Supporting Information: Toward Hyperpolarization of Oil Molecules via Single Nitrogen Vacancy Centers in Diamond

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Hamiltonian Derivation

Our system consists of one electronic spin, the NV center, coupled to a set of N nuclear $\frac{1}{2}-$spins via dipole-dipole magnetic interaction. The general Hamiltonian for such a system has the form ($\hbar = 1$)

$$H = \omega_s \sigma_z + \sum_{i=1}^{N} \gamma_N \mathbf{B} \mathbf{I}^i + \sum_i f_i(\mathbf{r}_i(t)) \left[\sigma \mathbf{I}^i - 3 \left(\sigma \hat{\mathbf{r}}_i(t) \right) \left(\mathbf{I}^i \hat{\mathbf{r}}_i(t) \right) \right], \tag{1}$$

where ω_s is the Zeeman splitting of the electronic spin, σ are the spin operators of the NV spin, which is spin-1, γ_N is the gyromagnetic ratio of the nuclei, $\mathbf{B}$ is an external magnetic field, $\mathbf{I}_i$ represent the spin operators of the nuclear spins, $f_i(\mathbf{r}_i(t)) \equiv \frac{\mu_0 \gamma_e \gamma_N}{4\pi \mathbf{r}_i^3}$, is the dipole-dipole force strength which depends on the relative position between the NV center and the $i-th$ nucleus, $\mathbf{r}_i$, the gyromagnetic ratios of the electron and nuclear spins γ_e, γ_N and the vacuum permeability μ_0 , and $\hat{\mathbf{r}}^i$ is the unitary vector joining the NV center with the $i-th$ nuclear spin. Interactions between the nuclear spins have been neglected since their effects are averaged out by the fast stochastic motion.

The nuclear spins move following a Brownian motion, which in turns make the dipole-dipole interaction to be a stochastic variable with certain correlation time τ_c. In our set-up, we consider that the particles move slowly enough such that $\omega_s \tau_c \gg 1$ and $\gamma_N |\mathbf{B}| \tau_c \gg 1$. In this regime, we can perform a secular approximation owning to the fact that $\omega_s \gg \gamma_N |\mathbf{B}|$, obtaining

$$H = \omega_s \sigma_z + \sum_{i=1}^{N} \gamma_N \mathbf{B} \mathbf{I}^i + \sigma_z \sum_i \mathbf{A}^i \left(\mathbf{r}_i(t) \right) \mathbf{I}_i. \tag{2}$$

With $\mathbf{A}^i(\mathbf{r}_i(t)) = f_i(\mathbf{r}_i(t)) \left(3\hat{x}_i \hat{z}_i, 3\hat{y}_i \hat{z}_i, 1 - 3\hat{z}_i^2 \right)$ the so-called hyperfine vector. If now a resonant microwave field resonant with the NV $m_s = 0 \rightarrow m_s = -1$ transition is applied, $H_{\mathrm{MW}} = \Omega \sigma_x \cos(\omega_s t)$, the Hamiltonian in the frame rotating with ω_s reads

$$H = \Omega S_z + \sum_i^N \left(\gamma_N \mathbf{B} - \frac{1}{2} A_z^i(t) \right) \mathbf{I}^i + S_x \sum_i \mathbf{A}_i \left(\mathbf{r}_i(t) \right) \mathbf{I}_i. \tag{3}$$

We have introduced $\mathbf{S}$ as the NV spin operator in the dressed state basis, $S_z = \frac{1}{2} \left(|+\rangle \langle +| - |-\rangle \langle -| \right)$, $S_+ = |+\rangle \langle -|$ and $S_- = S_+^\dagger$.

In the Hartmann-Hahn double resonance (HHDR) scheme, the Rabi frequency Ω is set resonant with the nuclear Larmor frequency $\omega_N \equiv \gamma_N |\mathbf{B}|$. Working with a high magnetic field such that $\Omega, \omega_N \gg |\mathbf{A}_i| \, \forall i$, and given that $\omega_N \tau_c \gg 1$ is also fulfilled in our set-up, we neglect fast oscillating terms together with magnetic field misalignment caused by $A_z^i(t)$,

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obtaining

$$H = \Omega S_z + \sum_i^N \omega_N I_z^i + \sum_i^N g_i(t) S_+ I_-^i + g_i(t)^* S_- I_+^i. \tag{4}$$

with $g_i(t) = \frac{1}{4}\left(A_x^i(t) + i A_y^i(t)\right)$. This Hamiltonian corresponds to Eq.(1) in the main text.

Master Equation derivation

In this section we derive the master equation that describes the whole system and, in particular, the dynamical evolution of the NV polarization $\langle n \rangle (t) = \frac{1}{2} + \mathrm{Tr}\left(\rho S_z\right)$. In these derivations we treat both classical and quantum noises for a multiparticle system, which extends previous results in this field.[1,2]

In order to have a more complete description we start with a Hamiltonian that consists of both flip-flop and flop-flop terms. For doing so, we rewrite the interaction Hamiltonian, $H_{int} = \sum_i^N g_i(t) S_+ I_-^i + g_i^*(t) S_- I_+^i$, in the interaction picture with respect to the energy part $H_\omega \equiv \Omega S_z + \sum_i \omega_N I_z^i$, obtaining

$$\tilde{H} \equiv e^{-iH_\omega t} H_{int} e^{iH_\omega t} = \sum_{i=1}^N g_i(t) L^i e^{-i\Delta t} + g_i^*(t) L^{i\dagger} e^{i\Delta t} + g_i(t) O^i e^{-i\omega' t} + g_i^*(t) O^{i\dagger} e^{i\omega' t}. \tag{5}$$

Where $L^i \equiv S_+ I_-^i$, $O^i \equiv S_+ I_+^i$ and $\Delta = \Omega - \omega_N$, $\omega' = \Omega + \omega_N$. For the sake of simplicity, we set $\Delta = 0$, that is, we assume the HHDR condition is always fulfilled and thus, $\omega' = 2\Omega$. Next, this Hamiltonian may be split into a time-independent and a time-dependent stochastic part as

$$\tilde{H}_0(t) = \sum_{i=1}^{N} \langle g \rangle \, L^i + \langle g^* \rangle \, L^{i\dagger} + \langle g \rangle \, O^i e^{-\mathrm{i}2\Omega t} + \langle g^* \rangle \, O^{i\dagger} e^{\mathrm{i}2\Omega t}. \tag{6}$$

$$\tilde{H}_1(t) = \sum_{i=1}^{N} \xi_i(t) L^i + \xi_i^*(t) L^{i\dagger} + \xi_i(t) O^i e^{-\mathrm{i}2\Omega t} + \xi_i^*(t) O^{i\dagger} e^{\mathrm{i}2\Omega t}. \tag{7}$$

Where $\langle g \rangle$ is the average of $g_i(t)$ over all possible stochastic trajectories and $\xi_i(t) = g_i(t) - \langle g \rangle = \frac{1}{4}\xi_x^i(t) + \mathrm{i}\frac{1}{4}\xi_y^i(t)$ are the stochastic fluctuations around the average, with $\xi_\alpha^i(t) = A_\alpha^i(t) - \langle A_\alpha^i \rangle$. Note that for $\tilde{H}_0$ we can neglect fast rotating terms obtaining

$$\tilde{H}_0 \approx \sum_{i=1}^{N} \langle g \rangle \, L^i + \langle g^* \rangle \, L^{i\dagger}, \tag{8}$$

which is a time independent Hamiltonian. The master equation, also in the interaction picture with respect to H_ω reads

$$\frac{\partial}{\partial t} \tilde{\rho} = \mathcal{L}\tilde{\rho} = (\mathcal{L}_0 + \mathcal{L}_1(t)) \, \tilde{\rho}, \tag{9}$$

where we have introduced the Liouvillian operators $\mathcal{L}_i \equiv -\mathrm{i}\left[\tilde{H}_i, \cdot\right]$. We look to the average density matrix over all possible stochastic trajectories, $\langle \tilde{\rho} \rangle$, which obeys

$$\frac{\partial}{\partial t} \langle \tilde{\rho} \rangle = \langle (\mathcal{L}_0 + \mathcal{L}_1(t)) \, \tilde{\rho} \rangle. \tag{10}$$

