

High-sensitivity optical detection of electron-nuclear spin clusters in diamond

L. Chambard¹, A. Durand¹, J. Voisin¹, M. Perdriat¹, V. Jacques², and G. Hétet¹

¹*Laboratoire De Physique de l'École Normale Supérieure, École Normale Supérieure,
PSL Research University, CNRS, Sorbonne Université, Université Paris Cité,*

24 rue Lhomond, 75231 Paris Cedex 05, France

²*Laboratoire Charles Coulomb, UMR 5221, CNRS-Université de Montpellier, 34095 Montpellier, France*



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We perform sensitive nuclear magnetic resonance (NMR) with spin ensembles that are polarized by nitrogen-vacancy (NV) centers in diamond at room temperature. Using stabilized lasers, a balanced detection, and a highly uniform magnetic field, we resolve sharp NMR features arising from multiple spin clusters. In particular, we investigate the coupling between nuclear spins and NV centers in the neutral and negatively charged states. Further, we perform high-precision NMR and coherent control of families of ^{13}C nuclear spin ensembles in the $|m_s = 0\rangle$ level of the NV ground state. Applying an off-axis magnetic field reveals the various sites associated with the otherwise degenerate couplings of the ^{13}C sites around the NV electronic spin, providing access to all the hyperfine tensor components. Finally, we observe spectroscopic signatures of pairs of nuclear spins coupled to the same NV center. These results are relevant for ensemble measurements of dynamical polarization that currently rely on expensive nuclear magnetic resonance systems as well as for recently proposed nuclear spin gyroscopes.

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I. INTRODUCTION

Harnessing ensembles of nuclear spins lies at the heart of a vibrant interdisciplinary effort, driven by applications in quantum information processing, secure communication, and nanoscale sensing [1–3]. Among the most promising platforms in this field of research is the negatively charged nitrogen-vacancy (NV^-) center in diamond, whose electronic spin state allows for efficient readout and polarization of proximal nuclear spins via optical means at room temperature. Notable breakthroughs using this hybrid electronic-nuclear platform include the realization of large-scale nuclear spin registers [4], high-precision gyroscopy [5–7], and nanoscale nuclear magnetic resonance (NMR) spectroscopy in microfluidic environments [8,9] or nanoscale magnetic resonance imaging [10]. Despite the unique ability of NV centers to detect nuclear spins optically, ensemble-based detection of bulk nuclear polarization—especially for ^{13}C spins—still often relies on conventional NMR setups that require strong (Tesla-scale) magnetic fields and cryogenic temperatures [11–14].

A promising alternative leverages optical detection of nuclear magnetic resonance (ODNMR), particularly via the nitrogen nuclear spin of the NV center itself. In this method, nuclear polarization is enhanced at the excited-state level anticrossing (ESLAC), where the NV photoluminescence becomes sensitive to the nuclear spin state [15–17]. While ^{14}N nuclei are commonly used in this context, the detection of other spin ensembles, such as ^{13}C , remains more challenging due, notably, to reduced polarization efficiency caused

by anisotropic hyperfine fields in the NV optically excited state and the inhomogeneous hyperfine coupling of the distant nuclear spins to the NV electronic spin. To date, most high-resolution studies of ^{13}C nuclear spins have relied on the probabilistic study of several single NV centers [18,19], which restricts throughput and scalability. Bulk readout of ensembles of ^{13}C nuclear spins generally still requires conventional NMR techniques. In the present work, we perform ODNMR with NV ensembles using amplitude and beam direction-stabilized, high-power green laser excitation in conjunction with balanced photoluminescence detection and highly homogeneous magnetic field conditions. By operating near the ESLAC, we achieve sensitive and high-resolution detection of weak nuclear spin signals. Our results show that even in a disordered system where all coupled ^{13}C -NV pairs are present, discrete families can be resolved. In particular, we detect distinct ^{13}C families (labeled A, B, C, and D) in the NV electronic ground-state manifold as well as site degeneracy lifting using a two-tone correlation spectroscopy method. We also report the optical detection of nuclear spins of the ^{14}N atom in the neutral NV^0 charge state. Finally, we study pairs of coupled carbon 13 spins that are indirectly connected by the NV center electronic spin. By driving to triplet states of the coupled system, we identify conspicuous features of these pairs of ^{13}C in good agreement with a numerical model, paving the way for a rich low-field ^{13}C NMR research landscape.

The measurements in this study are realized with a homemade confocal microscope (see Sec. I of the Supplemental Material [20]). Lasers delivering 200 mW in the green (either from Ventus-GEM or from a DPSS Cobolt Samba) are employed to excite the NV centers. Of central importance to this study is the noise reduction on the detected NV photoluminescence (PL), stemming mostly from the laser noise. Both lasers were found to be prone to beam pointing and amplitude noise

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translating directly to PL noise if no correction is applied. We reduced the low-frequency laser noise thanks to a balanced detection as well as an active correction of laser beam pointing and amplitude noise (see Sec. I of the Supplemental Material [20]). Such stabilization is crucial for long wideband NMR scans.

To minimize magnetic noise from paramagnetic impurities, we use a chemical-vapor-deposition (CVD)-grown diamond from the company element 6 (BNV14 diamond) containing 4.5 ppm of NV centers and a natural abundance of ^{13}C (i.e., 1.1%). With a laser spot size of about $5\ \mu\text{m}^2$ at the diamond surface, we detect up to $40\ \mu\text{W}$ of stable NV photoluminescence. Under these power conditions, the PL signal noise—referenced against a green laser—remains at $\sim 10^{-4}\ \text{V}$ for over an hour, enabling efficient NV signal averaging. The ground electronic state of the negatively charged NV center is a triplet state [22]. In the absence of an external magnetic field, the $|m_s = \pm 1\rangle \equiv |\pm 1_e\rangle$ states in the triplet manifold are at a frequency $D \approx 2.87\ \text{GHz}$ above the $|m_s = 0\rangle \equiv |0_e\rangle$ state at room temperature. The electronic spin of the NV centers can be optically polarized to the $|0_e\rangle$ state using green laser light. Additionally, the Stokes-shifted photoluminescence is stronger in the $|0_e\rangle$ state compared to the $|\pm 1_e\rangle$ states. Consequently, applying a microwave signal at the resonant frequency induces a drop in PL, which forms the basis of optically detected magnetic resonance (ODMR) spectroscopy.

To polarize the nuclear spins, a highly homogeneous magnetic field generated by a pair of 2 in. permanent magnets and mounted on a rotation stage is employed (see Sec. II of the Supplemental Material [20]). We will mostly be studying the $|I = 1/2, m_I = \pm 1/2\rangle \equiv |\pm 1/2\rangle$ spin of the ^{13}C atoms. Neglecting the coupling between the electronic spin and the nuclear spin of the ^{14}N , the Hamiltonian that describes a single coupled ^{13}C -NV pair is given by

$$\frac{H}{\hbar} = DS_z^2 + \gamma_e \mathbf{S} \cdot \mathbf{B} + \gamma_n \mathbf{I} \cdot \mathbf{B} + \mathbf{S} \cdot \underline{\underline{A}} \cdot \mathbf{I}, \quad (1)$$

where $D = 2.87\ \text{GHz}$, $\gamma_e = 2.8025\ \text{MHz/G}$, and $\gamma_n = -1.07\ \text{kHz/G}$. $\underline{\underline{A}}$ is the hyperfine tensor, whose components characterize the anisotropic interaction between the electronic and nuclear spins. In the NV center basis, it is possible to rewrite this Hamiltonian as

$$\begin{aligned} \frac{H}{\hbar} = & DS_z^2 + \gamma_e \mathbf{S} \cdot \mathbf{B} + \gamma_n \mathbf{I} \cdot \mathbf{B} + S_z I_z A_{\parallel} \\ & + \frac{A_{\perp}}{2} (S^+ I^- + S^- I^+) \\ & + \frac{A_{\text{ani}}}{2} ((S^+ I_z + S_z I^+) e^{-i\phi} + (S^- I_z + S_z I^-) e^{+i\phi}), \end{aligned} \quad (2)$$

where double quantum terms are neglected (see Sec. VI of the Supplemental Material [20]). The $\{e_x, e_y, e_z\}$ coordinate system is shown in Figs. 1(a) and 1(b). ϕ is defined as the angle that points to a ^{13}C site as depicted in Fig. 1(b). A_{ani} and $A_{\perp}$ are linear combinations of the components of the $\underline{\underline{A}}$ tensor (see Sec. VI of the Supplemental Material [20]). $A_{\perp}$ enables a flip-flop process, while A_{ani} couples the electronic and nuclear

