup>.

(iv) *Polarization sign*: – Sweeps over every part of the NV electronic spectrum produces hyperpolarization that constructively adds to the *same* polarization sign. The MW sweep bands can be optimally tuned to the simulated electronic spectral widths at any given  $B_{\text{pol}}$  field to optimize final hyperpolarization enhancements.

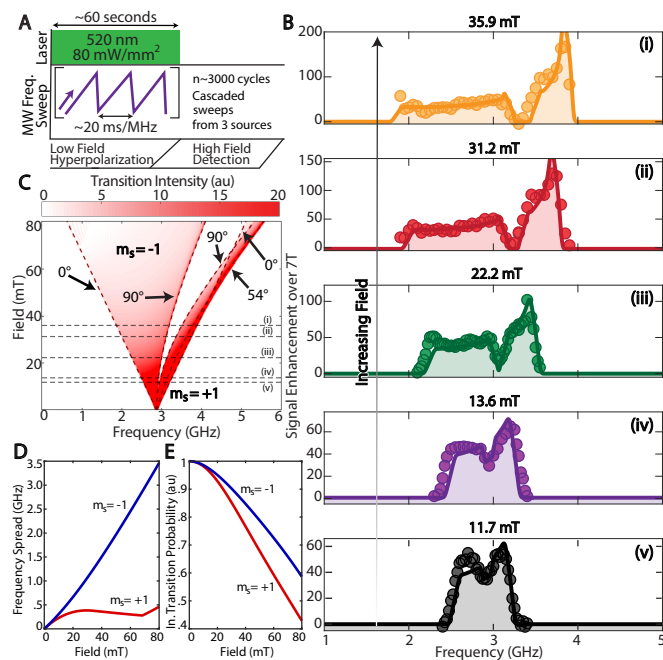
These attributes are consequences of the underlying DNP mechanism. We refer the reader to more detailed expositions elsewhere<sup>33</sup>, but briefly mention that DNP occurs when the nuclear Larmor frequency  $\omega_L = \gamma_n B_{\text{pol}} \approx 10\text{--}700\text{kHz}$  is smaller than the hyperfine coupling  $A$ , i.e.  $\omega_L \lesssim |A|$ . Here  $\gamma_n$  is the  $^{13}\text{C}$  gyromagnetic ratio,  $\gamma_n \approx 10.7\text{kHz/mT}$ . The swept MWs excite a sequential set of Landau-Zener (LZ) crossings between the electron-nuclear spin states in the rotating frame, and this drives a “ratchet” type process for polarization transfer. This at once results in lower laser and microwave powers requirements: MW power should be low enough to maintain adiabaticity of the LZ traversals, and the laser excitation of sufficiently low power to not break the coherence of the polarization transfer process. Indeed at optical powers that we operate under, the NV electronic repolarization occurs at a rate  $\approx 1/T_{1e}$ , and takes place predominantly during the long intervals far away from the LZ anti-crossings<sup>20,33</sup>.

### IV. ORIENTATION INDEPENDENT HYPERPOLARIZATION

In Ref.<sup>20</sup>, we had observed that every part of the NV electronic spectrum contributes to DNP, and that the sign of the resulting  $^{13}\text{C}$  polarization depends on the direction of the sweep. While this was a strong indication that DNP was excited for all orientations, it was not immediately evident that polarization builds up equally efficiently in every orientation of random crystallites in the diamond powder. In this paper, we perform new experiments that quantitatively answer this question in the affirmative. This stands in contrast to other proposals for nanodia-

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**Figure 3. Fully orientation independent hyperpolarization.** (A) DNP pulse sequence at low-field involving simultaneous laser and chirped MW irradiation over the NV center ESR spectrum. DNP enhancements are quantified by NMR detection at 7T. (B) Electronic spectra mapped via <sup>13</sup>C DNP on 200 $\mu$ m particles (Fig. 1C). Hyperpolarized <sup>13</sup>C NMR is performed on narrow 100MHz frequency windows to map the underlying NV ESR spectrum at various fields (i-v). Solid lines are fits to calculated spectrum (dashed linecuts in C) and show good agreement. Panels illustrate that *all* orientations of the particles contribute constructively to hyperpolarization, and all with the same sign. (C) Simulated NV electronic spectra, shown as a function of field, due to varying orientations ( $\vartheta$ ) of N-V axes in crystallites in the diamond powder with respect to the polarizing field  $\mathbf{B}_{\text{pol}}$ . Shading is proportional to electronic transition intensities  $P(\vartheta, B_{\text{pol}})$ . Exact orientations that contribute to the extrema of the patterns in  $m_s = \pm 1$  manifolds are indicated by arrows and the red dashed lines. (D) Frequency spread in either electronic manifold, showing an approximately linear fan out of transitions in the  $m_s = -1$  branch, as opposed to being constant ( $\approx 400$ MHz) in the  $m_s = +1$  branch at moderate fields. (E) Integrated transition intensity  $\mathcal{T}(B_{\text{pol}})$  averaged over all orientations of the powder, indicating that the net transition intensity falls with increasing field.

mond DNP<sup>34</sup>, where only spins in a narrow cone are polarized. These results also point to simple means to optimize hyperpolarization enhancements at any given polarizing field  $B_{\text{pol}}$ .

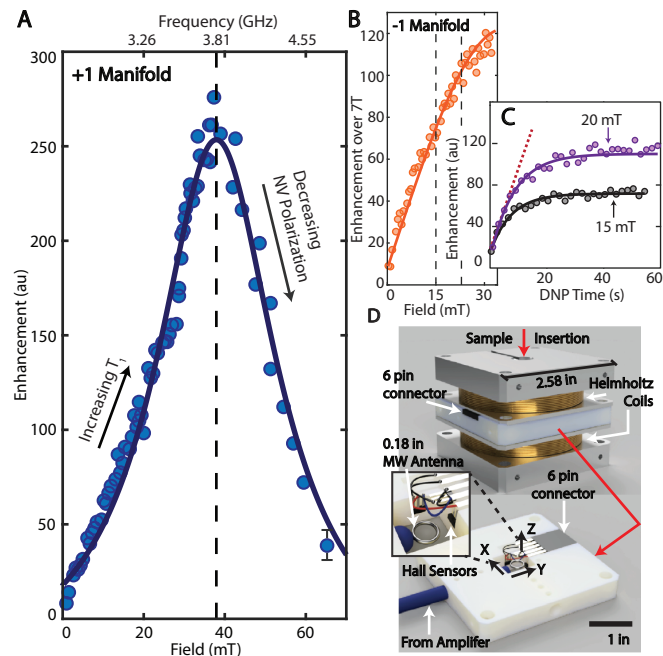
We perform experiments sweeping MWs in narrow 100MHz windows, using the obtained <sup>13</sup>C DNP enhancements to report on the underlying NV ESR spectra<sup>20</sup>. We employ a Helmholtz coil (see Fig. 4D) within the polarizer device to generate varying polarization fields in a background fringe field of a 7T NMR spectrometer. Embedded chip-scale Hall sensors measure the field along three axes, and the vector fields are reported in Fig. 3B. As expected the spectra become wider at higher fields. The key new result in this paper, however, is contained in the solid lines that provide good fits to the experimental data. These fits involve a single free parameter (overall amplitude), and are derived from a simple model of the NV center electronic spectrum alone, without having to include hyperfine couplings to the <sup>13</sup>C nuclei. The experiments reveal therefore that the <sup>13</sup>C hyper-