In order to obtain a proper master equation for $\langle \tilde{\rho} \rangle (t)$ we follow.[3-5] We start taking an interaction picture with respect to $\mathcal{L}_0$ in Eq.(9) obtaining

$$\frac{\partial}{\partial t} \tilde{\rho}^{(0)} = \mathcal{L}_1^{(0)}(t) \tilde{\rho}^{(0)} \tag{11}$$

Note that by $\cdot^{(0)}$ it is indicated that the operators are in the interaction picture with respect to $\mathcal{L}_0$. The formal solution to the last equation is simply

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$$\tilde{\rho}^{(0)}(t) = \mathcal{T} \exp\left(\int_0^t \mathcal{L}_1^{(0)}(\tau)d\tau\right) \tilde{\rho}^{(0)}(0), \tag{12}$$

where $\mathcal{T}$ represents the time ordering. Taking now the average over all possible stochastic trajectories we arrive to

$$\left\langle \tilde{\rho}^{(0)} \right\rangle(t) = \left\langle \mathcal{T} \exp\left(\int_0^t \mathcal{L}_1^{(0)}(\tau)d\tau\right) \right\rangle \tilde{\rho}^{(0)}(0). \tag{13}$$

We note that in our case the system is found always in the same initial state $\tilde{\rho}^{(0)}(0)$. Writing it explicitly, that is, making explicit the action of $\mathcal{T}$, the latter equation reads

$$\left\langle \tilde{\rho}^{(0)} \right\rangle(t) = \left[1 + \int_0^t dt_1 \left\langle \mathcal{L}_1^{(0)}(t_1) \right\rangle + \int_0^t dt_1 \int_0^{t_1} dt_2 \left\langle \mathcal{L}_1^{(0)}(t_1)\mathcal{L}_1^{(0)}(t_2) \right\rangle + \cdots\right] \tilde{\rho}^{(0)}(0). \tag{14}$$

Taking the time derivate in both sides leads us to

$$\frac{\partial}{\partial t} \left\langle \tilde{\rho}^{(0)} \right\rangle(t) = \left[\left\langle \mathcal{L}_1^{(0)}(t) \right\rangle + \int_0^t dt_1 \left\langle \mathcal{L}_1^{(0)}(t)\mathcal{L}_1^{(0)}(t_1) \right\rangle + \cdots\right] \tilde{\rho}^{(0)}(0). \tag{15}$$

In order to arrive to a master equation for the average density matrix the only thing needed is to invert Eq.(14), so we can express $\tilde{\rho}^{(0)}(0)$ in terms of $\left\langle \tilde{\rho}^{(0)} \right\rangle(t)$. Introducing the expression for the initial density matrix into the last equation we finally obtain

$$\frac{\partial}{\partial t} \left\langle \tilde{\rho}^{(0)} \right\rangle = \sum_n k_n \left\langle \tilde{\rho}^{(0)} \right\rangle \tag{16}$$

where the operators k_n are defined as

$$k_n = \int_0^t dt_1 \int_0^{t_1} dt_2 \cdots \int_0^{t_{n-2}} dt_{n-1} \left\langle\!\!\left\langle \mathcal{L}_1^{(0)}(t)\mathcal{L}_1^{(0)}(t_1)\mathcal{L}_1^{(0)}(t_2)\cdots\mathcal{L}_1^{(0)}(t_{n-1}) \right\rangle\!\!\right\rangle_c. \tag{17}$$

In the last expression we have used the brackets with subscript $\langle\!\langle \cdots \rangle\!\rangle\, c$ to denote ordered cumulants.[4]

We note that $\mathcal{L}_1$ is composed of a sum of N independent random variables, $\xi_i(t)$, with identical average properties, $\langle \xi_i \rangle = \langle \xi_j \rangle \equiv \langle \xi \rangle \ \forall i$. Due to the fact that for independent random variables all cross-cumulants vanish, each cumulant $\langle\langle \mathcal{L}_1(t) \cdots \mathcal{L}_1(t_{m-1}) \rangle\rangle_c$ is linear with N. A rough analysis of the $4-th$ cumulant allow us to make a prediction on the magnitude of the $n-th$ cumulant. For instance

$$\left\langle \left\langle \mathcal{L}_1^{(0)}(0)\mathcal{L}_1^{(0)}(0)\mathcal{L}_1^{(0)}(0)\mathcal{L}_1^{(0)}(0) \right\rangle \right\rangle_c \sim N \left\langle \left\langle \xi^4 \right\rangle \right\rangle_c = N \left[\left\langle \xi^4 \right\rangle - 3 \left\langle \xi^2 \right\rangle^2 \right]. \qquad (18)$$

Note that in our notation the single bracket, $\langle \cdots \rangle$ represents the moment and not the cumulant. These terms can be found by explicit integration over the interaction volume

$$N \left\langle \left\langle \xi^4 \right\rangle \right\rangle_c = \left\langle \xi^4 \right\rangle - 3 \left\langle \xi^2 \right\rangle^2 = N \left[\frac{1}{V} \int_V \xi^4 d\mathbf{r} - 3\frac{1}{V^2} \left(\int_V \xi^2 d\mathbf{r} \right)^2 \right] = \rho \int_V \xi^4 d\mathbf{r} - 3\frac{\rho}{V} \left(\int_V \xi^2 d\mathbf{r} \right)^2. \qquad (19)$$

Since the interaction fluctuations $\langle \xi_i \rangle$ decay with the distance, taking $V \to \infty$, we can see that the $4-th$ cumulant is proportional to the $4-th$ order moment. This analysis holds for every order, as will be explained in the next section. Therefore, we take the second order of the expansion as leading order. The general solution for the master equation in the non-interaction picture with respect to $\mathcal{L}_0$, becomes

$$\frac{\partial}{\partial t} \langle \tilde{\rho} \rangle = \left[\mathcal{L}_0 + \int_0^t \left\langle \langle \mathcal{L}_1(t) e^{t\mathcal{L}_0} \mathcal{L}_1(t-\tau) \rangle \right\rangle_c e^{-t\mathcal{L}_0} d\tau \right] \langle \tilde{\rho} \rangle. \qquad (20)$$

Now, under the assumption that $|\mathcal{L}_0|\tau_c \ll 1$, with τ_c the correlation time (see following section for an accurate definition), we approximate $e^{\pm\mathcal{L}_0} \approx 1$. This assumption is equivalent to $\sqrt{N} \langle g \rangle \tau_c \ll 1$, which is fulfilled in our set-up (see bellow). In our regime, the fluctuations are larger than the average value $\langle g \rangle$. In the following, we use that by definition $\langle \mathcal{L}_1(t) \rangle = 0$, obtaining

$$\frac{\partial}{\partial t}\langle\tilde{\rho}\rangle = \left[\mathcal{L}_0 + \int_0^t \langle\mathcal{L}_1(t)\mathcal{L}_1(t-\tau)\rangle\, d\tau\right]\langle\tilde{\rho}\rangle. \tag{21}$$

