

Supplemental Material for

Hyperpolarization-Enhanced NMR Spectroscopy with Femtomole Sensitivity Using Quantum Defects in Diamond

Dominik B. Bucher,^{1,2,8,*} David R. Glenn,¹ Hongkun Park,^{1,3,4} Mikhail D. Lukin,¹ and Ronald L. Walsworth^{1,2,4,5,6,7,†}

¹Department of Physics, Harvard University, Cambridge, Massachusetts 02138, USA

²Harvard-Smithsonian Centre for Astrophysics, Cambridge, Massachusetts 02138, USA

³Department of Chemistry and Chemical Biology, Harvard University, Cambridge, Massachusetts 02138, USA

⁴Center for Brain Science, Harvard University, Cambridge, Massachusetts 02138, USA

⁵Department of Physics, University of Maryland, College Park, Maryland 20742, USA

⁶Department of Electrical and Computer Engineering, University of Maryland, College Park, Maryland 20742, USA

⁷Quantum Technology Center, University of Maryland, College Park, Maryland 20742, USA

⁸Department of Chemistry, Technical University of Munich, 85748 Garching, Germany

*To whom correspondence and requests for materials should be addressed. dominik.bucher@tum.de

†To whom correspondence and requests for materials should be addressed. walsworth@umd.edu

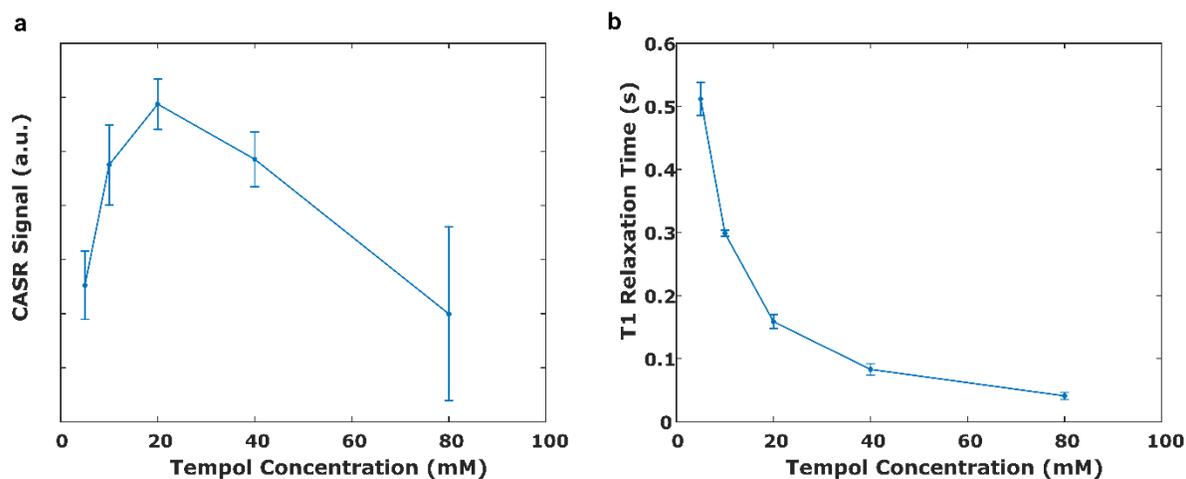


Figure S1 Tempol concentration dependencies. **a)** CASR signal from deionized water plotted against the TEMPOL concentration. We observe a maximum in enhancement around 20 mM. Due to slightly different MW antenna orientations in different experimental runs, we observe slightly varying DNP enhancement factors for the CASR signal. For that reason we mean subtracted the data before averaging. **b)** T₁ proton relaxation time as a function of TEMPOL concentration. At a TEMPOL concentration of 20 mM, the proton T₁ relaxation time is ~150 ms, well-matched to the operating linewidth of our NV-NMR sensor. Longer T₁ times can be achieved by reducing the TEMPOL concentration with only modest reduction in the CASR signal (see a). Error bars represent standard deviation (1σ) of the proton NMR T₁ relaxation time measured across three independent CASR experiments.

