Supplemental Information for "Probing Spin Defects via Single Spin Relaxometry"

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CONTENTS

Supplementary Note 1. Disentangling PL Signals from Optically Active Spin Defects

While we have proposed a method to probe a wide variety of spin-active quantum defects, there are cases such as that of using an NV to sense V_B^- spins when both the defect and the sensor emit PL. In this case, one must seek a method to differentiate changes in the PL of the sensor from that of the defect. Using a pulsed T_1 relaxometry protocol, there are three ways in which PL between the two can be distinguished. Firstly if there is a large enough difference of the emission wavelength, then optical filtering can be used to block PL from the defect while allowing PL from the sensor to be collected. In this work, a 750 nm shortpass filter was used to block the majority of the PL from the V_B^- centers when all measurements of the NV PL were performed (Fig. S1). Figure S2 and shows a spatial scan of the hBN sample comparing unfiltered versus filtered V_B^- PL. An order of magnitude decrease of PL intensity is observed when filtered, allowing changes in the NV PL to be seen more clearly.

In addition to differences between spin defect PL spectra, changes in the PL can be further separated if there is a difference between their radiative lifetimes. This method is also employed in our measurements, as depicted in Fig. 2c in the main text. A laser pulse is applied in order to excite the NV and read out its PL; however, this also excites nearby V_B^- centers which emit PL as well. Given the shorter radiative lifetime for V_B^- centers of $\tau_{\mathrm{BV}} = 1.6\,\mathrm{ns}$ compared to that for the NV of $\tau_{\mathrm{NV}} = 12\,\mathrm{ns}$, then introduction of a 6 ns delay time before the photon counting window is opened allows for most of the V_B^- PL to disappear before a measurement is made. Thus, even if both defects emit PL at the same wavelength precluding optical filtering, the PL signals can still be separated by engineering the counting window to take advantage of the difference in radiative lifetime.

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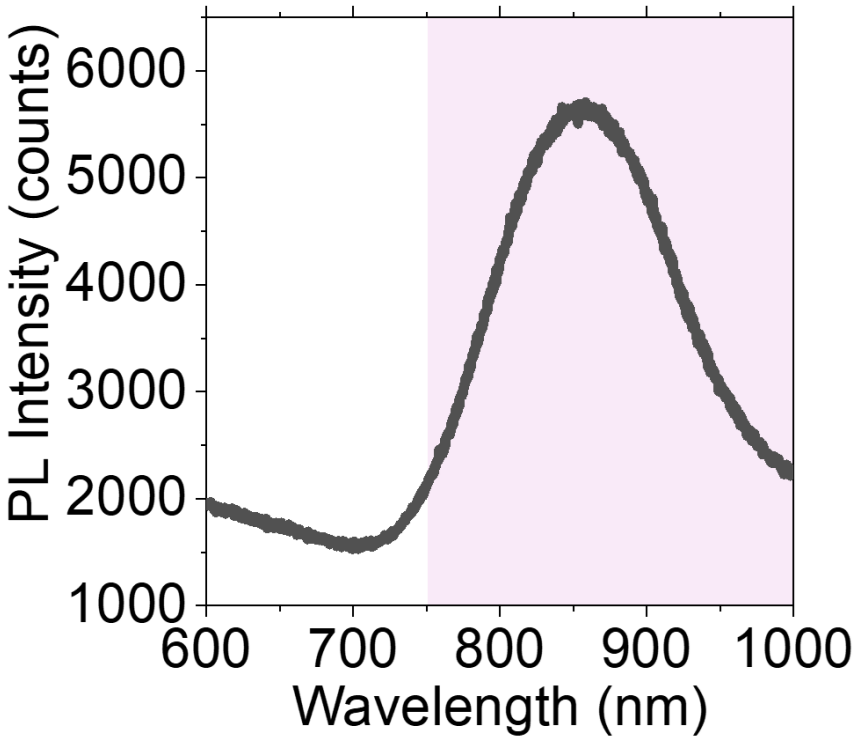

FIG. S1. **Boron vacancy center photoluminescence spectrum:** PL of hBN sample irradiated with He ions as a function of wavelength. A peak near 850 nm is consistent with the expected PL spectrum of BV centers. Placement of a 750 nm shortpass filter will block most of the BV PL as shown by the pink shaded region.