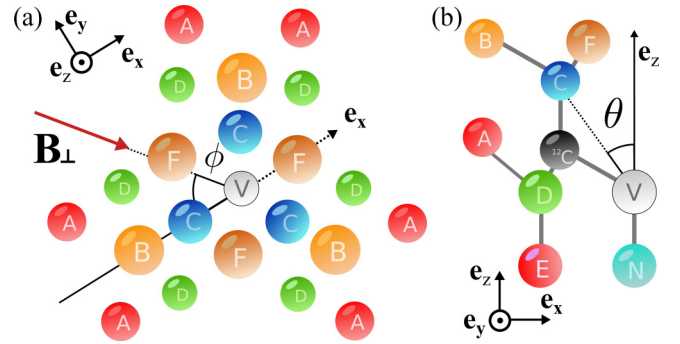


FIG. 1. (a) Schematics showing the repartition of ^{13}C atoms around the NV centers projected on a plane perpendicular to the NV axis. Families are defined according to their symmetries with respect to the NV axis, following the notation introduced in Ref. [21]. ϕ defines the angle between $\mathbf{B}_{\perp}$ and the axis ^{13}C -NV. (b) Schematics showing the ^{13}C families projected on a plane containing the NV axis. θ defines the angle between the perpendicular plane passing through the vacancy and ^{13}C families location.

spins by inducing spin flips of one system conditional on the z projection of the other.

At room temperature, the spin Hamiltonian has the same form in both the NV ground and excited states; only the parameters D and $\underline{\underline{A}}$ differ [22]. In the optically excited state, $D^{\text{ex}} \approx 1.4\ \text{GHz}$. A level crossing between $|0_e^{\text{ex}}\rangle$ and $|-1_e^{\text{ex}}\rangle$ takes place at a magnetic field of around 500 G. At such excited-state level anticrossing (ESLAC), some families of ^{13}C nuclear spins are polarized because of a joint flipping of the electron and nuclear spins $|0_e^{\text{ex}}, -1/2\rangle \rightarrow |-1_e^{\text{ex}}, +1/2\rangle$ induced by the perpendicular component $A_{\perp}^{\text{ex}}$ of the hyperfine tensor. After a few optical cycles, at relative angles between NV and magnetic axes below 1° , the nuclear spins of atomic species coupled to the NV center with $A_{\perp}$ larger than a few megahertz can then be polarized in one of the $|\pm 1/2\rangle$ states through their hyperfine coupling to the NV electronic spins, at room temperature [23]. ^{13}C families A, B, C, D, up to O have been observed using ODMR and partially polarized using single NV centers in CVD grown samples [19,21]. Figure 1(a) depicts a projected image of the position of 27 ^{13}C atoms around the NV centers on a plane perpendicular to the NV axis. Figure 1(b) is a schematics showing the ^{13}C families projected on a plane containing the NV axis. θ defines the angle between the perpendicular plane passing through the vacancy and ^{13}C families location. ϕ is the angle between $\mathbf{B}_{\perp}$ and the ^{13}C -NV axis (see Sec. VI of the Supplemental Material [20]).

The previous discussion focused on ^{13}C nuclear spins, but ESLAC polarization also applies to other nuclear species, such as the nuclear spin $I = 1$ of the ^{14}N , provided that the transverse component of the hyperfine tensor in the NV excited state exceeds a few megahertz.

II. ODMR AND SPIN ECHO AT THE ESLAC

Figure 2(a) shows an ODMR scan centered on the $|0_e\rangle \rightarrow |-1_e\rangle$ transition at a homogeneous magnetic field $B = 487\ \text{G}$ aligned to one of the four NV center families [24]. This value was chosen to maximize nuclear spin coupling to the NV

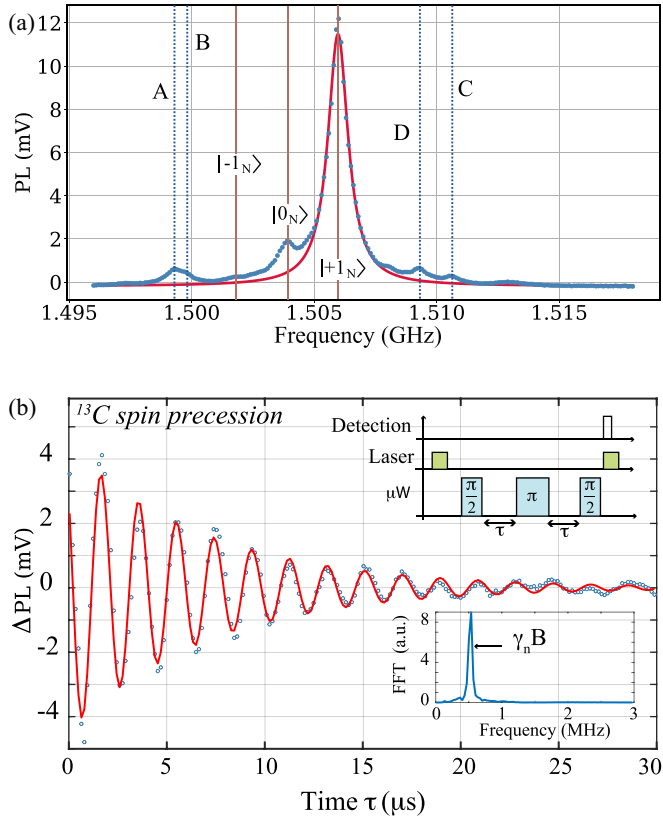


FIG. 2. (a) ODMR spectrum around the $|0_e\rangle \rightarrow |-1_e\rangle$ transition at $B = 487$ G. Blue points are experimental data, and red line is a Lorentzian fit to the resonance associated with the $|0_e, 1_N\rangle \rightarrow |-1_e, 1_N\rangle$ transition. Electronic spin transitions associated with the NV electron coupled to the A, B, C, and D ^{13}C nuclear spin families are indicated by vertical lines. (b) ESEEM signal subtracted from the slowly varying envelope (see main text). Insets: Spin echo sequence and Fourier transform of the spin echo curve.

center at the ESLAC [23], while ensuring no cross relaxation with P_1 centers [17]. Magnetic field alignment is achieved using a pair of 2 in. permanent magnets to minimize field gradients. The sample is mounted at the center of a goniometric system, where the field gradient is minimal—on the order of a few 0.06 T/m along z (see Secs. I and II of the Supplemental Material [20]).

The main peak at 1506 MHz corresponds to the electronic spin transition in the polarized $|m_I = +1\rangle \equiv |+1_N\rangle$ nuclear spin state of the ^{14}N at the frequency $\nu \approx D - \gamma_e B + |A_{||}|$. Here, $A_{||} = -2.16$ MHz is the longitudinal component of the hyperfine tensor describing the NV electron and the ^{14}N nuclear spin interaction. From the Lorentzian fit to this central line, we extract a resonance linewidth of ≈ 0.9 MHz, close to what is measured at smaller (≈ 50 G) magnetic fields, highlighting the negligibly small inhomogeneities in the B field (see Sec. II of the Supplemental Material [20] for more technical details).