polarization fully follows the underlying NV electron density of states, pointing to complete DNP orientation independence. They also reflect that it is the weakly coupled <sup>13</sup>C nuclei that are predominantly polarized.

To be more specific, Fig. 3C shows simulated NV ESR spectra at various fields, where the shading color is proportional to the transition intensity under applied MW excitation. The solid lines in Fig. 3B are line-cuts in this graph (dashed lines). We start with the spin-1 NV center Hamiltonian  $\mathcal{H}(\vartheta) = \Delta S_z^2 + \gamma_e B_{\text{pol}}(S_x \sin \vartheta + S_z \cos \vartheta)$ , where  $\Delta = 2.87$ GHz is the zero-field splitting,  $\gamma_e = 28$ MHz/mT is the electron gyromagnetic ratio, and  $S_j$  are Pauli matrices. We calculate the eigenvectors such that  $\mathcal{H}|v_k\rangle = E_k|v_k\rangle$ , and obtain the transition intensities  $P(\vartheta, B_{\text{pol}}) \sim \sum_{k<\ell} \sum_m |v_k|S_m|v_\ell|^2 [\langle v_k|\rho|v_k\rangle - \langle v_\ell|\rho|v_\ell\rangle]$ , where the first factor quantifies the transition probabilities in the randomly oriented powder where  $m \in \{x, y, z\}$ . The second factor describes the population difference between the eigenstates, with  $\rho = \mathbb{1} - S_z^2/3$ . The predicted spectra are then calculated by assuming a Gaussian spectral width  $\approx 28$ MHz (corresponding to a field inhomogeneity  $\approx 1$ mT) for each transition, averaging the effective  $P(\vartheta)$  over 300 random orientations in the powder, and then convoluting the result by the sweep window. The extremities of the spectra at low fields are easy to identify, at frequencies  $\Delta \mp \gamma_e B_{\text{pol}}$ , as originating from the crystallites aligned with  $B_{\text{pol}}$  ( $\vartheta = 0^\circ$ ) in the  $m_s = \mp 1$  manifolds. Similarly the perpendicular ( $\vartheta = 90^\circ$ ) orientations occur more centrally in the powder pattern, at frequencies  $\frac{1}{2}[\Delta + \sqrt{\Delta^2 + (2\gamma_e B_{\text{pol}})^2}]$  and  $[\sqrt{\Delta^2 + (2\gamma_e B_{\text{pol}})^2}]$  respectively. The region in-between the two manifolds has no electronic density of states and consequently produces no DNP enhancements, resulting in the apparent “holes” around 3GHz in Fig. 3B.

This simple model now allows simple means to optimize the DNP enhancement. Firstly, knowledge of the *vector* polarizing field, for instance through Hall probes embedded in the device near the sample, can point to the exact frequency band  $\mathcal{B}$  for the MWs to sweep over. This ensures that the applied microwaves are sweeping over electrons at every time instant during the full polarization period (constrained by nuclear  $T_1$ ). Moreover, as Fig. 3D demonstrates, the frequency spread in the  $m_s = -1$  manifold grows approximately linearly with field, while in the  $m_s = +1$  manifold it saturates after an initial quadratic rise. Since there is a relative reduction of electron density of states per unit frequency bandwidth in the  $m_s = -1$  manifold as opposed to the  $m_s = +1$  manifold, higher DNP enhancements are obtained by MW sweeps over the  $m_s = +1$  branch. This is also evident in the experiments in Fig. 3B. At 36mT, for instance, a single 100MHz sweep window in the  $m_s = +1$  manifold can provide DNP enhancements approaching 200 over 7T (Fig. 3B).

Finally the excited DNP is as a result highly robust to generate. (i) Any part of the frequency band can be swept over to produce hyperpolarization, in contrast to conventional DNP (solid/cross-effects), where misplaced frequency windows can lead to destructive polarization generation between various spin packets. (ii) Given that the ESR spectrum is orientationally broadened to start with, field inhomogeneities do not significantly alter the DNP enhancements. We estimate a inhomogeneity of 2mT over the sample volume (see Supplemental Information<sup>28</sup>) in our device. (iii) Moreover, since the NV electrons are quantized along randomly oriented axes in the powder,  $\mathbf{B}_{\text{pol}}$  can be applied in any direction. It can hence be generated by a vector combination of a single-axis Helmholtz coil and the



**Figure 4. Field dependent DNP profile.** (A) *Field dependence* of maximum hyperpolarization enhancements in 1-70mT range for the  $m_s=+1$  NV manifold. Experiments are performed at optimal MW sweep rates at each field (see *Methods*). We observe a steep decrease in DNP efficiency at ultralow fields  $<20$ mT and at fields  $>50$ mT, and a sharp optimum at  $\approx 38$ mT. We ascribe this to be due an interplay between low  $^{13}\text{C}$  lifetimes at low field, and inefficient optical polarization in a powder at high fields. Center of MW sweep bands are shown on top axis. Solid line is guide to the eye. Error bar  $\approx 11\%$  is shown representatively on last point. (B) Similar experiments performed on  $m_s=-1$  manifold. (C) Comparison of polarization buildup curves at 15mT and 20mT, showing longer saturation times for the latter, a reflection of longer nuclear relaxation times. Red dashed line shows identical rate of polarization buildup at both fields. (D) *Helmholtz coil* placed over the MW loop antenna onboard nanodiamond hyperpolarizer device (see also Fig. 8) can be used to apply the polarizing field in a variety of environments of NMR detection magnets. *Inset*: Three Hall probes measure the *vector* magnetic field in close proximity to the MW antenna and sample.

magnet fringe field. These favorable settings enable the simple installation of the device in the vicinity of detection magnets – one simply “dials-up” the current in the Helmholtz coil such that the net vector field seen by the sample is the optimal value  $|\mathbf{B}_{\text{pol}}| \approx 38$ mT.