Lastly, the PL signals can be differentiated through differences in the longitudinal relaxation rates T_1. The longitudinal relaxation time of the NV here ranges from 100 μs to 1 ms, while that of the V_B^- centers is on the order of 1 to 10 μs as shown in Fig. S3. Because of this, the PL as a function of τ is only affected by the relaxation of the V_B^- centers for roughly the first 20 μs. After that, the PL decay curve is entirely determined by the NV relaxation. Thus, the NV T_1 can be determined simply by omitting the first 50 μs of PL data in the curve fitting or, in the case of iso-T_1 measurements, by adding a delay before the reference PL readout is taken. In this way, NV relaxation can still be measured independently of V_B^- relaxation, even if optical filtering and radiative-lifetime differences cannot be exploited. In this work, all three methods are used to ensure that changes in V_B^- PL do not confound measurements of the NV relaxation rate or introduce a substantial static background PL.

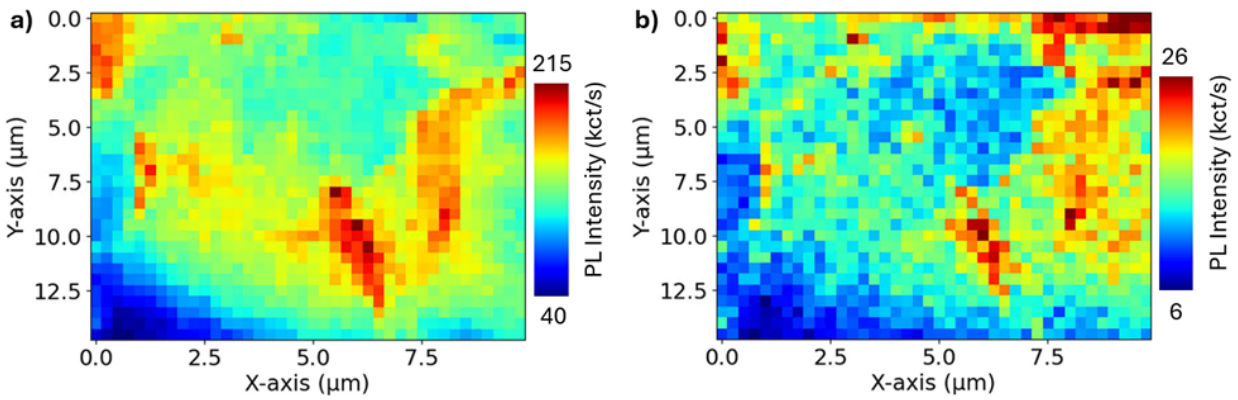

FIG. S2. **Spatial map of boron vacancy center photoluminescence:** (a) V_B^- PL as a function of position without optical filtering. (b) V_B^- PL with 750 nm shortpass filter showing an order of magnitude decrease in PL, allowing changes in the NV PL to be detected independently of changes in the V_B^- PL. Under the same measurement conditions, our NV center has PL intensity of approximately 600 kct/s (without filtering) and 500 kct/s (with filtering)