We recall that this is a second order approximation in terms of $\langle\xi_\alpha^{i\,n}\rangle\tau_c^{n-1}$, and thus, as we keep the cumulants till second order this approximation is valid for times $t \ll \tau_c/\left(N\left\langle\xi_\alpha^{i\,3}\right\rangle\tau_c^3\right)$. The action of the correlator on the density matrix gives

$$\int_0^t \langle\mathcal{L}_1(t)\mathcal{L}_1(t-\tau)\rangle\, d\tau\,\langle\tilde{\rho}\rangle = \frac{1}{4}\gamma(0,t)\sum_{i=1}^N\left[D\left(L^i\right) + D\left(L^{i\dagger}\right)\right]\langle\tilde{\rho}\rangle +$$
$$\frac{1}{4}\gamma(2\Omega,t)\sum_{i=1}^N\left[D\left(O^i\right) + D\left(O^{i\dagger}\right)\right]\langle\tilde{\rho}\rangle. \tag{22}$$

Where $D(\cdot)$ denotes the Lindblad superoperator, whose action on the density matrix is simply

$$D(A)\langle\tilde{\rho}\rangle = A\langle\tilde{\rho}\rangle A^\dagger - \frac{1}{2}\left\{A^\dagger A, \langle\tilde{\rho}\rangle\right\}, \tag{23}$$

where A is a given operator. In Eq.(22) all the fast oscillating terms have been neglected. We remark that since the particles move independently then $\xi_i(t)$ are independent random variables and thus, we have used that $\left\langle\xi_\alpha^i(\tau)\xi_\beta^j(0)\right\rangle = \left\langle\xi_\alpha^i(\tau)\xi_\alpha^i(0)\right\rangle\delta_{\alpha,\beta}\delta_{i,j}$. Also, as the diffusion is homogeneous, the correlation function does not depend on the direction of the hyperfine vector, α, or on the particle, i, $\left\langle\xi_\alpha^i(\tau)\xi_\alpha^i(0)\right\rangle \equiv \langle\xi(\tau)\xi(0)\rangle$. Moreover, we have introduced

$$\gamma(\omega, t) = \int_0^t \left\langle\xi_\alpha^i(\tau)\xi_\alpha^i(0)\right\rangle\cos\left(\omega\tau\right)d\tau. \tag{24}$$

Note that for $t \gg \tau_c$, with τ_c the correlation time, the upper limit of the integral may be extended to infinity, obtaining $\lim_{t\to\infty}\gamma_\alpha(\omega, t) = \frac{1}{2}S_\alpha(\omega)$, with $S(\omega)$ the spectral density function of $\xi_\alpha^i(t)$. A net polarization transfer is only possible if flip-flop induced relaxation

predominates over all the other effects. That is, $S(2\Omega)/S(0) \ll 1$. For a Lorentzian spectral density this condition translates into $\chi \equiv \Omega\tau_c \gg 1$. In our set-up $\tau_c \approx 10\,\mu\text{s}$, $\omega_N = 2.8\,\text{MHz}$, so $S(2\Omega)/S(0) \approx 10^{-4}$, that means that flip-flip terms may be neglected. In fact, following similar calculations other relaxations mechanisms related to Hamiltonian terms such as $S_\pm I_z^i$ or $\mathbb{I} \otimes \mathbf{I}^i$, may be neglected when $\Omega\tau_c \gg 1$.

Taking all mentioned conditions into account, the effective master equation back in the Schrödinger picture reads

$$\frac{\partial}{\partial t} \langle \rho \rangle = \langle \dot\rho \rangle = -\mathrm{i}\,[H_0, \langle \rho \rangle] + \frac{1}{4}\gamma(t) \sum_{i=1}^{N} D\left(S_+ I_-^i\right) \langle \rho \rangle + D\left(S_- I_+^i\right) \langle \rho \rangle, \qquad (25)$$

which is a master equation in Lindblad form with time dependent coefficient $\gamma(t) \equiv \gamma(0, t)$. The action of Eq. (25) is well understood. There are two main contributions. On the one hand, a Hamiltonian part, H_0, whose principal effect is a coherent transfer of polarization between the NV center and the nuclear spins. On the other hand, the Lindbladian term that generates an irreversible polarization transfer towards the nuclei caused by the stochastic motion.

In order to obtain a close equation for the population transfer, we first analyze the coherent part of the dynamics ruled by H_0, this will allow us to perform a Born approximation that will be fundamental for our following approach. First, we take a look into the form of H_0

$$H_0 = \Omega S_z + \sum_{i=1}^{N} \langle \omega \rangle I_z^i + \sum_{i=1}^{N} \langle g \rangle S_+ I_-^i + \langle g \rangle^* S_- I_+^i. \qquad (26)$$

It corresponds to the Hamiltonian of a single NV center interacting with a solid bath of N nuclear spins, all of them with the same energy splitting $\langle \omega \rangle$ and with the same coupling strength $\langle g \rangle$. We recall, $\langle \cdots \rangle$ is the average over the stochastic trajectories of the nuclei. More specifically, this solid bath is composed by the N spins that are enclosed in certain NV interaction volume V. As the nuclei diffuse rapidly in the whole space, we assume that they

only spend certain time τ_B inside the NV interaction volume V. This τ_B may be seen as the time that a particle needs to leave the interaction volume and thus, being replaced by some other particle. Therefore, the coherent evolution caused by H_0 takes place in a scale marked by $\sqrt{N}|\langle g \rangle|\tau_B$. Assuming that $\tau_B \approx \frac{1}{6}\frac{V^{2/3}}{\mathcal{D}_{oil}} \approx \tau_c$, where $\mathcal{D}_{oil}$ is the diffusion coefficient, and $V = L^3$ with $L \approx 2\,z_0$, we obtain for our set-up $\sqrt{N}|\langle g \rangle|\tau_B \approx 0.1 - 0.01 < 1$, depending on whether we use a shallow NV center, $z_0^1 = 3.2\,\mathrm{nm}$ or a deeper NV, $z_0^2 = 5.3\,\mathrm{nm}$. This condition is equivalent as being in the weak-coupling regime with the bath as described by.[5] Consequently, considering a time axis with time intervals larger than $\tau_c \approx \tau_B$, we can rewrite the average density matrix as

$$\langle \rho \rangle = \langle \rho \rangle_{NV} \otimes \rho_B, \tag{27}$$

where ρ_{NV} is the average density matrix for the NV center while ρ_B is the density matrix of the bath, which corresponds to a thermal state. We remark the latter equation is usually referred to as the Born approximation. This factorization of the density matrix allows us to trace out the nuclear spin space, obtaining a master equation solely for ρ_{NV}

$$\langle \dot{\rho} \rangle_{NV} = -\mathrm{i}[\Omega S_z, \langle \rho \rangle_{NV}] + \frac{1}{4}N\gamma(t)\left[\langle n \rangle_B D(S_+) + (1 - \langle n \rangle_B)D(S_-)\right]\langle \rho \rangle_{NV}. \tag{28}$$

with $\langle n \rangle_B$ is the average population of the spins in the bath. Moreover, we can derive the evolution equation for the NV population $\langle n \rangle = \frac{1}{2} + \mathrm{Tr}\,(S_z \langle \rho \rangle_{NV})$, obtaining

$$\langle \dot{n} \rangle + N\frac{1}{4}\gamma(t)\langle n \rangle = N\frac{1}{4}\gamma(t)\langle n \rangle_B. \tag{29}$$

This equation corresponds to Eq.(4) in the main text. We recall that this approximation is only valid for times $t \ll \tau_c/(N\langle \xi^3 \rangle \tau_c^3) \approx 100\,\mu s$ and $t \ll \tau_B\frac{1}{(\sqrt{N}\langle g \rangle \tau_B)^2} \approx 100\,\mu s$.