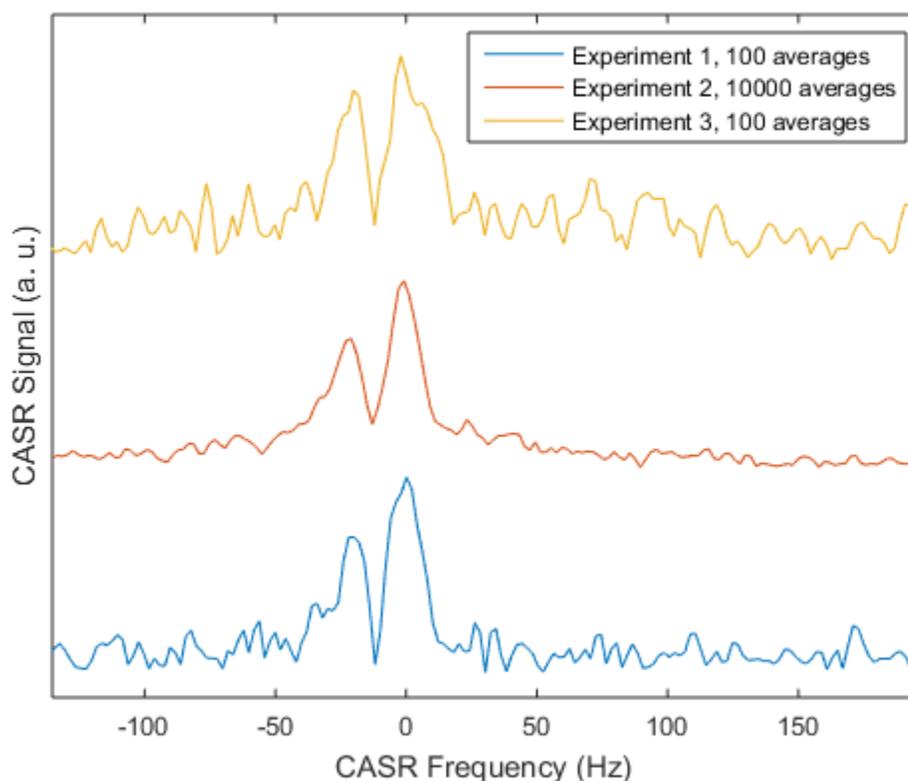


Figure S2 Reproducibility of experiments. We repeated each CASR experiment at least three times. Here we show an example dataset for Xylene. The amplitude of the CASR signal is scaled to our ac reference signal from a coil. Note that the sensitivity improvement for long acquisitions of Xylene CASR signals scales as somewhat less than the square root of the number of averages. We attribute this scaling to a slow reduction of the optical coupling between the quantum diamond sensor and lightguide, over repeated use, as the solvent degrades the optical epoxy used to join them. In future implementations of this technique, the sample should be physically isolated from all optical interfaces.

Supplementary Note 1

“The Overhauser enhancement can be written as¹

$$\varepsilon = -\xi \cdot f \cdot s \cdot \left| \frac{\gamma_S}{\gamma_I} \right|$$

Where γ_S and γ_I are the gyromagnetic ratios of the electron and the nucleus, respectively. ξ describes the coupling factor, f the leakage factor f and s the saturation factor.

For proton hyperpolarization $\left| \frac{\gamma_S}{\gamma_I} \right| \approx 660$. The saturation factor s describes how well the electron transition is saturated by microwave irradiation and ranges from 0 to 1. The leakage factor f accounts for the parametric relaxation of the nuclear spin and approaches 1 if the nuclear T1 relaxation time is dominated by the electronic

spins. The coupling factor ξ represents the efficiency of electron-nuclear cross relaxation and reaches 0.5 if the interaction is dipolar. Thus, the theoretical limit is ~ 330 for protons.

Our experimental results show that water has the highest enhancement factor (~ 230) which approaches the theoretical limit. The other organic molecules measured have a 2-3 lower enhancement factors. We assume that the leakage factor f and the saturation factor s are approximately constant for all samples, but the coupling factor is known to be strongly dependent on the sample as well as the solvent. One major factor is the molecular dynamics which governs the correlation time and determines the spectral density function. We ascribe the reduced enhancement for the organic molecules to their larger molecular size compared to water. A more detailed understanding the Overhauser mechanism for each molecular system would likely require numerical simulations beyond the scope of the present work.