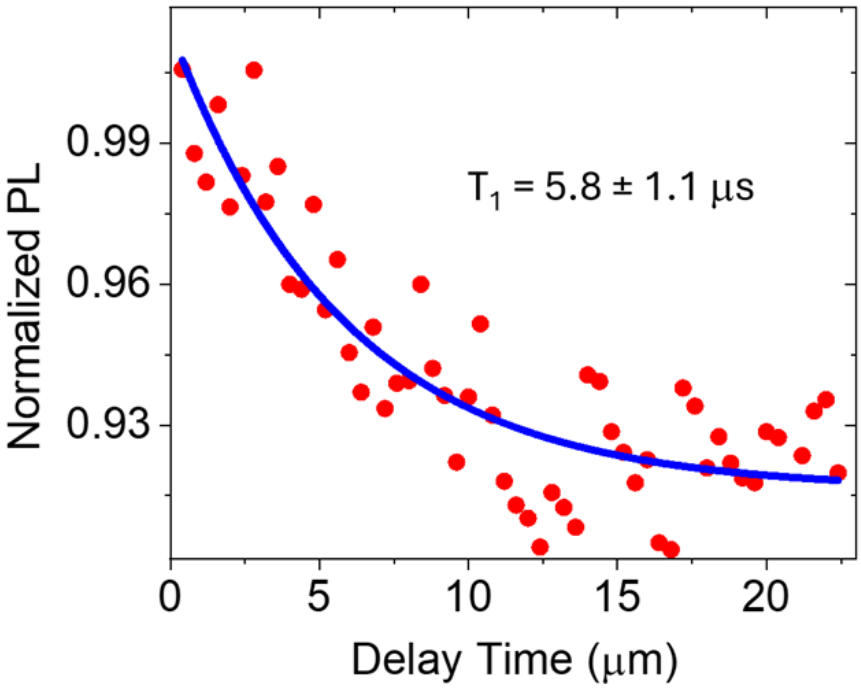

FIG. S3. **Relaxation time of boron vacancy centers in hBN:** Normalized PL as a function of delay time showing relaxation of BV spins to equilibrium.

Supplementary Note 2. Derivation of NV Relaxation Rate from Spin Noise in hBN

The longitudinal relaxation rate $\Gamma_1 = 1/T_1$ arises from the NV spin interacting with a randomly fluctuating magnetic field perpendicular to the NV spin quantization axis. The rate depends on the spectral density of the field fluctuations at the NV spin resonance frequency ω_{NV}. We start with the autocorrelation function and compute the relaxation rate. The spectral density $J(\omega)$ is the Fourier transform of the autocorrelation function:

$$J(\omega_{\mathrm{NV}}) = \int_0^\infty \langle B_\perp(t) B_\perp(t+\tau)\rangle \, e^{-i\omega_{\mathrm{NV}}\tau} \, d\tau, \tag{S1}$$

where $B_\perp(t)$ is the amplitude of the dipolar field fluctuations perpendicular to the NV. Assuming exponential autocorrelation (see Appendix C in Ref. 1):

$$\langle B_\perp(t) B_\perp(t+\tau)\rangle = \left\langle B_\perp^2 \right\rangle e^{-|\tau|/\tau_c} \tag{S2}$$

with a correlation time τ_c, then

$$J(\omega_{\mathrm{NV}}) = \left\langle B_\perp^2 \right\rangle \frac{\tau_c}{1 + (\omega_{\mathrm{NV}}\tau_c)^2} \, . \tag{S3}$$

By Fermi's golden rule,

$$\Gamma_1^{\mathrm{bath}} = \frac{3\gamma_e^2}{2\pi} J(\omega_{\mathrm{NV}}) = \frac{3\gamma_e^2 \left\langle B_\perp^2 \right\rangle}{2\pi} \frac{\tau_c}{1 + (\omega_{\mathrm{NV}}\tau_c)^2} \tag{S4}$$

where $\gamma_e = -2\pi \times 2.8\,\mathrm{MHz/G}$ is the electron gyromagnetic ratio. To obtain an expression for Γ_1^{bath}, one must find expressions for $\langle B_\perp^2 \rangle$ and τ_c.