## V. HYPERPOLARIZATION FIELD PROFILE

We now turn our attention to the field dependence of the DNP enhancements. Determining an *apriori* analytical model from microscopics of the “DNP ratchet”<sup>20,33</sup> is challenging since there are several factors at play simultaneously: different orientations in the powder, a continuum of hyperfine couplings within the diamond lattice, as well as always operational nuclear spin diffusion and relaxation effects. However one could generally state that the DNP mechanism is operational at low fields, since the critical hierarchy that we rely on,  $\omega_L \lesssim |A|$  flips at higher fields. Indeed in this regime, the mechanism will transition to the more conventional Integrated Solid Effect (ISE)<sup>35</sup>, with several con-

trasting features.

Before going forward, we do emphasize however, that these low-field regimes ( $\lesssim 70$ mT) have been traditionally inaccessible to DNP since typically electron polarization is also generated through a Boltzmann distribution at cryogenic conditions at high fields. Indeed, materials such as the diamond NV center provide a new paradigm on account of the fact that the electronic spins can be polarized optically independent of temperature and even at zero magnetic field. A hint of the possible field dependence (neglecting nuclear relaxation) is elucidated in the simulations of Fig. 3E. We plot here the integrated transition intensity of the electron spectra as a function of magnetic field,  $\mathcal{T}(B_{\text{pol}}) = \int_0^{\pi/2} P(\vartheta, B_{\text{pol}})$ . This suggests that the available NV density of states for hyperpolarization reduces with increasing field.

In this paper we furnish an experimental study, reporting in Fig. 4 the measured field dependence of the obtained DNP enhancements under optimal conditions. We use a combination of Helmholtz coil fields and background fringe fields over a wide range (1-70mT) to systematically map the field dependence under sweeps of the  $m_s=+1$  (Fig. 4A) and  $m_s=-1$  manifolds (Fig. 4B) respectively. In actuality, due to amplifier constraints, the data in Fig. 4A is obtained in two separate data sets (1-40mT) and (30-70mT) and pieced together by normalizing overlapping points. We estimate from this an  $\approx 11\%$  error through this (marked in the last point of Fig. 4A). We see a sharp field dependence, becoming optimal around  $B_{\text{pol}}=38\text{mT} \pm 4\text{mT}$ , and falling on either side of this value.

While a quantitative model is still beyond the scope of this paper, we ascribe this behavior to be arising from a competition between two factors with increasing  $B_{\text{pol}}$ : (i) a dominant rise in  $^{13}\text{C}$  nuclear  $T_1$  lifetimes and (ii) a fall in the NV center polarization<sup>36</sup> and integrated electron transition probability  $\mathcal{T}(B_{\text{pol}})$  in randomly oriented diamond powder. The nuclear  $T_1$  is set for the most part (see Fig. 5) by interactions with the spin bath of paramagnetic electron defects (primarily P1 centers) in the diamond lattice, which present to the  $^{13}\text{C}$  nuclei a spin-flipping noise spectral density centered at zero frequency and width given by approximately the inter-electron dipolar coupling. Increasing field allows the  $^{13}\text{C}$  nuclei to sample less of this noise, leading to an increase in  $T_1$  and the ability to buildup polarization for longer times before saturation. This is demonstrated in Fig. 4C (*inset*) where we report DNP buildup curves at 15mT and 20mT, and where the polarization curves saturate at longer times in the latter case. Simultaneously however, there is a reduced overall NV transition probability  $\mathcal{T}(B_{\text{pol}})$  at higher fields (Fig. 3E), and also (ignored by Fig. 3E) a reduction in number of  $^{13}\text{C}$  nuclei directly participating in the DNP process (satisfying the hierarchy  $\omega_L \lesssim A$ ). Due to these factors we expect a decrease in DNP efficiency at high fields.

Due to these competing factors, we expect that the optimal field value is sample dependent. Overall however, the low polarizing fields  $B_{\text{pol}} \approx 40$ mT, and the relatively benign range around this field  $\Delta B_{\text{pol}} \approx 10$ mT, mean that they are simple to generate through permanent magnet or coils. This feature is key to miniaturization of the hyperpolarizer. Moreover the MW bandwidth in the optimal  $m_s=+1$  manifold to sweep over is relatively narrow  $\mathcal{B} \approx 0.35$ GHz around 3.81GHz. We note that, in contrast, at high fields  $B_{\text{pol}} \gg 100$ mT, where the mechanism transitions to the standard ISE, one has to contend with far reduced electron density of states and the  $2\Delta \sim 5.9$ GHz wide electron spectral width which is technologically challenging to sweep over.

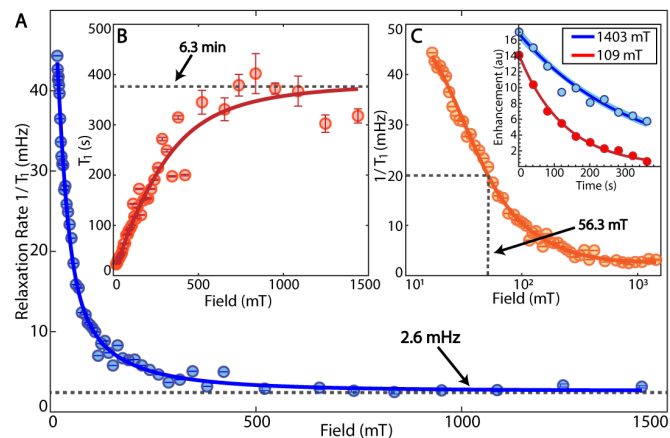


Figure 5. **Lifetimes of hyperpolarized  $^{13}\text{C}$  nuclei.** (A) *Field dependence* of nuclear relaxation rate  $R_1 = 1/T_1$  for hyperpolarized  $200\mu\text{m}$  particles in Fig. 1C. There is a steep rise in relaxation rate at low-fields below  $\lesssim 100\text{mT}$  mediated by interactions with paramagnetic impurities in the lattice. At higher fields the rate is approximately constant  $\approx 2.6\text{mHz}$ , allowing efficient retention of hyperpolarization for minute-long periods. Solid line is a Lorentzian fit. Error bars are estimated from monoexponential fits (see *Methods*<sup>28</sup>). (B) Measured  $T_1$  values showing lifetimes  $>6\text{min}$  at modest fields. (C) *Knee field* at which the rapid increase of nuclear lifetimes occurs can be quantified as the width in a logarithmic scale, here  $\approx 57\text{mT}$ . *Inset*: Signal decays at exemplary low and high fields. Shaded are 95% confidence intervals.