Relaxation of spin system

The measured data reveals that the NV center is affected by some environmental noise. Namely, this noise will make the NV center lose its polarization at a given rate. Normally, when the spin is driven and we are in the dressed state bases this rate is called $T_{1\rho}$.[6] Including these effects in our approach is straightforwardly done by adding a dissipation term to the master equation Eq.(28). Obtaining

$$\langle\dot{\rho}\rangle_{NV} = -\mathrm{i}[\Omega S_z, \langle\rho\rangle_{NV}] + \frac{1}{4}N\gamma(t)\left[\langle n\rangle_B D(S_+) + (1 - \langle n\rangle_B)D(S_-)\right]\langle\rho\rangle_{NV} + \frac{1}{2}\frac{1}{T_{1\rho}}\left[D(S_+) + D(S_-)\right]\langle\rho\rangle_{NV}.$$
(30)

This equation allow us to include the effects of $T_{1\rho}$ in our analysis and thus, have a complete perspective of the NV dynamics.

Hyperfine vector analysis

In the previous section we have seen the polarization dynamics is mainly determined by $\gamma(t) = \int \langle\xi(\tau)\xi(0)\rangle\, d\tau$. Despite the simple description of the nuclear trajectories, since they move in free-diffusion, a detailed analytical description of $\xi_\alpha^i(t)$ turns to be complicated. Aiming to derive an analytical solution for Eq. (29) we make two assumptions: i) Higher moments are negligible when compared to the average and variance, which is a necessary condition for Eq.(21). ii) The correlations are well approximated by an exponential curve.

The former assumption justifies the validity of using cumulants up to order two in the cumulant expansion performed in the previous section. We recall, that even in the absence of a correlation time, the $n-th$ order cumulant contribution is of order $\langle\xi^n\rangle t^{n-1}$.[4] In this case, we evaluate this time, t as the time in which most of the NV polarization is transferred to the nuclear spins. This can be estimated by: i) simulation of the system, and ii) evaluating this time assuming the second order is correct and then check for self-consistency. Both

methods yield the same time. Using the second method, the time for polarization should be - $\frac{1}{\langle\xi^2\rangle\tau_c N} \sim 10\mu s$. Numerical calculations suggest that indeed, the second term may be taken as the leading term and higher order terms decay exponentially with n. Numerical calculations are shown in Fig.(S1).

With regard to the correlation profile, we numerically calculate the normalized correlation function. The result is depicted in Fig.(S1). We see the correlation decay fast for short times and presents a heavy tail for larger times. In our set-up, nuclei interact with the NV center for a short-time before diffusing away and being reinitialize. Within this short-time interval an exponential decay accurately fits the numerical calculated correlation function. This approximation results in being accurate when tested against full numerical simulation with HPA, see Fig.(S3).
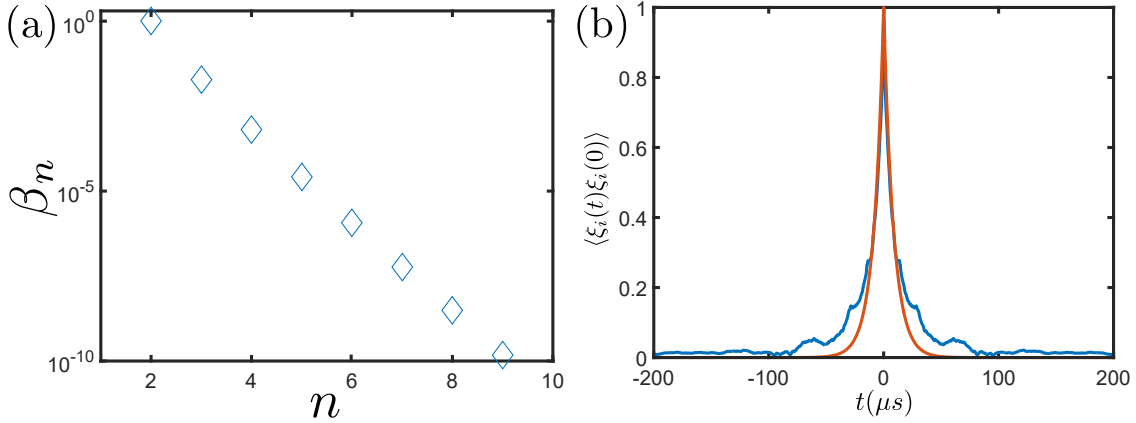

Figure S1: (a) Normalized contribution of the $n-th$ moment with respect to $\langle\xi^2\rangle$, $\beta_n \equiv \frac{\langle\xi^n\rangle t^{n-1}}{\langle\xi^2\rangle t}$. It decays rapidly with n, permitting us to accurately describe $\xi_\alpha^i(t)$ making use solely of its first and second moment. (b) Correlation profile of $\xi_\alpha^i(t)$ with an exponential fit.

Correlation function calculation

The correlation function of the coupling coefficient between the NV and each individual spin is important for determining the polarization rate. When the process is stationary, the correlation function is given by -

$$\langle \xi_\alpha^i(t)\xi_\alpha^i(0)\rangle = \int \xi_\alpha^i(\vec{r}_2;t)\xi_\alpha^i(\vec{r}_1;0)\rho(\vec{r}_2;t|\vec{r}_1;0)\rho(\vec{r}_1;0)d^3\vec{r}_1 d^3\vec{r}_2. \tag{31}$$

with $\xi_\alpha^i(t) = A_\alpha^i(t) - \langle A_\alpha^i\rangle$, $\rho(r_1;0)$ the distribution of the particle at the initial time (considered to be uniform) and $\rho(\vec{r}_2;t|\vec{r}_1;0)$ is the conditional probability of the particle being at $\vec{r}_2$ at time t given that it was in $\vec{r}_1$ at time $t = 0$. This conditional probability is nothing but the solution of the diffusion equation with the initial condition at $\vec{r}_1$ with a reflective boundary condition at $z = z_0$, satisfying $\frac{d\rho}{dz}|_{z_2=z_0} = 0$

$$\rho(\vec{r}_2;t|\vec{r}_1;0) = \frac{1}{(4\pi\mathcal{D}t)^{\frac{3}{2}}}e^{-\frac{(x_1-x_2)^2}{4\mathcal{D}t}}e^{-\frac{(y_1-y_2)^2}{4\mathcal{D}t}}\left(e^{-\frac{(z_1-z_2)^2}{4\mathcal{D}t}} + e^{-\frac{(z_1+z_2-2z_0)^2}{4\mathcal{D}t}}\right) \tag{32}$$

with $\mathcal{D}$ the diffusion coefficient. The correlation function can not be calculated analytically and therefore one must calculate it using a numerical approach, either by numerical integration or by using data obtained by a stochastic molecular dynamics simulation. While the former approach is rather straight forward, the latter requires to obtain a number of possible trajectories and then averaging the correlation function over all trajectories. This was done using the *MATLAB* function *xcorr*.

In this context, we define the correlation time such that when $t = \tau_c$

$$\langle \xi_\alpha^i(\tau_c)\xi_\alpha^i(0)\rangle \equiv \frac{1}{e}\left\langle \xi_\alpha^i(0)\xi_\alpha\alpha^i(0)\right\rangle = 1/e, \tag{33}$$

in other words, the correlation time is a characteristic time such that when $t > \tau_c$, $\xi_\alpha^i(t)$ and $\xi_\alpha^i(0)$ can be treated as statistically independent.