The other features correspond to the two other ^{14}N nuclear spin-conserving electronic transitions as well as the four electronic transitions related to hyperfine coupling with the nuclear spin of the A, B, C, and D ^{13}C families [19,21]. Proximal ^{13}C nuclei from family A have already been

observed in ODMR with a resolution of about 2 MHz (see, e.g., Refs. [7,24]). The frequencies of the four ^{13}C -NV transitions we observe can be approximated by $\nu \pm |A_{||} \pm \gamma_n B|$ far from level crossings in the ground state (the $\pm$ signs depend on the signs of the hyperfine tensor $A_{||}$ for each family). These analytical expressions provide a good estimate of the peak positions. In this measurement, the precision with which one can extract the ^{13}C -NV hyperfine tensor from ODMR spectra is nevertheless limited by $1/T_2^*$, where $T_2^* \approx 1 \mu\text{s}$ is the electron spin coherence time. Improving beyond this resolution is inherently challenging with highly doped NV ensembles.

To enhance spectral resolution, a common approach is to employ electron spin echo envelope modulation (ESEEM) [25]. The sequence is illustrated in the inset of Fig. 2(b). Figure 2(b) displays the PL as a function of the free precession time, after subtracting the slowly varying spin-echo envelope, which decays with a characteristic time of $T_2 \approx 7(3) \mu\text{s}$ (see Sec. III of the Supplemental Material [20]). The data reveal fast oscillations at a frequency of 521(5) kHz (see the Fourier transform below), corresponding to the ^{13}C Larmor precession at a magnetic field of 487(1) G. This is clear evidence that the electron spin experiences a periodically modulated hyperfine field from coupled ^{13}C nuclei. Applying a transverse magnetic field could, in principle, allow one to distinguish the contributions from the different ^{13}C families in the Fourier spectrum and extract the complete hyperfine tensors [18]. However, the achievable resolution would be limited to $1/T_2 \approx 140$ kHz. Moreover, inequivalent ^{13}C sites within the same family would precess at slightly different frequencies, leading to a broadening of the Fourier peaks.

In the rest of the article, we will use another method that is closer in spirit to NMR to measure nuclear spins and hyperfine tensor components with higher spectral resolution, enabling precise estimate of the full ^{13}C -NV hyperfine tensor. When a green laser is continuously applied to the NV centers, the fraction of the electronic spin population in a given electronic spin state will flip depending on the nuclear spin state. Applying an radio-frequency (RF) tone in the NV ground state to flip a polarized nuclear spin when at the ESLAC will indeed result in an electron-nuclear spin flip-flop in the optically excited state. The electron flip to the $|-1_e\rangle^{\text{ex}}$ state, will provoke a nonradiative decay to the NV metastable state, thus lowering the PL rate. In turn, the NV PL thus depends on the nuclear spin state [15,16]. The protocol will hereafter be called ODNMR [17]. As we shall see, detecting ^{13}C -NV couplings in the $|\pm 1\rangle$ states as well as in the $|0_e\rangle$ electronic states enables precise determination of the full hyperfine tensor.

III. ^{14}N NMR IN THE NV^- STATE

In this part, we study ODNMR under 10 mW of continuous-wave laser power. At this power level, the laser does not fully polarize the NV center in the $|0_e\rangle$ state so that nuclear spin transitions in the electronic states $|\pm 1_e\rangle$ can be detected without applying microwave [15] (see Sec. IV of the Supplemental Material [20]).

Figure 3(a) shows the NV PL as a function of RF drive frequency up to 14.4 MHz, featuring many sharp peaks. The first one, indicated by a downward pointing arrow, is close to $\gamma_n B = 521$ kHz under a magnetic field of 487 G. Thus,

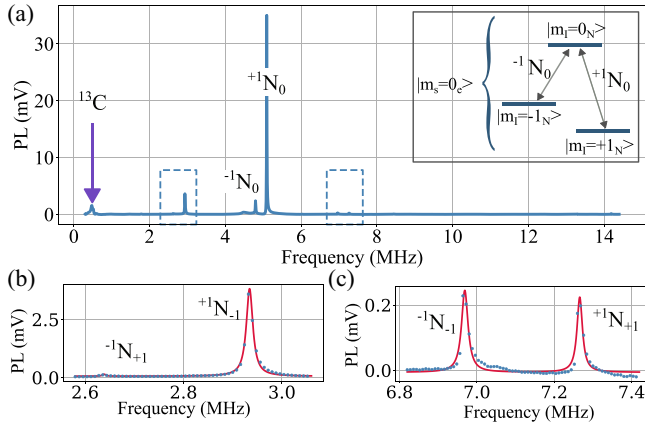


FIG. 3. (a) ODNMR spectrum at $B = 486.8$ G. Evolution of the PL as a function of the frequency of radio frequency field, from 400 kHz to 14.3 MHz. The upper right box show the ^{14}N nuclear spin in the $|0_e\rangle$ state. The ^{13}C down arrow shows the expected peak at the ^{13}C spin Larmor frequency. (b), (c) Enlarged spectra corresponding to the two dashed boxes in panel (a), showing resonances associated with the ^{14}N nuclear spins coupled to NV^- centers in the $|\pm 1_e\rangle$ manifolds.

this peak may be attributed to the ^{13}C NMR transitions in the $|0_e\rangle$ state. This will be confirmed in the next section. The other most pronounced peaks have already been reported [17,26] and are associated to ^{14}N spins in the three NV^- center electronic states.

Figures 3(b) and 3(c) show a close-up of the four nuclear spin transitions in the $|\pm 1_e\rangle$ manifolds of the NV^- center. The low employed optical power level permits observing all of the four transitions with high sensitivity, without requiring microwave pulses to drive the electron to the $|\pm 1_e\rangle$. Notably, the $^{-1}\text{N}_{-1}$ and $^{+1}\text{N}_{+1}$ transitions are both much lower than the $^{-1}\text{N}_{-1}$ transition and almost have the same contrast, although $|+1_N\rangle$ state is better polarized. This phenomenon is likely to be caused by the ODNMR readout protocol. At the ESLAC, the flip-flop only involves the $|-1_e\rangle$ and $|0_e\rangle$ states, so only nuclear spins in the $|-1_e\rangle$ are readout efficiently. This effect boosts the readout efficiency on the $^{-1}\text{N}_{-1}$ NMR transition and lowers it on the $^{+1}\text{N}_{+1}$ transition [17].

Using this spectrum, full information about the ^{14}N - NV^- hyperfine tensor can be obtained (see Sec. VIII of the Supplemental Material [20]).

IV. ^{14}N NMR IN THE NV^0 STATE

We now turn to observations of ODNMR in the *neutral charged state* of the NV center, written as NV^0 . Not visible in Fig. 3(a) are pairs of peaks around 2 and 8 MHz. Figure 4(b) shows two scans around these transitions. These are attributed to the driving of the nuclear spin of the nitrogen 14 atoms in the NV^0 state. In the NV^0 state, the electron spin of the defect can be $S = 1/2$ or $S = 3/2$ [27,28].

Neglecting second-order electron-nucleus flip-flop processes for now, the effective spin Hamiltonian for the ^{14}N nucleus in the $S = 1/2$ state of the NV^0 center reads

$$\mathcal{H}_N^{\text{NV}^0}/\hbar = Q_0 I_z^2 + \gamma_n^{(N)} B_z I_z + m_s A_{\parallel}^0 I_z, \quad (3)$$

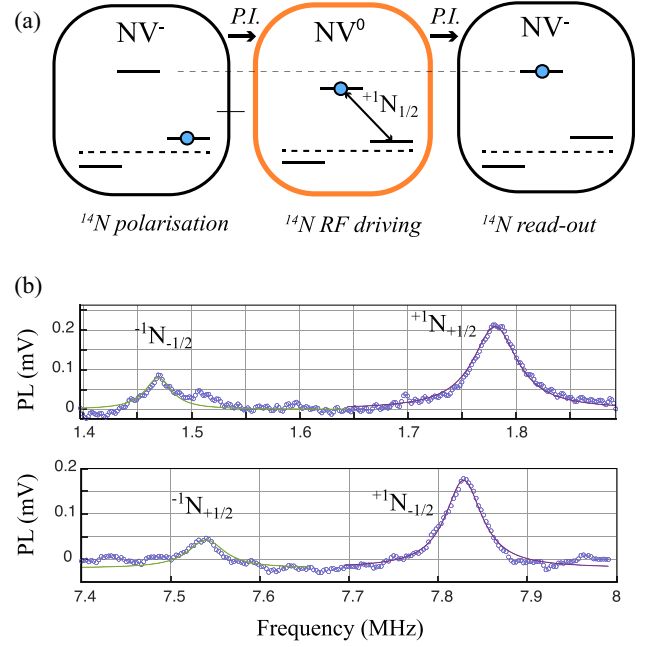


FIG. 4. (a) Suggested process enabling NMR in the NV^0 charge state : photoionization followed by radio frequency excitation of the ^{14}N spin in the NV^0 charge state and readout in the NV^- state. (b) ODNMR spectrum at $B = 486.8$ G showing resonances associated with ^{14}N nuclear spins coupled to the NV^0 center in the $|\pm 1/2_e\rangle$ manifolds.

where $Q_0 \approx -4.655$ MHz [29,30] is the nuclear quadrupolar interaction and $A_{\parallel}^0 \approx 6.06$ MHz is the hyperfine coupling constant between the $S = 1/2$ electron spin and the nuclear spin [30].