Supplementary Note 2

We seek to estimate the spin polarization achievable in a picoliter-scale liquid sample volume above the diamond surface, using shallow, optically-pumped NV centers for hyperpolarization. While a variety of schemes have been proposed for polarization transfer from NV electron spins to external nuclear spins, we consider the particular case of resonant polarization transfer using Hartmann-Hahn frequency matching, with spin exchange driven by random molecular motion. Our estimate captures the challenging features of all such techniques, namely (i) the relatively weak coupling between NV centers and sample protons, and (ii) the difficulty of achieving favorable NV/proton spin number ratios in a picoliter-scale sensing geometry.

The mechanics of the Hartmann-Hahn approach resemble those of “solid effect” polarization transfer in solid-state NMR. Following Chen et al.², detailed balance arguments³ yield the steady-state polarization of diffusing molecular spins close to the diamond surface:

$$\langle I_Z \rangle = \frac{N_{NV}}{N_{nuc}} (W_0 - W_2) T_{1,nuc} \langle S_Z \rangle$$

Here, N_{NV} and N_{nuc} are the number of NV electronic spins and nuclear spins in the system, respectively, W_0 is the rate of “zero quantum” $|\uparrow_{NV}\downarrow_{nuc}\rangle \leftrightarrow |\downarrow_{NV}\uparrow_{nuc}\rangle$ transitions, W_2 is the rate of “two quantum” $|\uparrow_{NV}\uparrow_{nuc}\rangle \leftrightarrow |\downarrow_{NV}\downarrow_{nuc}\rangle$ transitions, $T_{1,nuc}$ is the nuclear spin polarization lifetime, and $\langle I_Z \rangle$ and $\langle S_Z \rangle$ are the polarizations (normalized to one) of the nuclear and NV electronic spin populations, respectively. The transition rates for a particular NV center at depth d_{NV} below the diamond surface are calculated using time dependent perturbation theory, again following Chen et al.². The result is as follows:

$$W_{0,2} = \frac{3\pi}{10} \left(\frac{\mu_0 \hbar \gamma_e \gamma_n}{4\pi} \right)^2 \left(\frac{8 n_{nuc}}{27 D_T d_{NV}} \right) \frac{\Omega^2}{\Omega^2 + \Delta^2} J(\omega_{0,2})$$

In this expression, μ_0 is the permeability of free space, γ_e and γ_n are the electronic and nuclear gyromagnetic ratios, n_{nuc} is the density of target nuclear spins in the sample, D_T is the translational diffusion coefficient of the sample molecule, Ω and Δ are the Rabi frequency and detuning of the microwave field used for Hartmann-Hahn driving of the NV centers, and $J(\omega)$ is a spectral function with width approximately equal to the inverse correlation time of the magnetic noise at the NV center due to diffusing sample molecules, $1/\tau_c = D_T/d_{NV}^2$. Assuming that the Hartmann-Hahn matching condition is

satisfied (i.e., that the effective Rabi frequency $\Omega_{\text{eff}} = (\Omega^2 + \Delta^2)^{1/2}$ of the NV drive is equal to the nuclear spin Larmor frequency ω_{nuc}), then the frequency of the zero-quantum transition is $\omega_0 = \Omega_{\text{eff}} - \omega_{\text{nuc}} \approx 0$ and the frequency of the two-quantum transition is $\omega_2 = \Omega_{\text{eff}} + \omega_{\text{nuc}} \approx 2 \omega_{\text{nuc}}$. For simplicity, we assume that the experiment is performed at an optimal value of the bias field, such that $\omega_0 \ll (2\pi)/\tau_c \ll \omega_2$, and hence $J(\omega_0) \approx 1$ and $J(\omega_2) \approx 0$. We further assume that the NV drive is much stronger than the detuning from resonance, $\Omega \gg \Delta$. Finally, we take the NV steady state polarization to be $\langle S_z \rangle \approx 1$, assuming that the NV centers are optically repolarized much faster than they transfer polarization to the sample. Under these conditions, the steady-state nuclear spin polarization is approximated by

$$\langle I_z \rangle = \frac{3\pi}{10} \left(\frac{\mu_0 \hbar \gamma_e \gamma_n}{4\pi} \right)^2 \left(\frac{8 N_{\text{NV}}}{27 V_{\text{sense}} D_T d_{\text{NV}}} \right) T_{1,\text{nuc}}$$