Since the correlation time is inversely proportional to the diffusion coefficient, τ_c should also depend on a parameter with a dimension of length. This parameter was considered to be z_0. Intuitively, as the depth of the NV increases, an interacting nuclear spin has to be displaced more in order to change the interaction by a significant amount, increasing the correlation time. We can see in Fig.(S2) that the dependency of τ_c on the depth of the NV is indeed quadratic for shallow NVs ($z_0 \sim 6\,\mathrm{nm}$). For deeper NVs, due to the long range

interaction ($\sim \frac{1}{r^3}$) this dependency deviates because the interaction length is comparable to the NV's depth and takes part in the correlation time.
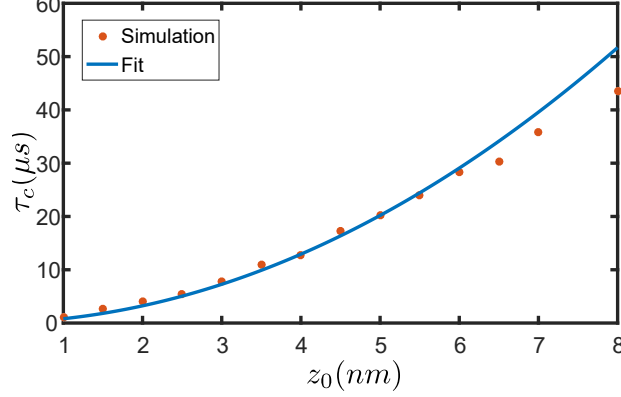

Figure S2: Correlation time vs NV depth. Results obtained from simulation. For Shallow NVs the data is fitted to a quadratic function.

Bosonic approximation and Gaussian states

In order to numerically simulate a large spin system we make use of the Holstein-Primakoff approximation (HPA),[7] which expresses the spin operators in terms of bosonic operators

$$S_+ = \sqrt{2S}a^\dagger\sqrt{1 - \frac{a^\dagger a}{2S}} \approx \sqrt{2S}a^\dagger, \tag{34}$$

$$S_- = \sqrt{2S}\sqrt{1 - \frac{a^\dagger a}{2S}}a \approx \sqrt{2S}a, \tag{35}$$

$$S_z = \left(-S + a^\dagger a\right), \tag{36}$$

Where, $S = \frac{1}{2}$ for spins-$\frac{1}{2}$. This approximation has been successfully used in other works for describing interacting spin baths in similar scenarios.[8] In fact, within the HPA a polarized spin is represented as a boson in its ground state. As far as only the ground and first excited states play a major role in the dynamical evolution of the system, the HPA yields satisfactory results. Since our system consists on numerous spins in thermal state with mainly flip-flop

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interactions and moreover strong correlations between nuclei are not built up owing to the stochastic motion, the HPA is expected to accurately describe the desired polarization dynamics in the regime we are interested in. Performing the same approximation for the nuclear spin operator $\mathbf{I}$ on Eq. (4), we directly obtain the bosonic Hamiltonian

$$H = \Omega a^\dagger a + \sum_i^N \omega_N b_i^\dagger b_i + \sum_i g_i\, a^\dagger b_i + g^*\, a b_i^\dagger, \tag{37}$$

This Hamiltonian corresponds to a system of two coupled harmonic oscillators under the rotating wave approximation (RWA). Introducing the bosonic operator vector, $\mathbf{R} = (a, b_i, \cdots, b_N)^T$, we express the total Hamiltonian as

$$H = \frac{1}{2}\mathbf{R}^\dagger V \mathbf{R}, \tag{38}$$

with $V = V_0 + V_1$, containing all the interactions between the operators

$$V_0 = \begin{matrix} & \begin{matrix} a^\dagger & b^\dagger \end{matrix} \\ \begin{matrix} a \\ b \end{matrix} & \begin{pmatrix} \Omega & 0 \\ 0 & \omega_N \end{pmatrix} \end{matrix}$$

$$V_1 = \begin{matrix} & \begin{matrix} a^\dagger & b^\dagger \end{matrix} \\ \begin{matrix} a \\ b \end{matrix} & \begin{pmatrix} 0 & g_i \\ g_i^* & 0 \end{pmatrix} \end{matrix}$$

In the last expressions, for the sake of simplicity, only the matrices for 2 interacting bosons are written down.

A quadratic bosonic Hamiltonian as Eq. (37) induces a Gaussian unitary evolution. This means, given a certain Gaussian state, its evolution under the action of a quadratic bosonic Hamiltonian will preserve its Gaussian character.[9,10]

All the quantum information of a Gaussian state is contained in the first and second moments of the quadratures operator $\mathbf{R}$: the mean, $\langle \mathbf{R} \rangle$, and the covariance matrix, γ.

Moreover, if the Hamiltonian has not linear terms, and for initial states with $\langle \mathbf{R} \rangle = 0$, the whole system is described by the covariance matrix, defined as

$$\gamma_{j,k} = \left\langle b_j^\dagger b_k \right\rangle, \tag{39}$$

with $j, k \in \{0, N\}$, being $b_0 = a$. Making use of the von Nuemann equation for the evolution of $\left\langle b_i^\dagger b_j \right\rangle$ in time,

$$\left\langle \dot{b_i^\dagger b_j} \right\rangle = +\mathrm{i} \left\langle \left[b_i^\dagger b_j, H \right] \right\rangle, \tag{40}$$

derive a evolution equation for γ results straightforward,

$$\dot{\gamma} = -\mathrm{i} \left[V, \gamma \right]. \tag{41}$$

We remark, γ has dimensions $N + 1 \times N + 1$, where N is the total number of nuclei. This is the main advantages of the Gaussian state formalism, while for a spin system we will need to compute the 2^N elements of the density matrix to describe the system, for a bosonic system it is sufficient to evolve γ. Therefore, while simulating a spin system of $N \approx 15$ spins already becomes computationally hard, the use of HPA allows us to simulate systems with thousands of bosons easily.

Relaxation of the bosonic system

In order to implement a relaxation process that will take the place of $T_{1\rho}$ effects in a spin system, we include a dissipation part on the evolution equation of the bosonic system

$$\dot{\rho} = -\mathrm{i} \left[H, \rho \right] + \frac{1}{T_{1\rho}} \left(\frac{3}{2} D(a) + \frac{1}{2} D\left(a^\dagger \right) \right) \rho, \tag{42}$$

where ρ is the density matrix of the whole bosonic system, and $D(a), D\left(a^\dagger \right)$ are the Lindblad dissipator on the creation and annihalition operators. The evolution of the covariance matrix,

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γ, under the action of such a master equation is given by

$$\dot{\gamma} = -\mathrm{i}\,[V, \gamma] + \frac{1}{2}\frac{1}{T_{1\rho}}\left[\Delta - \{\Delta, \gamma\}\right]. \tag{43}$$

where $\Delta_{i,j} = \delta_{0,i}\delta_{0,j}$ is a matrix that indicates the action of $T_{1\rho}$ affects only the NV center (labeled as 0). In addition to quadratic Hamiltonians, Lindblad equation of the form of Eq.(42) also maintains the Gaussian character of an initial Gaussian state.[11]

Numerical Simulation parameters

As stated in the main text, the numerical simulation based on HPA is performed considering N independently moving nuclei in a finite box with periodic boundary conditions and length l. This box represents the detection volume of the NV center. The simulation box sets a cut-off to other parameters such as the particle number, for a fixed particle density, ρ, then $N = \rho\,l^3$, or the interaction variance inside the box σ_l^2, with $\lim_{l\to\infty}\sigma_l^2 = \sigma^2$. That means, the selection of l is a compromise between the computational efficiency, set by N, and the ratio $\chi = \sigma_l^2/\sigma^2$, which should be $\chi \approx 1$ for a satisfactory description. Simulation results for different densities and lengths are depicted in Fig.(S3).