In contrast to the NV^- , the NV^0 state lacks spin-selective optical transitions, which restricts its applicability in coherent spin-control schemes. As illustrated in Fig. 4(a), however, photoionization (P.I.) may allow readout of the NV^0 nuclear spin states, provided that P.I. does not disturb the nuclear spins. In this protocol, ^{14}N nuclear spin polarization is first established in the NV^- charge state. A subsequent two-photon process [31] converts NV^- into NV^0 , where both the hyperfine interaction and quadrupole moment differ. Radio frequency driving can then flip the ^{14}N spin, after which a second P.I. process restores the NV to the negatively charged state, enabling optical readout of the ^{14}N nuclear spin.

The spectral positions of the four peaks in Fig. 4(b) are reported in the Table I. There is good agreement between the

TABLE I. Measured ODNMR transition frequencies (left) and ^{14}N nuclear spin parameters (right) in the NV^0 state.

NV ⁰ ODNMR resonances		¹⁴ N nuclear spin parameters	
Label	Frequency (MHz)	Param. in NV ⁰	Value (MHz)
⁺¹ N _{-1/2}	7.828(3)	Q ₀	4.655(5)
⁻¹ N _{-1/2}	1.472(9)	A _∥ ⁰	6.057(3)
⁺¹ N _{+1/2}	1.782(3)	A _⊥ ⁰	3.9(6)
⁻¹ N _{+1/2}	7.540(8)		

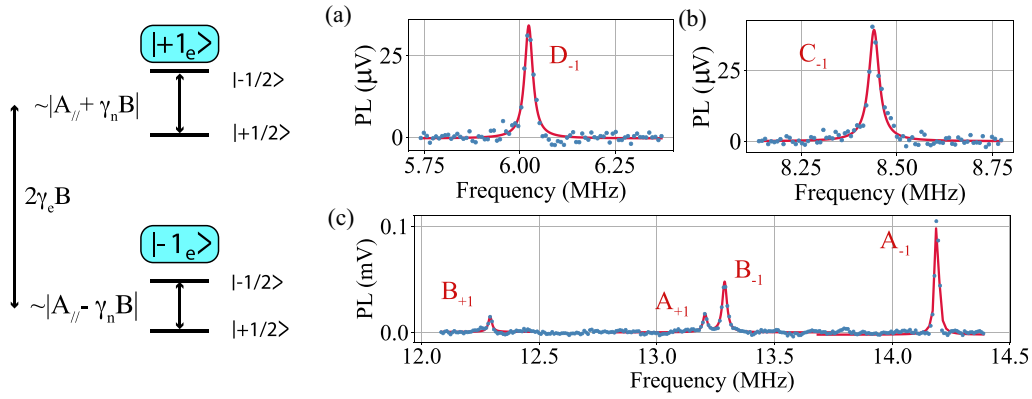


FIG. 5. (Left) Energy levels of the ^{13}C nuclear spins in the $|\pm 1_e\rangle$ states. Panels (a)–(c) are close-up of the ODNMR resonances arising from the coupling between ^{13}C nuclei and NV electronic spins in the $|\pm 1_e\rangle$ magnetic states. Blue dots correspond to experimental data and red lines to Lorentzian fits. The resonance frequencies are reported on Table II. Resonances are labeled by the ^{13}C family and using the NV electronic spin in index.

predicted positions of the peaks and the expectations found from Eq. (3). There is also good agreement with the reported values [30]. Interestingly, the contrast of the four ^{14}N nuclear spin transitions in the NV^0 state is fully consistent with a polarization of the nucleus in the $|1_N\rangle$ state. This shows that a large ^{14}N nuclear spin polarization is preserved after photoionization. Also, the P.I. transfer enables unambiguous CW readout of the spin polarization. This is to be compared with the readout of the ^{14}N nuclear spin in NV^- where ODNMR biases the readout contrast, as discussed in Sec. III.

We now seek to provide quantitative estimates of the NV^0 hyperfine and quadrupole tensors. To this end, we employ the formulas in the Sec. VIII of the Supplemental Material [20], which include nonsecular contributions. The values are reported in the Table I. We also extract the $A_\perp^0$ component, which has not been reported thus far to the best of our knowledge. Note that our method involves a subtraction of two frequencies that are very close to each other, so the uncertainty in $A_\perp^0$ is larger than in the estimation of Q_0 and $A_\parallel^0$.

V. ^{13}C NMR

A. ODNMR in the NV magnetic states

Let us now turn to additional peaks that are not visible in Fig. 3(a), which are displayed in Fig. 5. The central frequencies of these peaks, obtained by fitting Lorentzian functions, are reported in Table II (left). The peaks labeled A_{m_s} , B_{m_s} , and

D_{m_s} are in excellent agreement with the expected transitions in the $|\pm 1_e\rangle$ NV electronic states for the three families of ^{13}C spins, as previously observed by Smeltzer *et al.* [21] using pulsed ODMR with interleaved RF drive in the $|\pm 1_e\rangle$ manifolds. The position of each of the ^{13}C atoms with respect to the NV center is depicted in Fig. 1. The previously unreported peak at 8.45 MHz observed here can be attributed to C_{-1} , based on the ODMR results from Dréau *et al.* [19].

Interestingly, sharp NMR peaks are observed, with a width on the order of the one measured in the single-spin experiments [21], but here using many NV centers coupled to ^{13}C atoms at different sites, thus improving NMR sensitivity. All the sites—whose Hamiltonian differ one by ϕ [see Eq. (2)]—for a given family are indeed degenerate in the $|\pm 1_e\rangle$ states.

Diagonalizing the Hamiltonian Eq. (2) using the values of $A_\parallel$ from Refs. [19,21] and neglecting $A_\perp$ already yields a fair agreement with the observed transition frequency. We postpone the estimation of $A_\parallel$ to when $A_\perp$ will be extracted. The latter can indeed be estimated efficiently, independently on $A_\parallel$, in the $|0_e\rangle$ state.

B. ODNMR and coherent control in the $|0_e\rangle$ state

We now study ODNMR in the $|0_e\rangle$ state, where to the best of our knowledge, no ^{13}C spins have yet been detected. Since the $|0_e\rangle$ state is nonmagnetic, the NMR peaks for all ^{13}C families are expected to lie at around $\gamma_n B \approx 520$ kHz, with $B = 486.8$ G. This, in fact, almost coincides with the first broad peak observed in Fig. 3.

1. ODNMR in the $|0_e\rangle$ state theory

Figure 6(b) displays an ODNMR scan acquired with 30 dB lower RF power than in the data shown in Fig. 3, revealing four narrow peaks in the vicinity of $\nu = \gamma_n B$ now. To account for the origin of these peaks, one must consider second-order hyperfine interactions with the $|\pm 1_e\rangle$ NV spin states. Although the NV is nominally in a nonmagnetic state, the transverse component of the hyperfine interaction can induce an effective electronic magnetic moment, which in turn shifts the nuclear energy quasidegenerate levels [18,32,33].

TABLE II. ^{13}C ODNMR resonances in the three electronic spin states $|\pm 1_e\rangle$ and $|0_e\rangle$ of the NV^- center at $B = 486.8$ G aligned with the NV axis. Values and uncertainties are obtained from Lorentzian fits of each resonance.

