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Supplementary Information for

Enhanced dynamic nuclear polarization via swept microwave frequency combs


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Supporting Information Text

1. Linewidth limits of frequency comb DNP

In order to highlight the linewidth limitations when employing multiple cascaded sweepers, we performed detailed experiments mapping the NV center ESR spectrum via $^{13}$C DNP in a narrow 12.5 MHz sweep window for samples of different $^{13}$C enrichments (see Fig. S1). Similar to Fig. 6 in the main paper, the crystals are placed with the NV axes at the magic angle to the polarizing field, allowing the obtained spectra to be broadened predominantly by hyperfine couplings to $^{13}$C nuclei. We ascribe the slight asymmetry in the lineshape of Fig. S1B to crystal misalignment from the magic angle. The linewidth of the highly enriched samples are dominated by the hyperfine coupling to closeby $^{13}$C. A systematic discussion of the changes in lineshape is beyond the scope of this work and will be addressed in a forthcoming publication.

It is evident that the two cascaded sweepers provide a gain over a single one (right panels in Fig. S1) only when the comb teeth are separated by approximately the hyperfine mediated electron linewidth, which increases with $^{13}$C enrichment. This data was also used to report the exact optimal sweep bandwidths for one and two sweepers, plotted in the inset of Fig. 6C of the main paper.

Fig. S2 studies a similar bandwidth dependence of DNP gains with multiple cascaded sweepers for a 1% (natural abundance) microdiamond sample. The sweep bandwidth is centered at the center of the powder pattern (inset of Fig. S2). Once again, the enhancement gains are a strong function of the sweep bandwidth, decreasing sharply when the comb teeth spacing approaches the hyperfine mediated electron linewidth.

2. Hyperpolarized signal and buildup

Fig. S3 exhibits essential results from Ref. [1], demonstrated for a typical example of 200µm microparticles with natural abundance $^{13}$C containing about 1ppm of NV centers (Fig. S3C). We obtain $^{13}$C hyperpolarization over 116 times that of the...
We now briefly describe the low field DNP mechanism that governs the polarization transfer in our experiments. For more details, and experimental characterization of the mechanism, we point the reader to Ref. [1]. Consider for simplicity a NV center coupled to a single $^{13}$C nuclear spin. The Hamiltonian of the system is,

$$
\mathcal{H} = \Delta S_x^2 - \gamma_e B \cdot \vec{S} - \gamma_n B \cdot \vec{I} + A_{zz} S_z I_z + A_{yy} S_y I_y + A_{xx} S_x I_x + A_{xz} S_x I_z + A_{zy} S_y I_z + A_{zx} S_x I_y
$$

where $\vec{S}$ and $\vec{I}$ respectively denote the NV and $^{13}$C vector spin operators, and $\vec{B}$ is the magnetic field (10-30 mT) at angle $\vartheta$ ($\varphi$) to the NV axis. Within the $m_s = \pm 1$ states, the hyperfine coupling produces a $^{13}$C splitting,

$$
\omega_C^{(\pm 1)} = \sqrt{(A_{zz} \mp \gamma_n B \cos \vartheta)^2 + A_{xx}^2}
$$

For the $m_s = 0$ manifold, second-order perturbation theory leads to the approximate formula [2],

$$
\bar{\omega}_L \approx \gamma_n B \approx 2 \frac{(\gamma_e B)}{\Delta} \sin \vartheta \left( \sqrt{A_{xx}^2 + A_{zz}^2 \cos^2 \varphi} + A_{yy} \sin^2 \varphi \right)
$$

Fig. S2. Bandwidth dependence of multiplicative DNP gains in microdiamond powder. For varying sweep bandwidths centered on the NV center powder pattern, we obtain the $^{13}$C DNP signal employing a swept frequency comb of up to three cascaded sweepers at $\approx$20mT. Solid lines are guides to the eye. Inset: Experimentally determined powder pattern. Shaded region denotes an example 600MHz sweep bandwidth. Panel demonstrates electron linewidth limits on the obtained multiplicative DNP gain (see Fig. S1).