In our experiment, the oil density equals, $\rho_{oil} = 50\,\frac{\text{spins}}{\text{nm}^3}$. Therefore, it requires to consider a significantly large number of nuclei inside the simulation box. For a box length of $l = 20\,\text{nm}$, then $N = 4\cdot10^5$ and $\chi \sim 92\%$. Even for this length, N is still too large, so we consider effectively $N_{\text{eff}} = 5\cdot10^3$ spins with a effective interaction $g_{\text{eff}} = \sqrt{80}g$. This effective model has been proven to reproduce exactly the NV spin dynamics.

Determining the depth of shallow NV centers

In order to estimate the NV center depth z_0, the magnetic field noise produced by the Larmor precession of the hydrogen spins within the immersion oil (Fluka Analytical 10976)
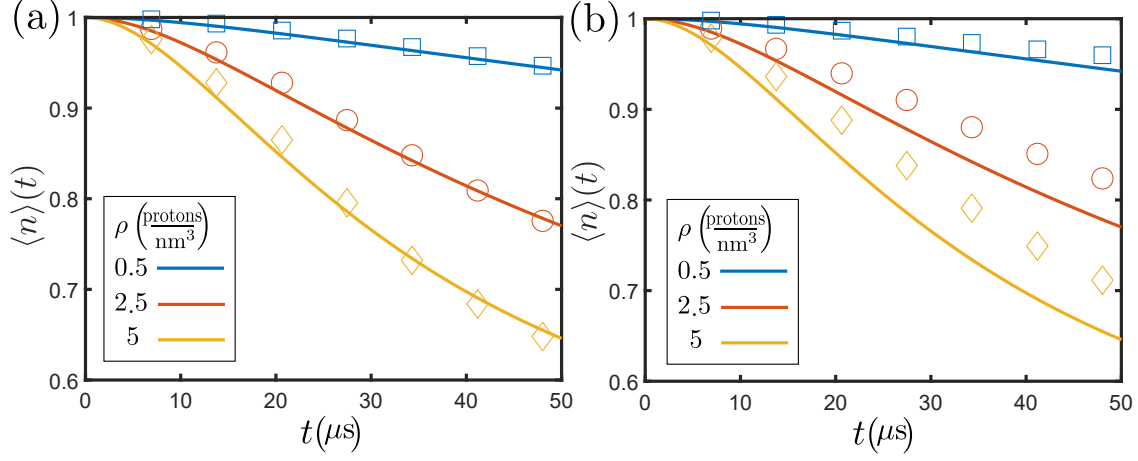
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Figure S3: Confrontation between full numerical simulation with HPA (markers) and theoretical prediction for spins (solid lines) for different densities and $z_0 = 3.2\,\mathrm{nm}$. (a) Simulations for bosons diffusing in a box with $l = 25\,\mathrm{nm}$, $\chi = 95\%$. (b) Simulation for $l = 12.5\,\mathrm{nm}$ and $\chi = 78\%$. For this box size the numerical simulation gives satisfactory results with fast computational time.

was measured via the XY8-N sequence. These measurements were performed at $660\,\mathrm{G}$, which corresponds to a hydrogen Larmor frequency of $\nu \equiv \omega_N/(2\pi) = 2.81\,\mathrm{MHz}$. We get the magnitude of the RMS magnetic field B_{RMS} from the measured XY8 signal by reconstructing the power spectral density $S(\nu)$ via a deconvolution process using the known filter function and then integrating the peak signal. From B_{RMS} the depth of the NV center can be calculated analytically (see e.g.[12]):
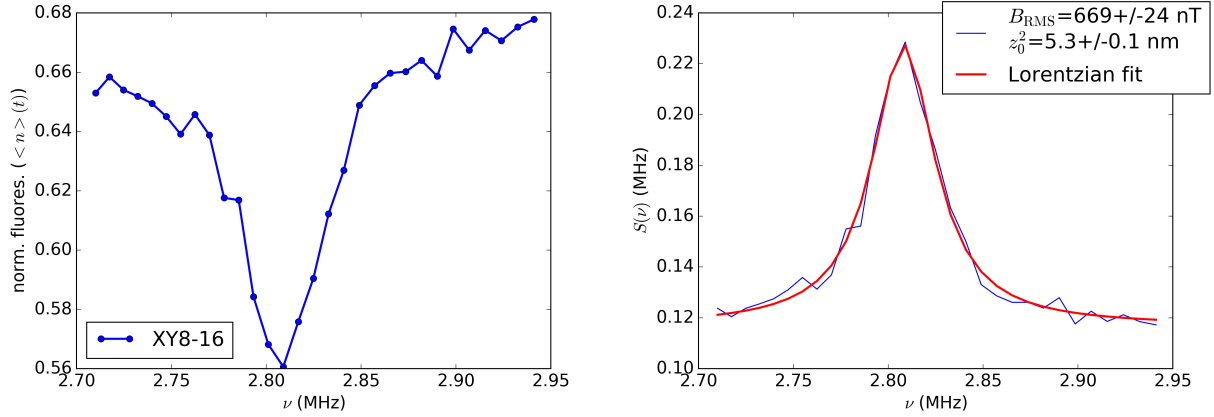
$$z_0 = \left[\frac{1}{B_{\mathrm{RMS}}^2} \frac{5}{1536\pi} \mu_0^2 h^2 \gamma_N^2 \rho_{\mathrm{oil}} \right]^{\frac{1}{3}}, \tag{44}$$

where $\gamma_N = 42.58\,\frac{\mathrm{MHz}}{\mathrm{T}}$ is the nuclear gyromagnetic ratio and $\rho_{\mathrm{oil}} = 50\,\mathrm{protons/nm^3}$ the proton density of the immersion oil.

Fig.(S4) shows the data of the XY8 measurements and the corresponding spectral density for the two NVs. From these measurements we can estimate the depths to be $z_0^1 = 3.2 \pm 0.2\,\mathrm{nm}$ and $z_0^2 = 5.3 \pm 0.1\,\mathrm{nm}$.
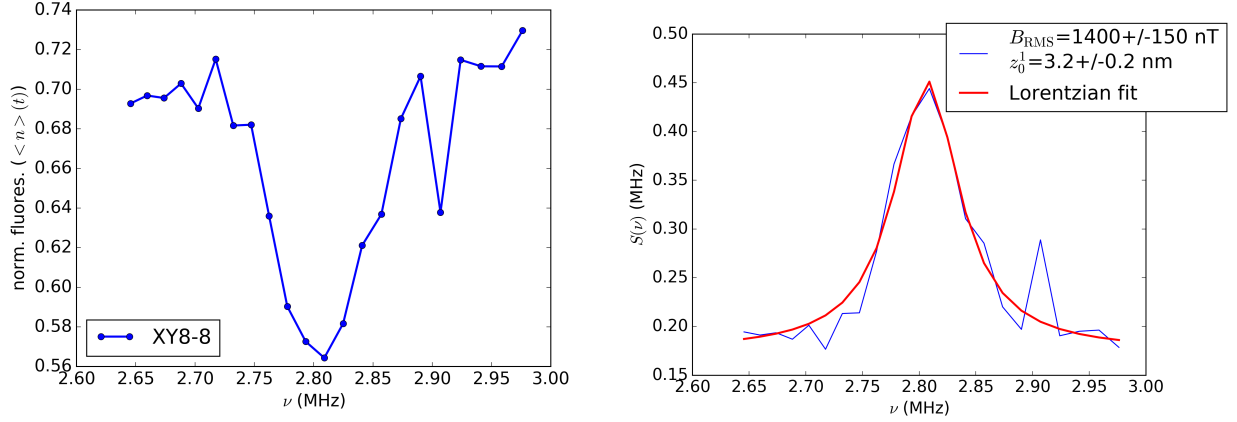
(a) Depth estimation for NV1