$ +1_e\rangle$		$ -1_e\rangle$		$ 0_e\rangle$	
Label	Freq. (MHz)	Label	Freq. (MHz)	Label	Freq. (kHz)
A_{+1}	13.2052(9)	A_{-1}	14.1907(4)	A_0	469.79(3)
B_{+1}	12.292(1)	B_{-1}	13.2985(3)	B_0	480.27(5)
		C_{-1}	8.4402(5)	C_0	499.29(9)
		D_{-1}	6.0235(5)	D_0	516.58(5)

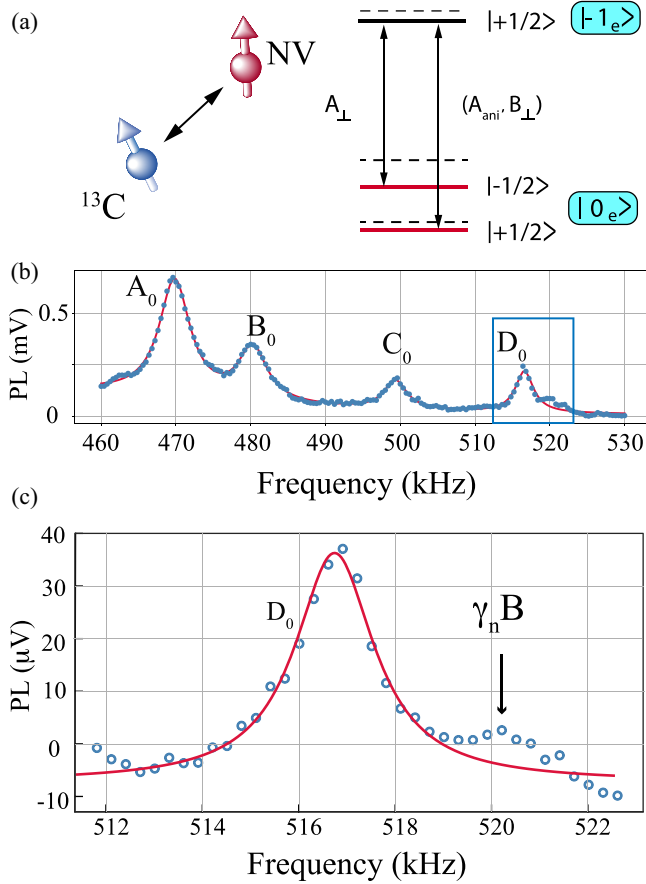


FIG. 6. (a) Coupled ^{13}C -NV spins and simplified level structure ($|+1_e\rangle$ state not depicted) showing the mechanism by which the two quasidegenerate ^{13}C states are coupled in the $|0_e\rangle$ state. (b) ODNMR of ^{13}C nuclei coupled to the NV center electronic spin in the $|0_e\rangle$ state. The magnetic field B is aligned along one NV axis. $B = 488.15$ G. Four resonances are fitted with Lorentzian profiles, the parameters are reported in Table III. (c) Enlarged scan around the peak D , showing an extra peak, possibility related to all other weakly coupled ^{13}C families.

Here, we derive an effective two-level Hamiltonian for a single ^{13}C spin in the subspace $|0_e\rangle$ taking into account the hyperfine interaction in all NV states. Using a second-order perturbation theory of degenerate states (see Secs. VI and VII

TABLE III. Values of the ^{13}C -NV hyperfine interaction terms for the families A, B, C, and D from the experiment and from the theory developed in Ref. [37]. The $A_{\perp}$ components are evaluated using data from Fig. 6(a). The A_{ani} components are extracted from Fig. 8(a) using a fit with Eq. (6). $A_{\parallel}$ are extracted from the transitions listed in Table II.

^{13}C Family (No. of sites)	$A_{\perp}$ (MHz)		A_{ani} (MHz)		$A_{\parallel}$ (MHz)	
	Exp.	Theo.	Exp.	Theo.	Exp.	Theo.
A (6)	15.6(1)	15.54	1.56(8)	1.62	13.7496(1)	13.38
B (3)	14.00(7)	13.88	1.8(1)	1.88	12.795(2)	12.62
C (3)	-10.4(1)	-10.17	0.9(2)	0.81	-8.9(2)	-8.84
D (6)	-5.2(2)	-5.64	-	0.90	-6.51(2)	-7.00

of the Supplemental Material [20]), we obtain

$$\frac{H_{\text{eff}}^{(0_e)}}{\hbar} = \frac{1}{2} \begin{pmatrix} \gamma_n B_z + \nu & \gamma_n B_x + h_{\perp} \\ \gamma_n B_x + h_{\perp}^* & -\gamma_n B_z - \nu \end{pmatrix},$$

in the basis $|\pm 1/2\rangle$, with

$$h_{\perp} = -\frac{\gamma_e A_{\perp}}{\Delta^2} (A_{\text{ani}} e^{i\phi} B_z + 2DB_x), \quad (4)$$

$$\nu = -\frac{\gamma_e}{\Delta^2} (2D \cos \phi A_{\text{ani}} B_x + A_{\perp}^2 B_z). \quad (5)$$

We wrote $\Delta^2 = D^2 - (\gamma_e B_z)^2$. The diagonal terms are due to virtual transitions through states $|1_e\rangle$ and $|-1_e\rangle$ by the combined action of $A_{\perp}$ and A_{ani} . This process is shown in Fig. 6 (note that the state $|+1_e\rangle$ is not depicted, but it also contributes to the frequency shifts). They involve flip-flop processes between the electronic and nuclear spins followed by electronic spin flips which preserve the nuclear spin. The Hamiltonian can in fact be recast in terms of an effective Zeeman Hamiltonian with a g tensor capturing the effects of the anisotropic and transverse components of the hyperfine tensor (see Refs. [18,34] and Sec. IX of the Supplemental Material [20]).

From this Hamiltonian, we can compute the shift in energy between the two $|\pm 1/2\rangle$ eigenstates. It is given by

$$\Delta E = \hbar \sqrt{(\gamma_n B_z + \nu)^2 + |\gamma_n B_x + h_{\perp}|^2}. \quad (6)$$

In the particular case where $B_x = 0$, we get

$$\Delta E = |\gamma_n B_z| \sqrt{\left(1 + \frac{\gamma_e A_{\perp}^2}{\gamma_n \Delta^2}\right)^2 + \left(\frac{\gamma_e 2A_{\perp} A_{\text{ani}}}{\gamma_n \Delta^2}\right)^2}. \quad (7)$$

We observe that the energy splittings, and consequently the RF resonance frequencies, differ for each ^{13}C family, due to variations in $A_{\perp}$ and A_{ani} .

2. Two-tone ODNMR spectroscopy

The values of $A_{\perp}$ have at present not been measured for the four families A, B, C, and D. We may tentatively attribute the resonances in the $|0_e\rangle$ manifold to families A_0 , B_0 , C_0 , and D_0 in ascending order of transition frequencies, following the $A_{\parallel}$ trend. The extra smaller peak that is seen at $\gamma_n B \approx 520$ G [a close-up is shown in Fig. 6(c)] would then likely correspond to the other weakly coupled ^{13}C families, including possible contributions from diffusive ^{13}C spins that are not coupled to the NV center directly.