## VI. LONG TIME HYPERPOLARIZATION RETENTION

While the DNP mechanism is optimum at low fields, we also find that modestly low fields are sufficient to retain this polarization for long periods, with typical cases approaching ten minutes. We demonstrate this in Fig. 5 by performing a full wide range ( $B_{\text{relax}}=10\text{mT}-7\text{T}$ ) field dependent mapping of the  $T_1$  relaxation of  $^{13}\text{C}$  nuclei in typical diamond microparticles (Fig. 1C). This is achieved by retrofitting a field cycling instrument constructed over a 7T magnet<sup>37</sup> with our optical hyperpolarizer device. One would naively expect a increase in relaxation rate that falls down as  $R_1 \propto 1/B_{\text{relax}}$ , due to a suppression in electron-nuclear overlaps due to the widening energy gap between the two reservoirs. We find, however, a step-like dependence on field (see Fig. 5A). There is a strong increase in  $T_1$  beyond a particular knee field  $\approx 57\text{mT}$  where lifetimes approach 6.3min and a steep fall below this field (see also Fig. 5B). Knee fields can be most easily quantified in a logarithmic field plot of the relaxation plots (Fig. 5C). We have observed that the dependence in Fig. 5 is typical of diamond particle samples employed for hyperpolarization. In recent companion work to this paper<sup>38</sup>, we have studied the origins of this relaxation behavior by studying various samples under field cycling and with ESR studies to map the electronic concentration. The data is borne out by a model that involves the interaction of the  $^{13}\text{C}$  nuclei with paramagnetic defects in the lattice, the knee field value being predominantly set by the dipolar electronic linewidth<sup>38</sup>.

That said the step-like dependence in Fig. 5A immediately opens the door to simplification of hyperpolarizer operation and deployment: by rapidly switching the field to  $\gtrsim 100\text{mT}$  after optical pumping by means of an electromagnet, one could retain the polarization for minute-long periods. The behavior in Fig. 5A also ensures that the hyperpolarization loss during sample

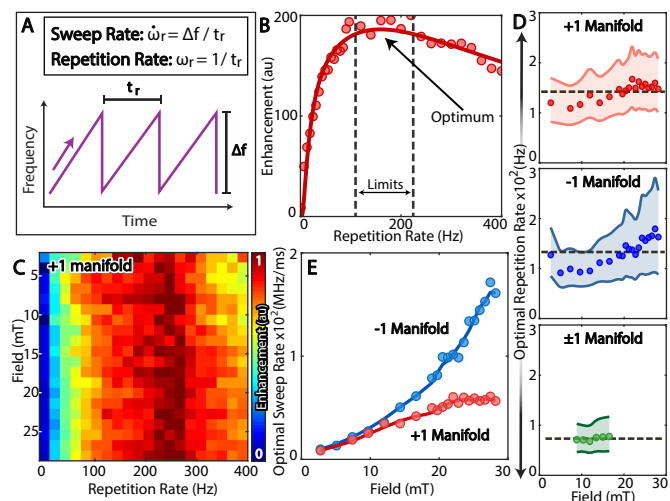


Figure 6. **MW sweep rates dependence** of hyperpolarization enhancements. (A) *Definitions.* We distinguish between MW repetition rates  $\omega_r$  and sweep rates  $\dot{\omega}_r$ . (B) Exemplary variation with MW repetition rate at  $28.8\text{mT}$  employing three cascaded MW sources sweeping a bandwidth  $\mathcal{B}=384\text{MHz}$ . Solid line denotes a fit to microscopic model<sup>20</sup> that qualitatively captures the observed behavior, with dashed lines denoting 5% confidence interval. (C) *Full dataset* as function of field for MW sweeps over the  $m_s=+1$  manifold. Color reflects obtained 7T DNP enhancements. (D) *Optimal MW repetition rates*  $\omega_r$  measured for sweeps over the  $m_s = \pm 1$  manifolds separately or together. Optimal value is obtained from fits. Data reveals relative field independence of observed optimal rates, with  $\omega_r^{(+1)} \approx 147\text{Hz}$ ,  $\omega_r^{(-1)} \approx 133\text{Hz}$ , and  $\omega_r^{(\pm 1)} \approx 73\text{Hz}$  (dashed lines). Shaded area represents 5% confidence interval around the optimal rates. Data suggests optimal repetition rates are dominated by the need to sweep each NV once during every optical repolarization cycle (E) *Optimal sweep rates*  $\dot{\omega}_r$  field dependence plotted for sweeps over the  $m_s = \pm 1$  manifolds individually. Data follows the spread of the underlying electronic spectra in both manifolds (see Fig. 3D).

shuttling can be exceedingly small ( $<1\%$  in our experiments), since it is only the traversal time through ultra-low field regions that predominantly contribute to deleterious loss.

## VII. FACTORS SIMPLIFYING MW SWEEPS

We now focus our attention on the factors affecting MW sweeps through the optimal electron bandwidths. For simplicity (see Fig. 6A), we distinguish between MW *sweep rates*  $\dot{\omega}_r = \mathcal{B}/t_r$ , where  $t_r$  is the time per sweep, and *repetition rates*  $\omega_r = 1/t_r$ , which are instead the rate of frequency chirps through the sweep band  $\mathcal{B}$ . Fig. 6B shows a typical dependence on the repetition rate, demonstrating a loss of polarization efficiency at slow and fast rates.

Microscopic predictions of the optimal MW sweep rates, and their dependence on polarizing magnetic field  $B_{\text{pol}}$ , are once again rather challenging. The Landau-Zener energy gaps and consequently the conditions for adiabatic travels of the level anti-crossings are functions of the applied Rabi frequency  $\Omega_e$ , NV center orientation, and importantly the hyperfine couplings<sup>20</sup>; and given the continuum of couplings and orientations in our sample, the optimal value is difficult to analytically compute. However, as Fig. 6B demonstrates, knowledge of this optimal rate is critical to obtaining optimized hyperpolarization

enhancements.