3. Hyperpolarization Mechanism

In our experiments, the sign of the polarization only depends on the direction of the microwave sweeps (Fig. S3C). Sweeping the microwaves in a ramp fashion from low-to-high frequency leads to nuclear polarization aligned to the polarizing $B$ which we term positive polarization. Anti-alignment can be achieved accordingly by sweeping from high-to-low-frequency. This allows on-demand control of the sign of polarization. As expected, a triangular sweep pattern with equal amounts of high-to-low and low-to-high frequency sweeps leads to destructive interference in alternate periods, and no net polarization buildup. Indeed, increasing the number of cascaded sweepers $N$ maintains the same optimal sweep rate set by adiabaticity constraints, and hyperpolarization sign dependence on the direction of the sweep (see Fig. S4).
From Eqs. 2 and 3 we conclude that each manifold (including the $m_s = 0$ manifold) has its own, distinct quantization axis which might be different from the direction of the applied magnetic field. In particular, the second term in Eq. 3 can be dominant for hyperfine couplings as low as 1 MHz (corresponding to nuclei beyond the first two shells around the NV) if $\theta$ is sufficiently large, implying that, in general, $^{13}$C spins coupled to NVs misaligned with the external magnetic field experience a large frequency mismatch with bulk carbons, even if optical excitation makes $m_s = 0$ the preferred NV spin state.

Assuming fields in the range 10-30 mT, it follows that $^{13}$C spins moderately coupled to the NV (300 kHz $\lesssim |A_{zz}| \lesssim$ 1 MHz) are dominant in the hyperpolarization process because they more easily spin diffuse into the bulk and contribute most strongly to the observed NMR signal at 7T. For sweep rates near the optimum ($\sim$ 40 MHz/ms), the time necessary to traverse the set of transitions connecting $m_s = 0$ with either the $m_s = -1$ or $m_s = +1$ manifolds is relatively short ($\lesssim$ 30 $\mu$s for weakly coupled carbons) meaning that optical repolarization of the NV preferentially takes place during the longer intervals separating two consecutive sweeps, as modeled in Fig. 3 of the main paper.

Nuclear spin polarization can be understood as arising from the Landau-Zener crossings in Fig.3. Efficient polarization transfer takes place when the narrower LZ crossings connect branches with different electron and nuclear spin quantum numbers, precisely the case in the $m_s = 0 \leftrightarrow m_s = -1$ ($m_s = 0 \leftrightarrow m_s = +1$) subset of transitions when the hyperfine coupling is positive (negative). When probing ensembles, both sets of transitions behave in the same way, i.e., $^{13}$C spins polarize positive in one direction, negative in the other. A more detailed exposition of the hyperpolarization mechanism and simulations are presented in Ref. [1].

4. Integrated Solid Effect

For completeness, here we review the principles of Integrated Solid Effect (ISE) (see [3, 4]) and the adiabaticity conditions for optimal polarization transfer (see Fig. 1 of main paper). The DNP mechanism we employ for the NV-$^{13}$C system shares several implementational similarities with ISE. Under swept MW irradiation with frequency $\omega$, the Hamiltonian of a coupled
The electron nuclear spin system is,

$$H = \omega_e S_z - \omega_L I_z + 2\Omega_z S_z \cos(\omega t) + \mathbf{S} \cdot \mathbf{A} \cdot \mathbf{I}.$$  \[[4]\]

The first two terms are electron and nuclear Zeeman term respectively, and the last term is hyperfine coupling between the electron and nuclei. In the rotating frame,

$$H = \Delta \omega S_z + \Omega_s S_z - \omega I_z + \frac{1}{2} S_z A_{zz} I_z + \frac{1}{2} S_x A_{xz} I_x - \frac{1}{2} S_y A_{xy} I_y$$  \[[5]\]

where $\Delta \omega = \omega_e - \omega_L I_z = I_x \pm I_y$. Assuming that the components of the hyperfine tensors are small. In this tilted rotating frame set by basis $|m_i\rangle$, the $\omega S_z$ term contributes to non-diagonal terms and induces states transitions. There are then effectively two level anti-crossings (LACs) at which polarization polarization transfer from the electron to nuclei can be affected, given by $\sqrt{(\Delta \omega)^2 + \Omega_s^2} - \omega_L \approx 0$. Assuming the rate for frequency sweep is $\dot{\omega}$, the probability of electron spin staying at the same state equals is $\exp\left(-\frac{\Omega_s^2}{\dot{\omega}^2}\right)$. Thus this results in the adiabatic condition for the frequency sweep $\frac{\Omega_s^2}{\dot{\omega}^2} \gg 1$.