(b) Depth estimation for NV2

Figure S4: The left plots show the raw XY8 data, normalized to the Rabi contrast. Right side: The power spectral density is calculated from the XY8 data and by the area of the function around the ^{1}H Larmor frequency the depth can be calculated (see Eq.(44)) (a) Measurement corresponding to shallower NV center $z_0^1 = 3.2$ nm. (b) Depth measurement outcomes for an slightly deeper NV center $z_0^2 = 5.3$ nm .

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# Relaxation in the dressed state basis $T_{1\rho}$

Besides the polarization transfer dynamics during the spin locking pulse there is also relaxation due to resonant magnetic noise. Since this decay happens in the same time scale as the polarization transfer process, the characteristic relaxation time in the dressed state basis $T_{1\rho}$ is detemined experimentally and taken into account in the theoretical predictions. This is done by measuring the decay of the NV spin state while the MW drive during the spin locking pulse is set off-resonant from the HHDR condition (by 500 kHz). In Fig.(S5) the NV decay during spin locking fulfilling HHDR condition (polarization transfer and relaxation) is compared to an off-resonant measurement (only relaxation). From a single exponential fit, $f(\tau) = a + b\exp[-\tau/T_{1\rho}]$, we obtain $T_{1\rho} = 10.8 \pm 0.6\,\mu$s for NV1 and $T_{1\rho} = 17.0 \pm 1.4\,\mu$s for NV2.

In all experimental data sets the fluorescence measured from a single NV center is normalized with the steady-state fluorescence at the end of the laser pulse and it scaled by the contrast of a by an additional Rabi experiment. The error bars are determined with photon shot-noise, error propagated with the fluorescence normalization and divided by the Rabi amplitude.

Steady-State polarization

Throughout this work we have focused on the polarization dynamics of one single NV center in one single cycle. In order to achieve significant polarization in the oil sample the protocol must be repeated numerous times, and the general set-up may be modified. The steady-state polarization, that is, the maximum achievable polarization using our protocol may be estimated as follows.

For hyperpolarization a diamond sample with high density of NV centers is needed. Given a bulk diamond with different NV centers distributed homogeneously through the whole volume, such that the interaction among different electronic spins is negligible, with a
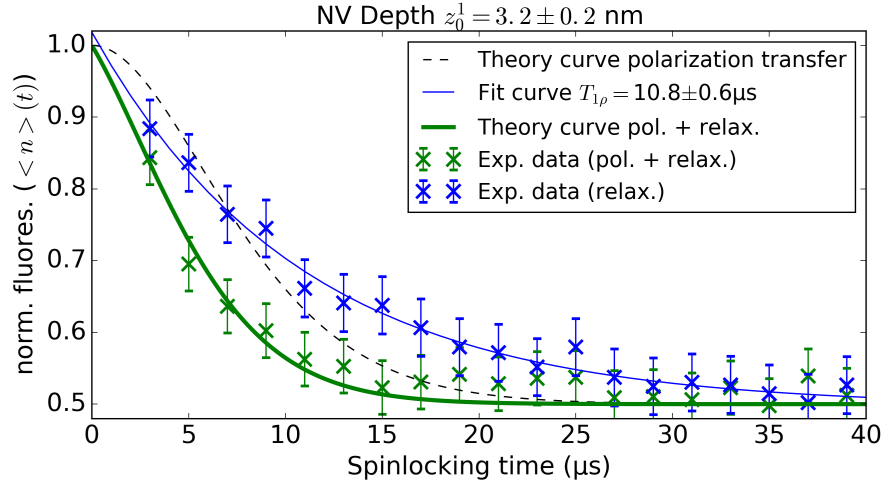
(a) Resonant and off-resonant decay for NV1
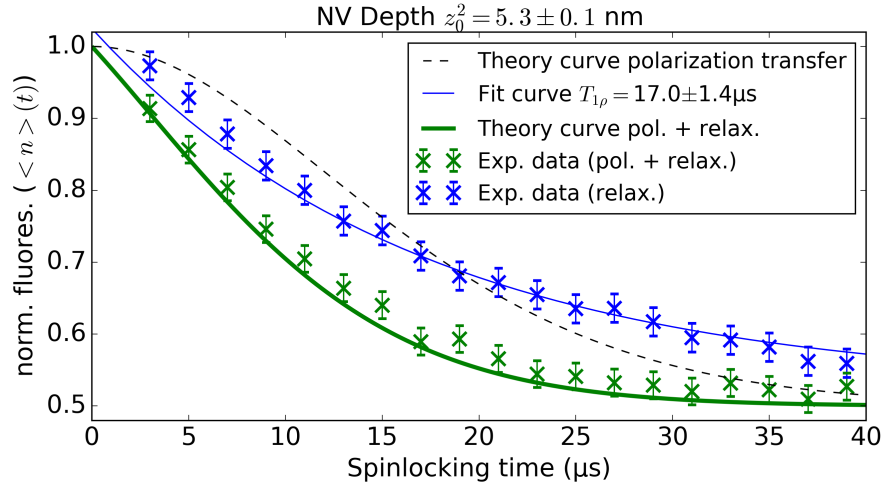
(b) Resonant and off-resonant decay for NV2

Figure S5: Decay of NV fluorescence under fulfilled HHDR conditions (green points) and under off-resonant conditions (blue points). The off-resonant decay is fitted by a single exponential decay (blue curve). The fitting curve is not forced to pass through $\langle n \rangle (0) = 1$ since the normalization in the plot for the off-resonant curve is solely illustrative; only the decay rate $T_{1\rho}$ is important. The corresponding time constant $T_{1\rho}$ is included in the theoretical predictions (green curve). Not taking $T_{1\rho}$ processes and thus only taking polarization transfer into account would lead to the black dotted theory curve. (a) Polarization loss, $T_{1\rho}$ relaxation and theoretical predicted polarization curve for an NV center at $z_0^1 = 3.2\,\mathrm{nm}$. (b) Same for NV center at $z_0^2 = 5.3\,\mathrm{nm}$.

superficial density σ_{NV}. If a thin layer of oil of thickness L_{oil} is deposited onto the diamond surface, then particle reservoir for a single NV centers consists of a volume $V_T = L_{oil}/\sigma_{NV}$.

On the other hand, during one cycle a single NV exclusively interacts with N nuclei, which are inside its own interaction volume V. Therefore, after a polarization cycle, whose duration is τ_p, the average polarization per nucleus is $\frac{1}{2}\frac{1}{N}\alpha$, as defined in the main text. Nonetheless, in a single cycle the NV center has only interacted with a fraction V/V_T of the total number of ^1H in the oil. For all the nuclei to interact at least once with the NV, the cycle must be repeated n times with $n = V_T/V$. Hence, the total required time is $T = n\tau_p$.