To derive $\langle B_\perp^2 \rangle$, consider a single NV center located at the Cartesian coordinate $(0, 0, d)$ above a 2D plane of spin-1 defects at $z = 0$ with surface density σ. The NV's quantization axis is $\mathbf{n} = (\sin\theta, 0, \cos\theta)$. We derive the variance of the magnetic field perpendicular to $\mathbf{n}$, denoted $B_\perp^2$. The magnetic field at the NV location due to a bath spin $\mathbf{S}_i$ at position $(x_i, y_i, 0)$ is given by the dipole interaction [2]:

$$\mathbf{B}_i = \frac{\mu_0 \gamma_e \hbar}{4\pi r_i^3} \left[3(\mathbf{S}_i \cdot \hat{\mathbf{r}}_i)\hat{\mathbf{r}}_i - \mathbf{S}_i\right], \tag{S5}$$

where $\mathbf{r}_i = (x_i, y_i, -d)$ is the vector from the bath spin to the NV center, $\mu_0 = 4\pi \times 10^{-7}\,\mathrm{H/m}$ is the vacuum permeability and $\hbar = 1.054 \times 10^{-34}\,\mathrm{J\,s}$ is the reduced Planck constant.

The bath spins are in a fully mixed state, with density matrix $\rho = \frac{1}{2S+1}\mathbf{1}_{2S+1} = \frac{1}{3}\mathbf{1}_3$ for spin-1 particles. The expectation values are

$$\langle S_{i,\alpha} \rangle = 0 \qquad \text{and} \qquad \langle S_{i,\alpha} S_{i,\beta} \rangle = \frac{2}{3}\delta_{\alpha\beta}, \tag{S6}$$

where $\alpha, \beta = x, y, z$, and $\delta_{\alpha\beta}$ is the Kronecker delta. The covariance of the magnetic field components from a single spin is

$$\langle B_{i,\alpha} B_{i,\beta} \rangle = \left(\frac{\mu_0 \gamma_e \hbar}{4\pi r_i^3} \right)^2 \langle [3(\mathbf{S}_i \cdot \hat{\mathbf{r}}_i)\hat{r}_{i,\alpha} - S_{i,\alpha}] \, [3(\mathbf{S}_i \cdot \hat{\mathbf{r}}_i)\hat{r}_{i,\beta} - S_{i,\beta}] \rangle \tag{S7}$$

$$= \frac{2}{3} \left(\frac{\mu_0 \gamma_e \hbar}{4\pi r_i^3} \right)^2 [3\hat{r}_{i,\alpha}\hat{r}_{i,\beta} + \delta_{\alpha\beta}] \, . \tag{S8}$$

The total covariance for the 2D plane is obtained by integrating over all bath spins:

$$\langle B_\alpha B_\beta \rangle = \sigma \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \left(\frac{\mu_0 \gamma_e \hbar}{4\pi r^3} \right)^2 \frac{2}{3} \, [3\hat{r}_\alpha \hat{r}_\beta + \delta_{\alpha\beta}] \, dx \, dy, \tag{S9}$$

where $r = \sqrt{x^2 + y^2 + d^2}$, and σ is the surface density of bath spins. The diagonal components of the variance are

$$\left\langle B_x^2 \right\rangle = \left\langle B_y^2 \right\rangle = \sigma \left(\frac{\mu_0 \gamma_e \hbar}{4\pi} \right)^2 \frac{\pi}{2d^4}, \tag{S10}$$

$$\left\langle B_z^2 \right\rangle = \sigma \left(\frac{\mu_0 \gamma_e \hbar}{4\pi} \right)^2 \frac{\pi}{d^4}. \tag{S11}$$

The total magnetic field variance is

$$\left\langle \mathbf{B}^2 \right\rangle = \left\langle B_x^2 \right\rangle + \left\langle B_y^2 \right\rangle + \left\langle B_z^2 \right\rangle = 2\sigma \left(\frac{\mu_0 \gamma_e \hbar}{4\pi} \right)^2 \frac{\pi}{d^4}. \tag{S12}$$