5. Experimental design

During our DNP process, 1W laser (520nm LasterTack) light is applied continuously for a fixed time (~60s) to polarize the NV centers. Simultaneously applied swept microwave (MW) irradiation (MiniCircuits ZHL16W-43S+ 16W) across the NV center spectrum at 1-30mT transfers the polarization to \(^{13}\)C nuclei (see Fig. 2A in the main paper). A mechanical field cycler then rapidly carries the sample from the low field magnetic shield (NETIC S3-6 alloy 0.062” thick, Magnetic Shield Corp) where hyperpolarization is excited to a 7T superconducting magnet (see Fig. S5A) in a total travel time of 648±2.6ms. Inductive detection of the \(^{13}\)C NMR signal starts immediately after the sample is in position at high field. The entire hyperpolarization...
6. Electronics for swept MW frequency combs

Setup. Microwave (MW) sweeps are applied across the NV center powder pattern to drive the DNP process (see Fig. 2A in the main paper). For the experiments in this work, we employed voltage controlled oscillator (VCO) (MiniCircuits ZX95-3800A+ (1.9-3.7 GHz)) sources to generate the frequency sweeps, by employing DC shifted ramp input voltages to produce the sweeps (see Fig. S6). The microwaves are finally amplified by a 16W amplifier into a stub antenna that produces either longitudinal or transverse fields.

Fig. S6. Schematic circuit for DNP excitation. Low field DNP from NV centers to $^{13}$C is excited by microwave sweeps produced by employing voltage controlled oscillators (VCOs) with ramp generator inputs (see Fig. S7). Multiple VCOs are employed in a cascade to increase polarization transfer efficiency. A spectrum analyzer is used to implement a feedback algorithm that exactly matches the VCO bandwidths to $\sim$2 MHz (see Fig. S8). The microwaves are finally amplified by a 16W amplifier into a stub antenna that produces either longitudinal or transverse fields.

Fig. S7. Feedback matching of VCO sweep bandwidths. Frequency-voltage characteristics of two MiniCircuits ZX95-3800A+ VCO frequency sources measured with an in-situ spectrum analyzer (Fig. S6), showing dissimilarity in frequency output with tuning voltage by $\approx$ 3MHz/V (inset A). (B) Feedback is now implemented to match their swept bandwidths to 500± 1 MHz, shown in the insets for 2kHz sweep frequency (see Fig. S8). This allows the VCOs to be cascaded to simultaneously sweep over the NV center powder pattern to enhance DNP efficiency.

procedure is relatively easy to conduct on account of the low laser and MW powers employed, as well as absolutely no requirement for alignment of diamond samples to the magnetic field. The field cycling consists of a high-precision actuator (Parker HMRB08) with a twin carriage mount carrying a carbon fiber rod (8mm, Rockwest composites) into which the NMR tube (8 mm, Wilmad) containing the sample is pressure fit. Single crystal or powder samples are immersed in water (Fig. S5B), and a plunger firmly holds the sample solution to prevent changes in sample orientation and position during shuttling (Fig. S5C). Single crystals have the NV axes oriented at magic angle (see Fig. 6) to the polarizing field. Fig. S5D details the hyperpolarization setup in the low field shield. The laser beam is collimated to a $\sim$4mm diameter and irradiated at the bottom of the NMR tube carrying the sample. The microwaves are delivered by means of a stub antenna (loop) employed below the tube. The motion and subsequent detection is controlled and sequenced with pulse generator (SpinCore PulseBlaster USB 100 MHz) using a high voltage MOSFET switch (Williamette MHVSW-001V-036V). For more details on the device construction and performance we point the reader to Ref. [5].
1022A), in a high-pass configuration with a $\sim 1$Hz cutoff frequency. The input ramps are programmed to carefully tune the VCO outputs to the target sweep bandwidths corresponding to the NV center powder pattern [1]. Lastly, after being power combined (MiniCircuits ZN4PD1-63HP+), a 16W amplifier (MiniCircuits ZHL16W-43S+) transmits the microwaves to a stub antenna matched to the diameter of the tube containing the sample [1] to excite the $^{13}$C hyperpolarization.