This interpretation is not entirely satisfactory, however. Theories suggest that the $A_{\perp}$ ordering between families can differ significantly from that of $A_{\parallel}$ [35,36]. To resolve this ambiguity, we perform two-tones correlation spectroscopy involving the $|-1_e\rangle$ electronic states in which each ^{13}C family was previously unambiguously identified (see Sec. V A). The idea is to record demodulated PL (DPL) lock-in signals by scanning an RF tone close to resonances in the $|-1_e\rangle$ manifold while a second modulated RF tone is on resonance with one of the peaks in the $|0_e\rangle$ state. First, we perform a lock-in detection close to the A_0 , B_0 , C_0 , and D_0 peaks with a frequency-modulated RF signal. Figure 7(a) shows the corresponding DPL scan, where all peaks seen in Fig. 6(b)

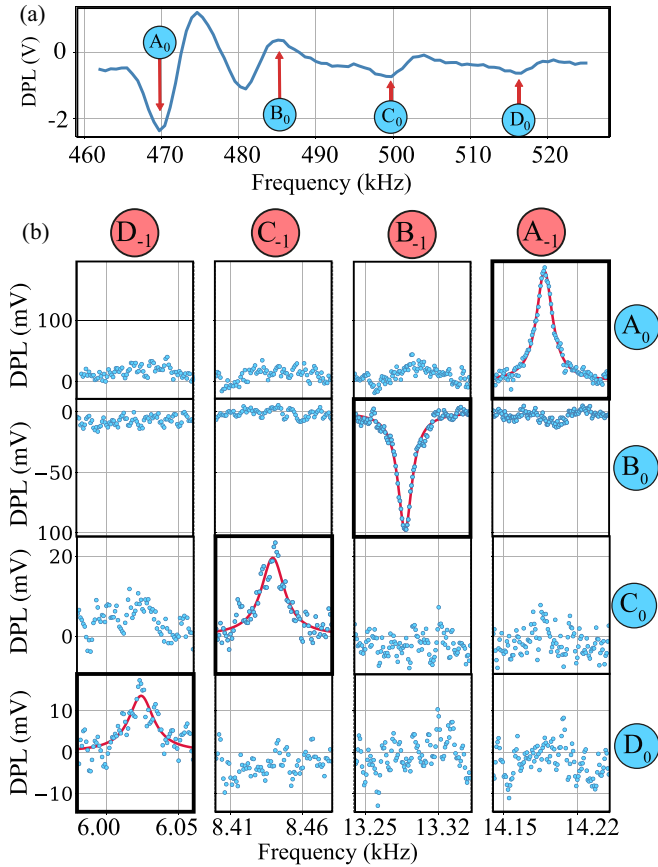


FIG. 7. (a) ODNMR recorded from 460 to 525 kHz, using a lock-in detection. The FM modulation frequency of the RF field is 2 kHz. Frequencies shown with arrows are the one chosen to realize the two-tone spectroscopy shown below. (b) DPL scans around ^{13}C transitions in the $| - 1_e \rangle$ states (indicated by the red circles on top) with a second modulated RF near one of the four ^{13}C families in the $| 0_e \rangle$ manifold (indicated by blue circles on the right). Red continuous curves are Lorentzian fits to the data.

are clearly identified. Next, as indicated by the red arrows, we park the modulated RF signal around one of the four transitions in this $| 0_e \rangle$ manifold. We then detect a DPL around the four A, B, C, and D transitions in the $| \pm 1_e \rangle$ state for four different pump frequencies using a second RF generator.

The principle of this technique is that a demodulated detection scan around one of the four nuclear transitions—for instance B_{-1} —yields a signal only if a modulated pump is applied on B_0 , thereby depleting the $| 0_e \rangle$ state. Since the lock-in detection is sensitive exclusively to resonances involving ^{13}C nuclei from the same spin family, a DPL signal should thus appear solely for the B_{-1} - B_0 combination.

Figure 7(a) presents the results of sixteen measurements obtained with the two-tones correlation spectroscopy technique. A signal within a given family appears only when the pump is tuned to that same spin family, with no cross signals observed. This allows us to unambiguously identify the families in the $| 0_e \rangle$ subspace and confidently assign the four resonances in Fig. 6(b) to the A, B, C, and D families, in ascending order.

One essential feature in the theory presented in the Sec. V B 1 is that the central positions of the A_0 , B_0 , C_0 , and D_0 peaks depend solely on $|A_{\perp}|$ to lowest order. The third term under the square root in Eq. (7) is indeed negligibly small as we shall see. This fact greatly facilitates the reconstruction of the hyperfine tensor. From the central position of these peaks, we can thus extract the absolute value of $A_{\perp}$ independent on $A_{\parallel}$. This is reported in Table III, setting the sign of $A_{\perp}$ to be the same as the sign of $A_{\parallel}$ (see Sec. VIII of the Supplemental Material [20]).

Once the $A_{\perp}$ are extracted, another identification check can be done by comparing the amplitude of each of the four peaks. Their amplitudes are proportional to $p \times \Omega^2 \times N_{\text{site}}$, where p is the polarization of the ^{13}C spin, Ω the RF Rabi frequency, and N_{site} the number of sites. One can use the formulas in Ref. [33] to estimate $\Omega = \gamma'_n B_{\text{RF}}$, where γ'_n is the hyperfine enhanced gyromagnetic ratio—related to $A_{\perp}$ —and B_{RF} is the RF magnetic field amplitude. Using the polarization p measured in Ref. [19], we find that the amplitude ratios between each peak match very well this prediction (see Sec. IX B of the Supplemental Material [20]).

3. Lifting site degeneracy

Theory also predicts that there is a dependency of the frequency of the various sites *within the same family* [see Fig. 1(a)] to a transverse magnetic field. As is manifest in Eq. (6), when both ϕ , namely, the azimuthal angle that identifies a site in the same family, and B_x are included in the theory, the energy levels depend on ϕ . ^{13}C nuclear spins states of the same family are then no longer degenerate in a transverse B field. A_{ani} then contributes at leading order to the shift, allowing specific spatial ^{13}C -NV configurations to be distinguished spectrally. In order to show this effect while still retain sufficient signal to noise, we performed an experiment where the transverse component of the magnetic field is set as sketched in Fig. 8(a). The magnetic field direction is set in the middle of two A carbon ^{13}C atoms so that only two B field projections onto the ^{13}C -NV axes differ, instead of six for the family A and three for the family B. A clear splitting of the A and B transitions due to the transverse component of the magnetic field is observed in 8(b) as it is stepped up to 0.085 mT. Figure 8(c) shows a scan of the transition frequencies in families A and B, when the transverse component of the B field spans -0.15 to 0.15 mT. The evolution of the transition frequencies as a function of B_x is shown in Fig. 8(d). Each of these four curves are fitted by Lorentzians, thus providing a precise and unvalued measurement of A_{ani} . The hyperfine components, including the $A_{\parallel}$ components obtained from the transitions frequencies in the Table II, are recorded in the Table III and are compared to the theory performed in Ref. [37]. A good agreement between the theory and the experiment is obtained, highlighting the accuracy of the ODNMR and of the theoretical methods used in Ref.[37].

4. Coherent control of ^{13}C nuclear spins

To use the ^{13}C nuclear spins for applications, achieving quantum coherent control of their spin states is essential. Here, we show coherent control of ^{13}C nuclear spin ensembles in the $| 0_e \rangle$ manifold.

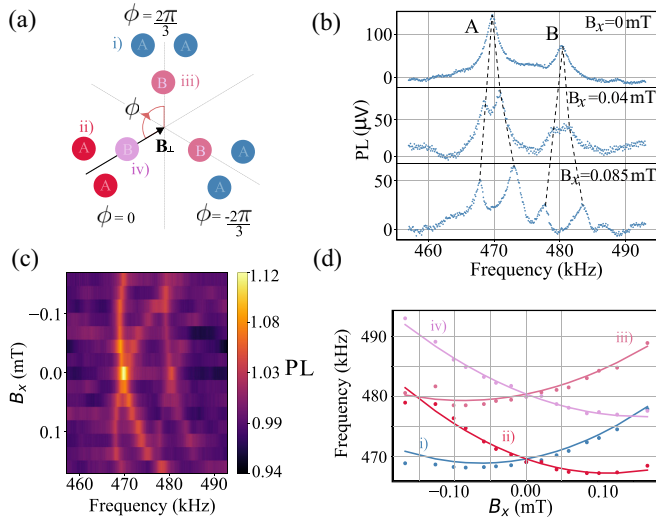


FIG. 8. (a) Schematic representing the ^{13}C repartition, of families A and B around an NV center (not shown). The direction of $\mathbf{B}_\perp$ shown here is the one employed in the measurements shown in panels (b)–(d). (b) ODNMR spectra for families A and B for the three values of B_x shown on the top right (here $\phi = 0$, so $\mathbf{B}_\perp = B_x \mathbf{e}_x$). Dashed lines indicate the evolution of the peaks' maxima obtained using Lorentzian fits. (c) Two-dimensional plot showing the photoluminescence as a function of the transverse magnetic field amplitude and RF frequency for families A and B. (d) Transition frequencies as a function of the transverse magnetic field B_x . The data points (dots) are extracted from the maxima in the ODNMR spectra of Fig. 6(b). Continuous lines correspond to the fit using Eq. (6), where ϕ is set to 0 for traces (i) and (iii) and $2\pi/3$ for traces (ii) and (iv). A_{ani} is used as a free parameter in these fits. Each trace is associated to a ^{13}C as labeled in panel (a).