In this paper, we experimentally address this question, by determining dependence on MW sweep rates for various polarizing fields. Fig. 6C shows these results, concentrating first on the  $m_s=+1$  manifold, and employing a frequency comb constructed out of three cascaded MW sweepers. For each polarizing field, we sweep over the full NV ESR band  $\mathcal{B}$  given by Fig. 3C. We find that the MW repetition rates  $\omega_r^{(+1)}$  are (to a good approximation) independent of magnetic field. To demonstrate this more clearly, in Fig. 6D, we extract the optimal repetition rates for fields  $B_{\text{pol}}=1\text{-}30\text{mT}$ , considering sweeps over the  $m_s=+1$  and  $-1$  manifolds separately, as well as over both manifolds together. These optimal values are obtained from fits of the observed dependence (eg. solid line in Fig. 6B) to the expected behavior from microscopics of the Landau-Zener process<sup>32</sup>,  $\varepsilon = A \exp(-\Lambda^2/\omega_r)(1 - \exp(-\Omega^2/\omega_r))$ . The lines in Fig. 6D indicate 95% confidence intervals, showing additionally that the repetition rates exhibit a relatively benign dependence, with width  $\Delta\omega_r \sim 50\text{Hz}$ . In contrast, by plotting the MW sweep rates  $\dot{\omega}_r$  in Fig. 6E, we find that they increase with field, and closely follow the underlying spread in the electronic density of states (see Fig. 3D).

It is somewhat confounding that the system microscopics conspire to produce relative field independence. Strong hints to the origin of this behavior is provided by the results in Fig. 6D, where we observe that the optimum repetition rates for sweeps over both  $m_s = \pm 1$  manifolds simultaneously  $\omega_r^{(\pm 1)} \approx 73\text{Hz} \pm 29\text{Hz}$ , is approximately *half* that of sweeps over the individual manifolds, for instance,  $\omega_r^{(+1)} \approx 147\text{Hz} \pm 53\text{Hz}$ . Indeed, several factors contribute to determining optimal MW rates. There is the need to maximize: (i) the polarization transfer efficiency *per sweep* (ii) the *total* number of sweeps in a period bounded by nuclear  $T_1$ , and (iii) and the NV electron polarization at the start of every sweep event. Experiments in Fig. 6B suggest that the last factor is the most critical, pointing to relative field independence. Indeed, at the laser powers we employ the NV repolarization rate  $t_{\text{repol}} \sim T_{1e} \approx 1\text{ms}$ <sup>39</sup>, and sweeping MWs at a rate  $\omega_r \approx 1/(NT_{1e})$ , ( $N=3$  being the number of sweepers) ensures the largest NV polarization is available to transfer to the  $^{13}\text{C}$  nuclei per sweep. This observation once again simplifies hyperpolarizer miniaturization. Sweep times (5-10ms) are relatively slow, and can easily be generated by using microcontrollers to provide voltage ramps that when interfaced with the chip-scale VCOs provide the frequency chirped MWs (see Supplemental Information<sup>28</sup> for a miniaturized custom-built frequency-chirp circuit used in our hyperpolarizer).

Indeed miniaturization is the key behind the ability to cascade multiple frequency sources in a frequency comb in order to provide multiplicative enhancement gains<sup>32</sup>. This works on the principle that since while employing a single MW sweeper, the sweep rate also directly sets the total number of sweeps events that can be applied to the sample. However, the use of multiple sweepers allows one to decouple these two factors: it allows the maintenance of a fixed sweep rate per NV center spin “packet” and hence adiabaticity constraints, but increases effectively the number of total number sweeps applied on the spins. Since the total polarization time is bounded by the nuclear  $T_1$ , this can lead to a linear increase in the polarization levels by the use of multiple sweepers<sup>32</sup>. However, this increase is operational only in the regime where NV spins are predominantly inhomogeneously broadened, and when the sweepers are separated

by more than the inhomogeneous electronic linewidth. Indeed, when the number of sweepers is increased further, their spacing in frequency space approach the homogeneous NV linewidth, and there are no gains in hyperpolarization enhancements to be gained further. We found a saturation in hyperpolarization gains upon using  $\approx 3$  sweepers for a  $\sim 300\text{MHz}$  sweep bandwidth<sup>32</sup>.

## VIII. BACKGROUND SUPPRESSION VIA SIGN-REVERSALS

The DNP mechanism allows additional SNR gains in the detection of hyperpolarized signals, especially in the presence of large background signals. We refer to “*background*” as those signals that are not arising directly or indirectly from the optically hyperpolarized diamonds. We exploit the observation that the sign of the  $^{13}\text{C}$  polarization depends only upon the direction of the MW sweep<sup>20</sup>. Polarization is aligned (anti-aligned) to  $\mathbf{B}_{\text{pol}}$  for low-to-high (high-to-low) frequency sweeps over the NV ESR spectrum (Fig. 7A). In this paper, we quantify the *inversion fidelity*  $\mathcal{F}$  of the sign reversals. We find that when all NV orientations are swept over, the sign reversal is extremely robust, the amplitude of the  $^{13}\text{C}$  polarization inverts to within  $(1 - \mathcal{F}) = 2\%$  of its original value (see Fig. 7B). In reality, this is an underestimate of the inversion fidelity since it also includes (weak) repolarization during sample shuttling.

This ability to invert hyperpolarization signals on-demand and at high fidelity, with no change of hardware infrastructure, opens the door to background suppression of the DNP signals. Performing successive experiments with alternate MW sweep direction and subtracting the result, one can suppress the background and exclusively recover the DNP signal although it maybe initially impossible to discern. Applications for this idea are more powerful in case the polarization from the  $^{13}\text{C}$  spins in the diamond powder can be transferred to external liquids, for example  $^1\text{H}$  spins in water, through cross polarization<sup>13</sup> or the Overhauser effect<sup>40</sup>. Such hyperpolarized water, with a polarization that is sign invertible at will, could then be used as a bright-field MRI contrast agent in imaging applications, suppressing  $^1\text{H}$  signals from thermally polarized water in the body, and significantly boosting image contrast-to-noise.

In this paper, we demonstrate a restricted proof-of-concept experiment along these lines. We perform DNP on diamond microparticles embedded in a large volume of  $^{13}\text{C}$  labeled Fmoc-Gly-OH- $^{13}\text{C}_2$ , a compound<sup>41</sup> with a chemical shift that completely overlaps with the diamond signal at 7T. In Fig. 7C, we increase the concentration of this “background” signal, so that the hyperpolarized diamond signal is completely enveloped by it and typically impossible to discern. In fact, in the final panel of Fig. 7C, the background signal is over hundred times larger than the diamond peak. However background suppression using polarization sign inversions performs well (see Fig. 7C), and we can extract the diamond peak from the 112 times larger background (zoomed in Fig. 7D) with high fidelity.