**Generating swept frequency combs.** Cascaded sweeps utilizing multiple VCOs ($N_{\text{VCO}}$) are generated by using input voltage ramps that are phase shifted by $2\pi/N_{\text{VCO}}$. The VCO output frequency $f(V)$ and input voltage $V$ has approximate linear relationship, $f(V) = b \cdot V + F$, where $b$ is a constant coefficient and $F \approx 1.9$GHz is the frequency when $V = 0$. However, the VCOs have slightly differing $f$-$V$ characteristics, even when of the same family, due to inter-device variation and temperature dependence (see Fig. S7). In order to match all the VCOs to sweep the target band, and to generate the equally spaced frequency comb, we implemented a gradient descent feedback algorithm employing a fast spectrum analyzer (SignalHound USB-SA44B).

Let us define the DC and AC voltage inputs to the VCOs for the $i$th iteration ($i=1, 2, 3,...$) to be $V_{\text{pp}}$ and $V_{\text{dc}}$. We define center of the spectrum $f$ for the $i$th iteration, and bandwidth of the spectrum $\Delta f$, while the target spectrum center and width are $f_0$, $\Delta f_0$ respectively. Given the linearity of the VCO response, $V_{\text{dc}}$ and $V_{\text{pp}}$ are predominantly related to $f$ and $\Delta f$ respectively. The following equations are applied to update $V_{\text{pp}}$ and $V_{\text{dc}}$ level for each iteration:

\[
\begin{align*}
V_{\text{pp}}^{i+1} &= \frac{\Delta f_0}{\Delta f} \cdot V_{\text{pp}}^i, \\
V_{\text{dc}}^{i+1} &= V_i + \frac{f_0 - f_i}{b},
\end{align*}
\]

During each feedback loop, $V_{\text{pp}}$ is adjusted based on the assumption that bandwidth $\Delta f$ is approximately proportional to $V_{\text{dc}}$, and $V_{\text{dc}}$ shifted to approach the target band center. To ensure VCO receiving reasonable input, initial values are set to $V_{\text{pp}}=2V$ and $V_{\text{dc}}=6V$, based on empirical $b$ and $F$. The pre-set deviation we typically use is 2MHz, which is approximately the VCO output linewidth when input is a single constant voltage. The efficiency of the algorithm is highlighted in Fig. S8.

**Intermodulation Distortion limits.** The multiplicative DNP gains of our microwave frequency comb technique will be limited by hyperfine mediated electron broadening, and also practical constraints such as non-linear distortions set by amplifier intermodulation distortion (IMD). Here we highlight the latter and discuss its effect on our hyperpolarization technique.

IMD appears in a wide range of RF and microwave systems, and particularly affects our experiments in the power amplifier stage Fig. S6. When input a two-tone signal, an ideal linear amplifier would produce an output signal of the amplified two tones at exactly the same frequencies as the input signal. A realistic amplifier, however, will produce additional signal content at frequencies other than the two input tones. As one can tell from Fig. S9, two fundamental tones, $f_1$ and $f_2$, injected into the amplifier mix to produce interfering signals with the most notable interference given by third order products, which are $2f_1 - f_2$ and $2f_2 - f_1$. The power in these intermodulation products depends on how close the amplifier is to saturation. After saturation, the gain becomes nonlinear and enters a compression regime where the output power becomes independent of the input power. In this compression regime, intermodulation products and distorted signals arise from the mixing of fundamental signals which can adversely alter the signals of the amplified bandwidth. Since in our DNP mechanism the transfer efficiency falls rapidly with MW power, as long as one operates far below the amplifier compression point, these harmonics do not play a significant role in hyperpolarization process. However, when the two tones approach a frequency separation $<10$MHz (Fig. S9C), the nonlinearity of the amplifier substantially distorts the output signal and deleteriously affects the DNP efficiency. In general, cascading more frequency sweeps lead to a larger number of spurious IMD harmonics, all of which take away MW