As a preliminary step, we demonstrate Ramsey oscillations on the $|+1_N\rangle \rightarrow |0_N\rangle$ transition of the ^{14}N nuclear spin in the $|0_e\rangle$ electronic state. The duration of a $\pi/2$ pulse is first calibrated via Rabi oscillation measurements. We then perform a standard Ramsey sequence using a radio frequency tone detuned by approximately 8 kHz from the central transition frequency at 5.091 MHz. Figure 9(a) displays the resulting decaying Ramsey oscillations. A fit with an exponentially decaying sinusoid yields a detuning of 8 kHz and a dephasing time T_2^* of approximately 864(7) μs . This value is close to the T_1 time of the NV electronic spins (see Sec. V of the Supplemental Material [20]). It is also close to the decay time estimate that one can derive from the electronic T_2^* and ratio of the nuclear to electronic gyromagnetic ratios.

We now move on to performing coherent control of the ^{13}C ensemble in the $|0_e\rangle$ state. One difference with the nitrogen nucleus is the nondegeneracy of the A, B, C, and D peaks, even in the $|0_e\rangle$ state (see Fig. 6). Figure 9(b) shows a Ramsey measurement with an RF tone set at 460 kHz. We fit these data by a sum of two sinusoids with frequencies $\omega_A = 9.87(3)$ kHz and $\omega_B = 20.34(6)$ kHz and a single exponential decay. The Fourier transform of the signal in Fig. 9(b) features these two frequencies, plus another one around 40 kHz from family C. From the fit, we extract a decay time for the ^{13}C nuclear spins coherence time $T_2^* \approx 203(9)$ μs . The ratio of the decoherence

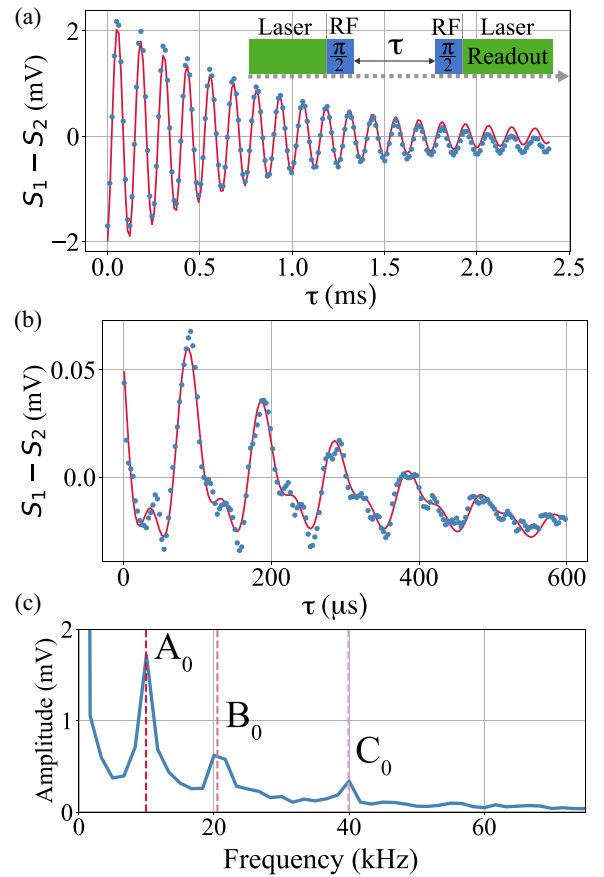


FIG. 9. (a) Ramsey oscillation of the ^{14}N nuclear spin state at a frequency detuning of 8 kHz. The sequence is detailed in the top right of the figure. (b) Ramsey oscillation of the ^{13}C nuclear spin. The RF is fixed at 460 kHz. Experimental data are fitted with a sum of two sinus with exponential decay. (c) Fourier transform of the Ramsey oscillation signal. Three resonances corresponding to families A, B, and C in the $|0_e\rangle$ state are visible.

time of ^{13}C and ^{14}N nuclear spins is of the same order of magnitude as the ratio of their gyromagnetic ratios indicating that the decoherence times have the same origin in both species.

We conclude this section by noting that, in principle, all-optical pulsed detection of ^{13}C nuclear spins can be performed in a similar manner to that of the NV center's ^{15}N nucleus, as demonstrated in Ref. [38] (both having a spin 1/2), albeit with a smaller contrast and with multiple frequency components instead of just one.

C. Coupled pairs of ^{13}C spins

Individual NV centers can act as efficient mediators for coupling nearby nuclear spins, offering a more effective mechanism than direct nuclear-nuclear interactions, as the electronic spin of the NV provides both a stronger magnetic interaction and a controllable interface that enables coherent, long-range coupling between otherwise weakly interacting nuclear degrees of freedom. Figure 10(a) illustrates how the NV center facilitates the interaction between ^{13}C pairs. This picture can be naturally extended to larger clusters of nuclei, where the NV center mediates complex multispin interactions

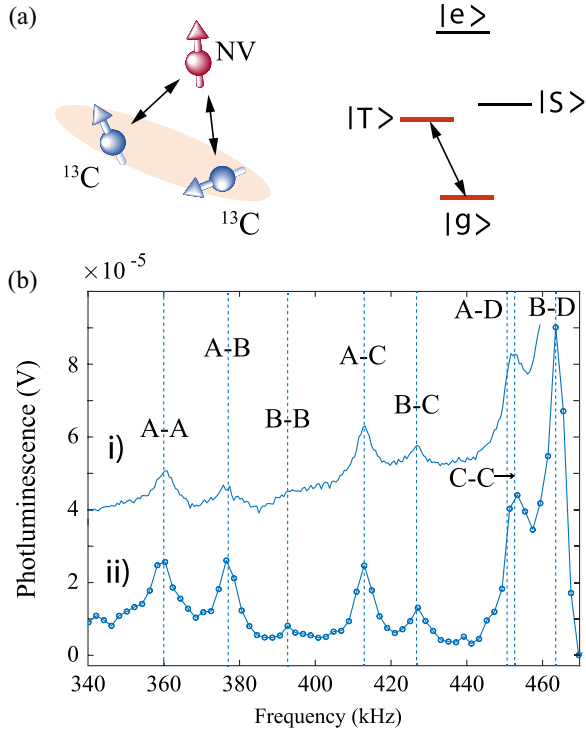


FIG. 10. (a) Left: Schematics showing ^{13}C spins coupled through the NV electronic spin. Right: Energy levels of the coupled ^{13}C spins in the $|0_e\rangle$ state. $|T\rangle$ and $|S\rangle$ denote the triplet and singlet states, respectively. The double arrow shows the transition that is detected experimentally. The transition to the singlet state is forbidden by selection rules. (b) Trace (i): ODNMR spectrum in the 340–460 kHz range, showing the coupled homo- and heteronuclear couplings between the ^{13}C spins. The bottom curve (ii) was obtained by lowering the RF signal by 10 dB. Trace (i) and (ii) have been offset for clarity.

with potential applications in quantum information processing and quantum metrology [4,39–41]. Such coupled spins are expected to exhibit eigenfrequencies distinct from those of uncoupled nuclei [4,39] and allow access to first-order magnetic field insensitive transitions [42].