An instructive representation of SNR gains through a *combination* of hyperpolarization and background suppression is in the lower axis of Fig. 7E. We are able to discern the diamond peak with high SNR, although every  $^{13}\text{C}$  nucleus in diamond is immersed in a background of more than  $10^4$  more  $^{13}\text{C}$  nuclei. This large factor is a multiplicative effect of DNP that renders every  $^{13}\text{C}$  in the diamond roughly 100 times “brighter” than



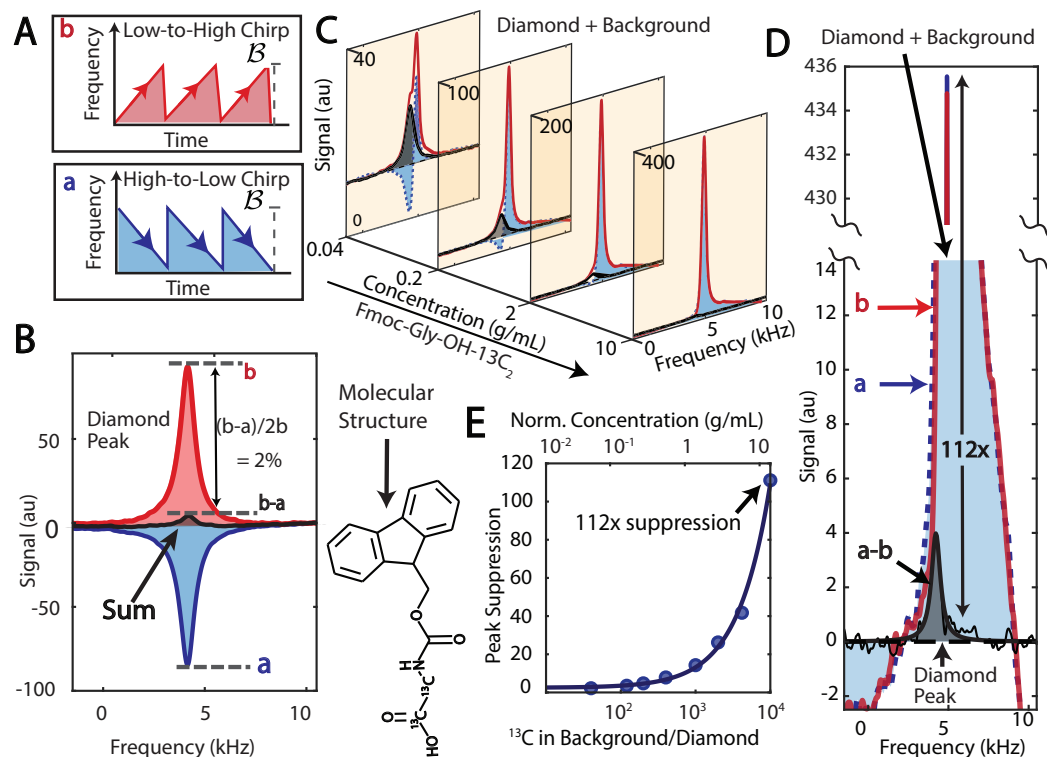


Figure 7. **“Background suppressed”  $^{13}\text{C}$  hyperpolarization** employing polarization sign reversals. (A) Schematic of polarization sign control. Sign of  $^{13}\text{C}$  hyperpolarization, aligned or anti-aligned to  $B_{\text{pol}}$ , depends only on the direction of the MW sweep. (B) Sign reversal fidelity  $\mathcal{F}$  is evaluated by MW sweeps at  $B_{\text{pol}} = 22\text{mT}$ . Results demonstrate that hyperpolarization sign can be reversed on-demand to better than  $(1-\mathcal{F}) = 2\%$ . (C) Background suppression by exploiting successive sign-reversals of  $^{13}\text{C}$  hyperpolarization. Diamond particles in Fig. 1C are immersed in increasing concentration (panels) of Fmoc-Gly-OH- $^{13}\text{C}_2$  (“background”) that overlaps the diamond spectrum. Red (blue shaded) line is the obtained spectrum under low-to-high (high-to-low) MW sweeps, each averaged 20 times. Subtracting the results allows one to extract the diamond spectrum (black shaded) although initially indiscernible. Concentrations of the background compound are displayed normalized to 50 diamond particles (see Methods). (D) Zoomed signal when employing highest relative concentration (final panel in C). Diamond signal (black) is recovered with high fidelity although initially enveloped by a 112 times stronger background signal, which is now completely suppressed. (E) Scaling of background suppression with compound concentration (upper axis). In final panel of C, suppression exceeds two orders of magnitude, corresponding to the detection of diamond  $^{13}\text{C}$  nuclei immersed in  $\sim 10^4$  more  $^{13}\text{C}$  nuclei in the background (lower axis).

7T thermally polarized nuclei, and polarization sign-reversals that suppress the  $^{13}\text{C}$  signatures in the background by over 100 times. The high fidelity recovery of the hyperpolarized signal in Fig. 7D indicates that the trend in Fig. 7E can be continued further; we expect one could suppress background signals over 1-2 more orders of magnitude.

## IX. CONCLUSIONS

In conclusion, by uncovering new physics underlying the DNP mechanism first introduced in Ref.<sup>20</sup>, we have constructed a compact solid-state room-temperature “optical nanodiamond hyperpolarizer”. The ability to construct such a device rests on a unique confluence of factors underlying the DNP mechanism requiring low fields, low laser and MW powers, and being robust to field inhomogeneity, optical excitation modes, and MW inhomogeneity. Hyperpolarization is on-demand sign invertible with high-fidelity, can be excited with very modest resources, and retained for long periods approaching tens of minutes. We employed the device to obtain best reported values of  $^{13}\text{C}$  hyperpolarization in diamond micro- and nanoparticles through optical means. We have also highlighted engineering aspects that,

leveraging the physics, make our nanodiamond hyperpolarizer device easy to build and operate, and with a small footprint that can retrofit any existing magnet system.