In summary, at time $T = n\tau_p$ the average polarization per nucleus is $P = \frac{1}{2}\frac{1}{N}\alpha$. The same procedure can be repeated m times, and since the polarization acquisition is only limited by the nuclear relaxation time, T_{1n}, then for an optimal performance $m = T_{1n}/T$. Assuming that for small amounts the polarization is additive, we obtain that the maximal average polarization per nuclei is

$$P_{max} = \frac{T_{1n}}{T}\frac{1}{2}\frac{1}{N}\alpha = \frac{1}{2}\alpha\frac{T_{1n}}{\tau_p}\frac{\sigma_{NV}}{L_{oil}\rho_{oil}}, \tag{45}$$

For realistic values, $\alpha = 0.8$, $\tau_p \approx 5\,\mu s$, $T_{1n} \approx 1\,\mathrm{s}$, $\rho_{oil} \approx 50\,\frac{\mathrm{protons}}{\mathrm{nm}^3}$, $L_{oil} \approx 1\,\mu\mathrm{m}$, $\sigma_{NV} \approx 2\cdot 10^{-3}\,\frac{\mathrm{NV}}{\mathrm{nm}^2}$, the calculations yield $P_{max} = 10^{-3}$, which severally exceeds the thermal average polarization $P^{Th} = 10^{-7}$.

Measurement outcomes for rigid and semi-rigid samples

The dynamical behavior of oil molecules in the vicinity of the diamond sample is unknown. Chemical reactions such as adsorption may occur, hence blocking the stochastic motion of the molecules resulting in an effective rigid bath for the NV center. Nonetheless, in our model we consider the protons as randomly moving particles in free diffusion with certain diffusion coefficient $\mathcal{D}_{oil}$. This description is expected to be accurate when the detection volume is big enough and thus, the big majority of the molecules diffuse freely while only an

small fraction may participate in adsorption.

Still, using HPA and Eq.(43) we can estimate the measurable polarization loss from a NV center when interacting with a rigid or semi-rigid oil. The outcome of these simulations helps us to discriminate whether the measured polarization loss may be also attributable to a solid sample or if it is exclusively inherent to liquid oil.

Since molecular simulations with the used oil (Fluka Analytical 10976) are not available, we explore different proton configurations with different orderings. For the sake of simplicity, we start from an initial configuration in which all protons form a cubic lattice with lattice parameter a. From this starting point, different configurations are achievable by displacing each of the protons by a random quantity δ_i. In this context, the magnitude of δ_i sets the amount of disorder with respect to the initial cubic lattice, hence we quantify the disorder by $\chi \equiv \frac{2|\delta_i|}{a}$.

Consequently, we can study the different signals on the NV center coming from different types of bath: from a complete ordered crystal, $\chi = 0$, to homogeneously distributed non-overlapping protons, $\chi = 80\%$. We remark that our aim is not to predict the exact NV center dynamics but rather the general behavior for a given kind of bath.

For the numerical simulations we have used Eq.(43) with a time-independent Hamiltonian. The electronic spin relaxation, $T_{1\rho}$, is described by a local Lindblad equation. This description is accurate and valid for non correlated systems such as liquid oil. Nonetheless, here it is used for highly-correlated baths such as rigid oil since it is expected to give satisfactory results.[13] Further details on the simulation techniques may be found in the Secs. *Bosonic approximation and Gaussian states* and *Numerical Simulation parameters*.

The outcomes of the simulation are depicted in Fig.(S6). For a rigid bath, the amount of possible configurations of the protons is infinite and therefore we have chosen to present the average signal (obtained by averaging over all the plausible polarization loss curves), together with the standard deviation. Moreover, the average signal (blue curve Fig.(S6)), coincides with the signal that a semi-rigid solid produces on the NV center. In this context, a

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semi-rigid solid consists of and ensemble of protons that are fixed during the duration of the spin-locking time, t, but move by a random quantity δ_i between two different measurements.
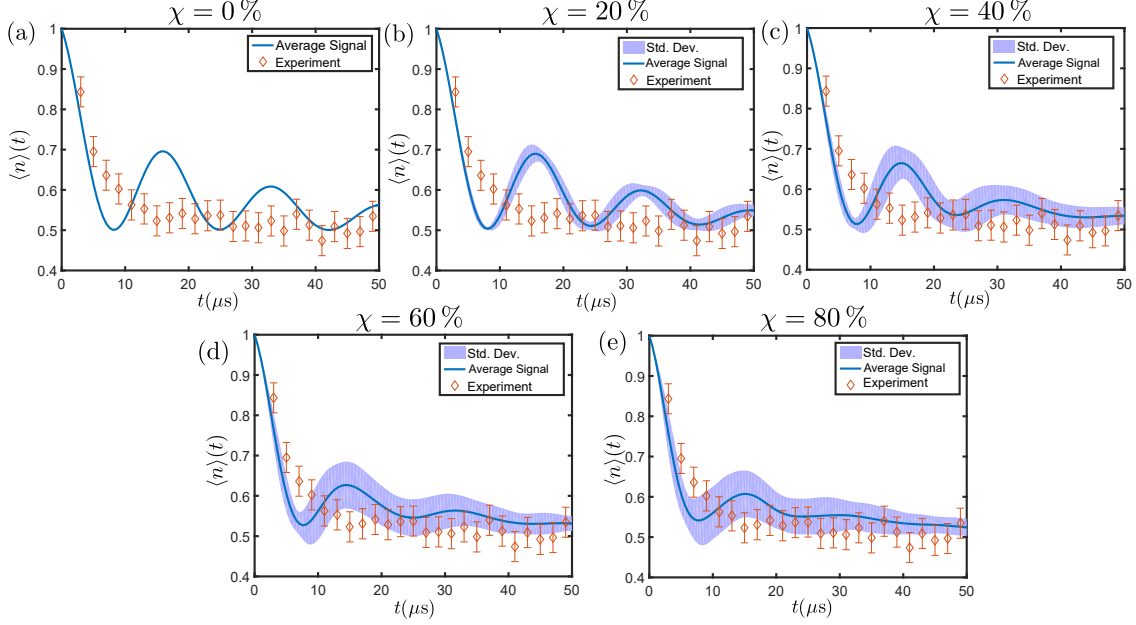

Figure S6: Comparison between rigid and semi-rigid baths and experimentally measured polarization loss for a shallow NV center at $z_0^1 = 3.2\,\mathrm{nm}$ and $T_{1\rho} = 11\,\mu\mathrm{s}$. For each order parameter, χ, infinite configurations are possible; in the figure there are shown the average value (blue line) and the standard deviation (blue shadow). (a) The protons are found at fixed positions conforming a cubic lattice with lattice parameter a. The NV center coherently interchanges polarization with the bath. Nuclear-nuclear interaction effectively detunes the nuclei from the HHDR and therefore full-oscillations are not seen.(b-e) Disorder models with different disorder parameter χ. The protons are assumed to be at random positions inside the detection volume, that is, disordered. Still, the coherent oscillations are appreciable. For larger disorder factors, the number of plausible nuclear configurations increase hence leading to a bigger standard deviation. {In the calculations, have been used, $N = 800$, $L = 20$, $\rho_{oil} = 50\,\mathrm{spins/nm^3}$, $T_{1\rho} = 11\,\mu\mathrm{s}$.}

The simulations suggest that for both rigid and semi-rigid baths the NV experiences coherent oscillations. Nonetheless, this behavior is attenuated when disorder dominates. When compared to the experimental measured data, none of the examined scenarios, neither rigid nor semi-rigid, can reproduce the observed behavior. Hence, we conclude that the description of the oil molecules as a liquid is adequate.

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