Here, we have also substituted $n_{\text{nuc}} = N_{\text{nuc}} / V_{\text{sense}}$, for sensing volume V_{sense} . (This assumes a constant density of the polarized nuclear spins in the sensing volume. A more realistic calculation would include diffusion of the polarized spins away from the diamond surface, resulting in an exponentially decaying density distribution. We performed such a calculation and obtained numerically similar results to the ones given below for the overall sample spin polarization and NMR signal enhancement.) The above expression describes polarization transfer from a single NV center or an ensemble of NV centers at fixed depth d_{NV} . If necessary, it can be integrated over a range of depths to describe an NV ensemble of finite thickness. However, the polarization transfer is dominated by the shallowest NV centers, and the quadratic increase in noise correlation time with d_{NV} in any case sets a stringent bound on the maximum depth of NV centers that can contribute without violating the condition $\omega_0 \ll (2\pi)/\tau_c$, for finite NV drive detuning due to inhomogeneous broadening of the NV resonances.

To obtain realistic numerical estimates of the polarization transfer rate, we consider a shallow implanted NV surface layer with density $\sigma_{\text{NV}} = 10^{12} / \text{cm}^2$ and characteristic depth $d_{\text{NV}} = 5 \text{ nm}$. The total number of NV centers contributing to the polarization is then $N_{\text{NV}} = \sigma_{\text{NV}} A = 10^6$, for diamond-sample interface area $A = 10 \mu\text{m}^2$. Then, for sensing volume $V_{\text{sense}} \approx 10 \mu\text{m}^3$, the expression for the steady-state sample spin polarization reduces to

$$\langle I_z \rangle = \alpha \frac{T_{1,\text{nuc}}}{D_T}$$

Here, the dimensional constant containing all sample-independent factors is $\alpha = 1.4 \times 10^{-14} \text{ m}^2/\text{s}^2$. Thus, for small molecules dissolved in water, with $T_{1,\text{nuc}} \approx 1 \text{ s}$ and $D_T \approx 10^{-9} \text{ m}^2 / \text{s}$, the maximum achievable polarization is $\langle I_z \rangle \approx \mathbf{1.4 \times 10^{-5}}$. We note that, to satisfy the condition for efficient polarization transfer, $(2\pi)/\tau_c \ll 2 \omega_{\text{nuc}}$ requires operation at minimum bias field $B_0 \gg \pi / (\gamma_n \tau_c)$. We have $\tau_c = d_{\text{NV}}^2 / D_T \approx 25 \text{ ns}$ and, for proton NMR, $\gamma_n = 2.675 \times 10^8 \text{ rad/s/T}$, so that the requirement becomes $B_0 \gg 0.5 \text{ T}$. If we choose to operate at $B_0 = 1.5 \text{ T}$, then the thermal proton polarization is approximately $\langle I_z \rangle_{\text{Thermal}} \approx 5.1 \times 10^{-6}$. Therefore, the expected signal enhancement due to hyperpolarization using the NV centers is less than a factor of 3. Using Overhauser DNP with TEMPOL radicals dissolved in the sample is expected to provide a signal enhancement factor of ~ 200 above the thermal polarization at bias fields B_0 up to about 1 T.

Other published estimates of achievable polarization transfer from NV centers to sample nuclear spins via the diamond surface claim up to two orders of magnitude higher polarization enhancement⁴, which would make them comparable to the Overhauser technique demonstrated in the present work. However,

these estimates assume a very slowly-diffusing pure sample of oil molecules in a volume extending only μm above the surface, rather than small molecules diffusing in a standard NMR solvent.

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