Our work opens the door to many intriguing new future directions. *First*, variants of the hyperpolarizer device could enable efficient polarization transfer relayed from the long-lived surface  $^{13}\text{C}$  nuclei to external liquids. While challenges remain requiring paramagnetic defect free surfaces and long relaxation time of surface  $^{13}\text{C}$  nuclei of the nanodiamonds, recent materials advances provide optimism on prospects for external polarization transfer<sup>42</sup>. Importantly the hyperpolarization so generated optically is replenishable, and could also be employed with NV sensors for the optical detection of magnetic resonance<sup>43,44</sup>. This may open new possibilities for miniaturized NMR spectrometers for chemical analysis. *Second*, from a technological standpoint, the device can be easily miniaturized further. A more efficient MW delivery scheme will allow the use of a lower power amplifier that currently occupies the largest footprint. All other MW components can be replaced by chip-scale ones, and a palm-top sized hyperpolarizer can easily be envisioned. Integrating low-field inductive NMR readout<sup>45</sup> into the device will enable an in-situ measurement of the  $^{13}\text{C}$  hyperpolarized signals without the need for sample shuttling. *Finally*, it should be possi-

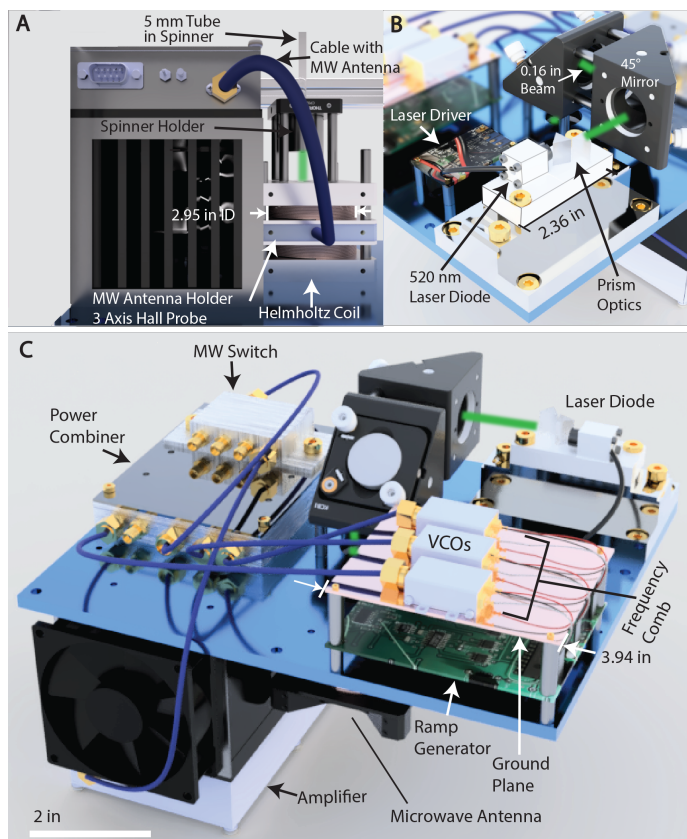


Figure 8. **Nanodiamond hyperpolarizer schematic** (to scale) showing component parts assembled on a single 10in $\times$ 10in aluminum plate (blue). (A) *Sample attachment*. Diamond particles to be hyperpolarized are placed at the confluence of the laser and MW excitation in a weak polarizing field generated by the Helmholtz coil pair. Amplified MWs are delivered by means of a stubbed loop antenna (see Fig. 4D). (B) *Optical excitation* is provided by a small (2.36in) 520nm 1W laser diode placed on the plate underside. Minimal optics direct the beam to the sample. Alternatively, multi-mode optical fibers can deliver the light from one or more laser diodes mounted in the device. (C) *MW generation and excitation* circuitry (also on plate underside) involves miniature VCO sources interfaced with a custom-built voltage ramp generator to produce the MW frequency sweeps. Chirped MWs are subsequently power combined, amplified, and finally delivered to the MW antenna. The ultracompact, modular, design allows easy customization and enhances device portability.

ble to produce similar low field hyperpolarization in other wide bandgap semiconductor materials. Pioneering recent work<sup>46,47</sup> has demonstrated that the V1 defect center in Silicon Carbide can be hyperpolarized through infrared light. Employing these spins for DNP will allow *in-vivo hyperpolarization* of  $^{29}\text{Si}$  nuclei and background-free imaging of nanoparticles targeting disease locations.

## SUPPLEMENTAL INFORMATION

In the accompanying Supplemental Information, we include more details about the construction of the miniature hyperpolarizer device, including the electronics for frequency sweep generation required to excite dynamic nuclear polarization (DNP). We also characterize the performance of the device under field and

MW inhomogeneity, and provide details of an integrated Hall probe system to measure the magnetic field at the site of the polarizer device. This aids in its use as a retrofit for existing NMR and MRI systems. We characterize enhancement levels when the diamond particles are hyperpolarized while being immersed in different solutions, including solvents, and biological liquids such as blood and saline. Finally, we detail measurements of the  $^{13}\text{C}$  lifetimes in diamond as a function of magnetic field, and for completeness include an overview of the DNP mechanism operational in our device.

## ACKNOWLEDGMENTS

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## APPENDIX A: MATERIALS AND METHODS

### A. Hyperpolarizer construction

The hyperpolarizer (Fig. 1A, Fig. 2) is a stand-alone device fully operational at room-temperature, composed from non-magnetic solid-state components and requiring almost zero user maintenance. We choose a modular design that allows a compact and rapid assembly of the various components (see Fig. 8). The device has a small footprint (12 $\times$ 10 $\times$ 10in.) and light weight (<10lb), making it ultraportable, and compatible with any NMR spectrometer. This small hyperpolarizer is testament to the technological ease of optical DNP at low fields.

The aluminum chassis supports three distinct modular blocks (see Fig. 2): optics, MW sweep generation, and a sample holder that contains the diamond particles to be hyperpolarized (Fig. 8). The densely packed and double-sided design supports easily customizable modalities for sample placement and removal. For instance, the device can contain a hollow bore to allow shuttling of the sample into a high field NMR magnet. For more experiments, we employ a miniature 1W 520nm diode laser (Lasertack PD-01289) in a feedback loop with an integrated thermoelectric cooler for adequate thermal control (TE Inc. TE-63-1.0-1.3). Very few optical components are required (see Fig. 8B): an aspheric lens and a set of anamorphic prisms collimate the beam to a circular 4mm diameter. Two mirrors redirect the beam towards the sample, typically irradiating it from below. We note however that the modular design of the device engenders the use of multiple laser sources (fiber coupled with Thorlabs M35L01) to illuminate large masses of the sample, or to ensure better illumination coverage on densely packed diamond powder. We have employed unto 9 sources simultaneously on the sample at a total power of  $\sim 400\text{mW}/\text{mm}^3$  without significant sample heating.