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The DNP enhancement in our experiments is quantified by scaling the hyperpolarized signal to the corresponding thermal power from the main frequency comb that drives the hyperpolarization process. This is evident for instance in Fig. S9D, where we consider three frequency tones.

This technical obstacle can be overcome by employing multiple cascaded amplifiers, each amplifying a component of the frequency comb, which are then subsequently combined. This exploits the fact that power splitters have significantly lower nonlinearity, are not prone to IMD, and can yield a distortion-free combination of frequency tones. While the overall MW power increases linearly with the number of comb teeth, the ability to combine several low-power amplifiers to obtain multiplicative gains in DNP enhancements also has serious advantages in overall cost of the electronic infrastructure required.

**MW frequency combs at high field.** Let us now describe how the swept frequency combs can be constructed in the context of high field DNP with radicals. The availability of arbitrary waveform generators with bandwidths that reach into the microwave range, combined with solid-state millimeter wave mixers, now permits arbitrary pulse shaping up to Terahertz frequencies.

There are two approaches possible. At frequencies below about 100GHz, it is possible to directly mix a high frequency carrier with a modulated microwave signal, filter it, and feed the resulting modulated millimeter waves into an amplifier. Solid-state amplifiers with up to 1W of power are commercially available below 100GHz. At even higher millimeter wave frequencies, an active multiplier chain (AMC-Virginia Diodes) is used to generate the millimeter wave signal, with a microwave input to the AMC in the 10-20GHz range. These AMC’s are available with up to about 100mW of power at 270GHz, dropping to about 10mW at 500GHz and 1mW at 1THz. By modulating the input to the AMC, it is possible to create arbitrarily modulated millimeter waves. Note that in this case it is necessary to scale the desired modulation down by the multiplication factor of the AMC.

The use of solid-sources at higher frequencies is typically constrained by the available power and the significant increase in cost with increased power output. At liquid helium temperatures, the electron spin relaxation times become much longer, and it is possible to excite DNP at lower millimeter wave power. At liquid nitrogen temperatures typically used for DNP-MAS experiments, the electron spin relaxation times are short, and high millimeter wave powers are needed to ensure good DNP. Gyrotrons are used to generate sufficient millimeter wave power for DNP in this regime. While gyrotrons have typically been narrow band (resonant devices), voltage-tunable gyrotrons that enable frequency modulation are being developed [6].

**7. Data Analysis**

The DNP enhancement in our experiments is quantified by scaling the hyperpolarized $^{13}$C signal to the corresponding thermal signal at 7T for each sample. The spectra are all phased, baseline corrected, and scaled to have an average noise of 1. This allows comparison between signals taken with a different number of averages. The areas of each peak area was calculated, and the ratio between them determines the enhancement factor. Zero-order phase correction is applied by multiplying the spectrum by a phase value that maximizes peak height.
A fitted absorptive Lorentzian curve identifies the peak in each spectra with the real portion of the data. Standard Lorentzian formulas were used to calculate the area under the fitted curve, and peak limits were designated such that the area between the limits encompassed 90 percent of the entire spectrum area. The portion outside of the peak limits was defined as noise. To flatten the baseline, a 12th order polynomial was fitted through these parts, and subtracted from the spectrum. For comparison between DNP and thermal spectra, the average noise of both spectra was scaled to 1 by dividing the noise section by its standard deviation. The area of each peak was then obtained through a Riemann sum across the peak limits, and the DNP enhancement factor given by the equation:

$$
\varepsilon = \frac{\text{SNR}_{\text{DNP}}}{\text{SNR}_{\text{Thermal}}} \sqrt{\frac{N_{\text{DNP}}}{N_{\text{Thermal}}}}
$$

[8]

References