The longitudinal component along $\mathbf{n} = (\sin\theta, 0, \cos\theta)$ is

$$\left\langle (\mathbf{B} \cdot \mathbf{n})^2 \right\rangle = \sin^2\theta \left\langle B_x^2 \right\rangle + \cos^2\theta \left\langle B_z^2 \right\rangle = \sigma \left(\frac{\mu_0 \gamma_e \hbar}{4\pi} \right)^2 \frac{\pi}{d^4} \left(\frac{1}{2} \sin^2\theta + \cos^2\theta \right). \tag{S13}$$

The transverse variance is then

$$B_\perp^2 = \left\langle \mathbf{B}^2 \right\rangle - \left\langle (\mathbf{B} \cdot \mathbf{n})^2 \right\rangle = \sigma \left(\frac{\mu_0 \gamma_e \hbar}{4\pi} \right)^2 \frac{\pi}{2d^4} (3 - \cos^2\theta). \tag{S14}$$

The correlation time τ_c is defined as $\tau_c = 1/R_{\text{dip}}$, where R_{dip} is the fluctuation rate of the bath spins due to intra-bath dipolar interactions.

$$\hbar R_{\text{dip}} = \sqrt{\sum_{j \neq i} \left\langle H_{ij}^2 \right\rangle}, \tag{S15}$$

where the dipolar Hamiltonian is

$$H_{ij} = \frac{\mu_0 \gamma_e^2 \hbar^2}{4\pi r_{ij}^3} \left[\mathbf{S}_i \cdot \mathbf{S}_j - 3(\mathbf{S}_i \cdot \mathbf{u}_{ij})(\mathbf{S}_j \cdot \mathbf{u}_{ij}) \right], \tag{S16}$$

and $\mathbf{u}_{ij} = \mathbf{r}_{ij}/r_{ij}$. For spin-1 systems in a mixed state, the expectation value of the square of the Hamiltonian becomes

$$\left\langle H_{ij}^2 \right\rangle = \left(\frac{\mu_0 \gamma_e^2 \hbar^2}{4\pi}\right)^2 \frac{16}{3r_{ij}^6}. \tag{S17}$$

For a 2D plane with spin density σ,

$$\sum_{j\neq i} \frac{1}{r_{ij}^6} \approx \sigma \int_{r_{\min}}^{\infty} \frac{2\pi\rho\, d\rho}{\rho^6} = 2\pi\sigma \left[-\frac{1}{4\rho^4}\right]_{r_{\min}}^{\infty} = \frac{\pi\sigma}{2r_{\min}^4}, \tag{S18}$$

where $r_{\min}$ is the minimum spin separation. Thus,

$$\sum_{i\neq j} \left\langle H_{ij}^2 \right\rangle = \frac{8}{3}\left(\frac{\mu_0 \gamma_e^2 \hbar^2}{4\pi}\right)^2 \frac{\pi\sigma}{r_{\min}^4} \tag{S19}$$

and so

$$\tau_c = \frac{r_{\min}^2}{\mu_0 \gamma_e^2 \hbar}\sqrt{\frac{6\pi}{\sigma}}. \tag{S20}$$

The cross-relaxation (CR) contribution to the relaxation rate Γ_1 occurs when the NV and a V_B^- center exchange energy due to near-resonant transitions, mediated by dipolar coupling. The contribution to the relaxation rate is [3]

$$\Gamma_1^{\mathrm{CR}} = \frac{W_d^2}{2\pi} \frac{\Sigma_2}{\Sigma_2^2 + \delta^2} \tag{S21}$$

The dipolar coupling strength can be related to $\langle B_\perp^2 \rangle$ of Eq. (S14) by $W_d^2 = \gamma_e^2 \langle B_\perp^2 \rangle$. At the CR condition, $\delta = 0$ and therefore

$$\Gamma_1^{\mathrm{CR}} = \frac{1}{(2\pi)^2} \frac{\gamma_e^2 \langle B_\perp^2 \rangle}{\Gamma_2^{\mathrm{NV}} + \Gamma_2^{\mathrm{BV}}}. \tag{S22}$$

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