Microwaves are generated by miniature voltage controlled oscillator (VCO) sources (Minicircuits ZX95-3800A+, 1.9-3.7GHz, output power  $p = 3.1\text{dBm}$ ). Frequency sweeps are

produced by controlling the VCO frequency by a homebuilt quad-channel voltage ramp generator controlled by a PIC microprocessor (PIC30F2020). Fig. 8C shows the connectorized VCOs mounted on a copper sheet that serves as a good ground plane. Given the relatively slow MW sweeps required,  $\omega_r \approx 164\text{Hz}$ , translating to sweep times of 6ms for the typical sweep bandwidths  $B=100\text{MHz-1GHz}$ , the 50kHz clock speeds of the microprocessor provide sufficiently fast control for the sweep circuitry. The sweep generator employs dual multiplying digital-to-analog converters (MDACs, Linear Technology LTC1590) to generate the sawtooth voltage ramps. The sweeps from the individual sources are time-cascaded, generating a MW frequency comb that sweeps different parts of the NV ESR spectrum at once. This allows multiplicative gains in the obtained DNP enhancements. The VCO outputs are power-combined (Minicircuits ZN4PD1-63HP-S+,  $p = 2.2\text{dBm}$ ), passed through a high-isolation switch (Minicircuits ZASWA- 2-50DR+,  $p = -0.46\text{dBm}$ ) and delivered to a low-cost amplifier (Minicircuits ZHL16W-43S+,  $p = 37.9\text{dBm}$ ) that transmits the microwave irradiation to the sample via a stubbed loop antenna (4mm diameter, reflected power  $p = 36.3\text{dBm}$ , radiation efficiency = 24%). The radiated MW powers required are extremely low, estimated to be below 1.5W. To estimate the Rabi frequency, we assume an upper limit of microwave output power  $P \approx 1.5\text{W}$  at a frequency  $\nu = 3\text{GHz}$ . Since the circuit is broadband, the magnetic energy is at most  $W_B = P/\nu$  and equal to  $w_B V = \frac{B^2}{2\mu_0} \frac{4\pi}{3} R^3$  where  $w_B$  is energy density of the magnetic field and we approximate the volume by a sphere with radius  $R=2\text{mm}$ . To generate the weak field  $B_{\text{pol}}$  used for hyperpolarization, as described in Fig. 4A, we employ a single axis Helmholtz coil (25 turns, 10 layers, 0.8mm diameter) mounted around the sample, generating 14mT fields with  $\approx 2\text{A}$  of current, and with minimal heating. The coil also helps in the hybrid scenario supplementing detection magnet fringe fields. A set of three small Hall sensors (AsahiKASEI EQ-731L, magnetic sensitivity 65mV/mT) are placed in the polarizing window near the sample, and provide an in-situ measurement of the field. A simple feedback loop can match the field with any desired value.

## B. Materials

While we have focused entirely on the physics of the hyperpolarization mechanism, and the constriction of the hyperpolarizer device, the material properties of the diamond particles employed can themselves play a critical role in setting the ultimate hyperpolarization levels. The particles employed for hyperpolarization can be HPHT and CVD grown and generally have a high density ( $\sim 1\text{-}10\text{ppm}$ ) of NV centers<sup>48</sup>. In Ref.<sup>31</sup> we studied these materials factors in detail across different dimensions including electron irradiation doses, sample annealing conditions and particle size. We observed that the quality of the lattice plays a critical role, and sets directly both the NV centers  $T_1$  and  $T_2$  coherence time, but also the  $^{13}\text{C}$   $T_1$  lifetimes. In general, a more pristine lattice free from paramagnetic defects can lead to higher hyperpolarization enhancement levels. Through combined ESR and NMR studies, we demonstrated that rapid annealing of the diamond particle sample at high temperature (1700-1800°C for 15min) can substantially relieve lattice damage stemming from electron irradiation and improve the hyperpolarization levels by an order of magnitude when compared to standard annealing

conditions (850°C for 2hrs). We point the reader to Ref.<sup>31</sup> for a more detailed exposition on these aspects.

## C. Experimental methods

In the experiments of Fig. 1B-E, we employed in the hyperpolarizer device a fiber coupled excitation involving an octagonal arrangement of eight 800mW diode lasers to ensure all particle surfaces were maximally exposed to the illumination. The field dependence experiments in Fig. 4A over the wide field range were obtained as a combination of two datasets accessing (1-40mT) and (30-70mT) ranges, and normalizing points in the overlapping regime. From this we obtain the error bar of 11% indicated in Fig. 4A. For the latter range, we employed the Synergy DCRO330500 VCOs and AR50S1G6 amplifier combination. For background suppression experiments in Fig. 7, Fmoc-Gly-OH- $^{13}\text{C}_2$  was successively added in a NMR tube containing 0.5ml DMSO (Fisher Scientific) and 50 particles of 200 $\mu\text{m}$  diamonds at the beginning. After reaching saturation at 1g/ml, the amount of diamonds was halved from step to step. The concentrations in Fig. 7C are displayed normalized to 50 particles. The calculated ratio between the number of  $^{13}\text{C}$  atoms in Fmoc-Gly-OH- $^{13}\text{C}_2$  and diamond was based on mass considerations. Considering that the Fmoc-Gly-OH- $^{13}\text{C}_2$  mass  $m_F$  (g), and having molar mass  $M_F = 299.29\text{g/mol}$ , the molar mass of diamond  $M_D=12.01\text{g/mol}$ , the density of diamond  $\rho = 3.52\text{g/cm}^3$ , the edge length of the truncated octahedral crystallites  $a = 87 \pm 3\mu\text{m}$ , and the number of diamonds  $n$ , the ratio of  $^{13}\text{C}$  nuclei outside the diamond to within it can be calculated as  $\frac{m_F M_D}{8\sqrt{2}a^3 \rho n M_F} \frac{100}{1.1}$  (upper axis in Fig. 7E).

Experiments in Fig. 5 are carried out by interfacing the hyperpolarizer with a mechanical field cycling instrument constructed over a 7T detection magnet, and consisting of a sensitive conveyor belt actuator stage (Parker HMRB08) with 50 $\mu\text{m}$  precision and 1.5m travel range in the fringe field of the magnet, allowing a rapid ( $\sim 700\text{ms}$ ) and wide field sweep range from 10mT-7T<sup>37</sup>.

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