Predictions about the frequencies of the transition of coupled pairs can be performed by diagonalizing numerically the Hamiltonian

$$\frac{H}{\hbar} = DS_z^2 + \gamma_e \mathbf{S} \cdot \mathbf{B} + \gamma_n (\mathbf{I}_1 + \mathbf{I}_2) \cdot \mathbf{B} + \mathbf{S} \cdot \underline{\mathbf{A}}_1 \cdot \mathbf{I}_1 + \mathbf{S} \cdot \underline{\mathbf{A}}_2 \cdot \mathbf{I}_2. \quad (8)$$

Here, $\mathbf{I}_{1,2}$ denote the nuclear spin operators, and $\underline{\mathbf{A}}_{1,2}$ are the hyperfine tensors describing the interaction of nuclear spins 1 and 2 with the electronic spin $\mathbf{S}$ of the same NV center. The values of $\underline{\mathbf{A}}_{1,2}$ are taken from Table III. The frequency difference between the transitions of two coupled ^{13}C and uncoupled ^{13}C in the $|\pm 1_e\rangle$ states was found to be too small to be detectable are thus not listed.

In the case of two ^{13}C nuclei that are coupled identically to the NV centers with a positive A_{zz} component, the four

TABLE IV. Theoretical predictions and experimental observations for transitions between the ground and triplet states in the ^{13}C spin pairs (in kHz) for homo- and heteronuclear pairs in the $|0_e\rangle$ state of the NV center.

Intrafamily transitions frequencies (kHz)		
Pair	Theory	Experiment
A-A	359.2(1)	360.1(3)
B-B	391.2(1)	392.0(6)
C-C	455.5(1)	452.2(4)
D-D	504.7(1)	
Interfamily transitions frequencies (kHz)		
A-B	375.1(1)	376.2(6)
A-C	409.0(1)	412.9(3)
A-D	449.3(1)	452.2(4)
B-C	422.5(1)	426.8(2)
B-D	460.4(1)	462.1(7)

eigenstates in the coupled basis are given by

$$\begin{aligned} |g\rangle &= \left| +\frac{1}{2}, +\frac{1}{2} \right\rangle, \\ |T\rangle &= \frac{1}{\sqrt{2}} \left(\left| +\frac{1}{2}, -\frac{1}{2} \right\rangle + \left| -\frac{1}{2}, +\frac{1}{2} \right\rangle \right), \\ |S\rangle &= \frac{1}{\sqrt{2}} \left(\left| +\frac{1}{2}, -\frac{1}{2} \right\rangle - \left| -\frac{1}{2}, +\frac{1}{2} \right\rangle \right), \\ |e\rangle &= \left| -\frac{1}{2}, -\frac{1}{2} \right\rangle. \end{aligned} \quad (9)$$

For pairs of inequivalent ^{13}C nuclei, however, the states $|T\rangle$ and $|S\rangle$ are no longer perfectly symmetric and antisymmetric, due to their different hyperfine couplings to the NV center.

Importantly, the transition $|g\rangle \rightarrow |T\rangle$ is allowed whereas transitions to the singlet state are RF forbidden by selection rules as shown in Fig. 10(a). Numerical simulations of the $|g\rangle \rightarrow |T\rangle$ transition frequencies for all possible pairs of strongly coupled ^{13}C spins in the $|0_e\rangle$ states are listed in the Table IV.

The number of clusters of spins around each NV under the laser focal spot is calculated in Sec. IX of the Supplemental Material [20]. It is shown that there is a ratio of 1/10 between double occupancy and single occupancy of ^{13}C nuclear spins close to NV centers in our sample. Such pairs should thus be detectable in about an hour with our setup. Figure 10(b) shows two scans taken in the region where such transitions between the $|g\rangle$ and triplet states $|T\rangle$ are expected. Most of the transitions are indeed observed, and reported in Table IV, showing good agreement with theoretical modeling. Further experiments are planned to investigate the coherence of these coupled spin pairs. At present, our sensitivity is insufficient to perform spin-echo measurements on such weak signals.

VI. CONCLUSION

In conclusion, we perform high-sensitivity detection of nuclear spins in a CVD-grown diamond crystal under modest magnetic fields at room temperature. The identification of

nuclear spin environments around ensembles of NV center lays the groundwork for further dynamical control of the state of nuclear spins families, opening up the possibility to test and optimize various polarization transfer protocols with ^{13}C spins that are currently only accessible using high-field NMR, even at the single-spin level. This includes coherent population trapping [43–46], pulse-pol [12], and adiabatic sweeps techniques [11,13], which are central for improving spin initialization and readout in diamond-based quantum sensors. Another promising avenue arises from the temperature-dependent variations observed in all spectral features [47–49], which provide a means to investigate the spin-phonon interactions of the newly detected clusters with high precision.

Importantly, our results are relevant in the context of gyroscopy. Nuclear spins have been proposed as promising candidates for the next generation of compact and precise gyroscopes [5,6,50]. While the gyroscopic signal associated with ^{13}C nuclear spin precession could in principle be enhanced

using ^{13}C -enriched samples, our findings suggest that additional experimental and theoretical efforts will be required to fully assess the feasibility and ultimate performance of such implementations, particularly in comparison with established ^{14}N -based approaches [7,51].

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DATA AVAILABILITY

The data that support the findings of this article are not publicly available. The data are available from the authors upon reasonable request.

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- [1] M. H. Appel, A. Ghorbal, N. Shofer, L. Zaporski, S. Manna, S. F. C. da Silva, U. Haeusler, C. Le Gall, A. Rastelli, D. A. Gangloff, and M. Atatüre, Many-body quantum register for a spin qubit, *Nat. Phys.* **21**, 368 (2024).
 - [2] J. C. Marcks, B. Pingault, J. Zhang, C. Zeledon, F. J. Heremans, and D. D. Awschalom, Nuclear spin engineering for quantum information science, *J. Mater. Res.* **40**, 1433 (2025).
 - [3] J. Kenny, F. Zhou, R. He, F. Jelezko, T. S. Koh, and W. Gao, Quantum sensing enhancement through a nuclear spin register in nitrogen-vacancy centers in diamond, *Appl. Phys. Rev.* **12**, 021323 (2025).
 - [4] C. E. Bradley, J. Randall, M. H. Abobeih, R. C. Berrevoets, M. J. Degen, M. A. Bakker, M. Markham, D. J. Twitchen, and T. H. Taminiau, A ten-qubit solid-state spin register with quantum memory up to one minute, *Phys. Rev. X* **9**, 031045 (2019).
 - [5] M. P. Ledbetter, K. Jensen, R. Fischer, A. Jarmola, and D. Budker, Gyroscopes based on nitrogen-vacancy centers in diamond, *Phys. Rev. A* **86**, 052116 (2012).
 - [6] A. Ajoy and P. Cappellaro, Stable three-axis nuclear-spin gyroscope in diamond, *Phys. Rev. A* **86**, 062104 (2012).
 - [7] A. Jarmola, S. Lourette, V. M. Acosta, A. G. Birdwell, P. Blümler, D. Budker, T. Ivanov, and V. S. Malinovsky, Demonstration of diamond nuclear spin gyroscope, *Sci. Adv.* **7**, eabl3840 (2021).
 - [8] J. Smits, J. T. Damron, P. Kehayias, A. F. McDowell, N. Mosavian, I. Fescenko, N. Ristoff, A. Laraoui, A. Jarmola, and V. M. Acosta, Two-dimensional nuclear magnetic resonance spectroscopy with a microfluidic diamond quantum sensor, *Sci. Adv.* **5**, eaaw7895 (2019).
 - [9] J.-P. Tetienne, L. T. Hall, A. J. Healey, G. A. L. White, M.-A. Sani, F. Separovic, and L. C. L. Hollenberg, Prospects for nuclear spin hyperpolarization of molecular samples using nitrogen-vacancy centers in diamond, *Phys. Rev. B* **103**, 014434 (2021).
 - [10] R. Budakian *et al.*, Roadmap on nanoscale magnetic resonance imaging, *Nanotechnology* **35**, 412001 (2024).
 - [11] A. Ajoy *et al.*, Room-temperature optical ^{13}C hyperpolarization in powdered diamond, *Sci. Adv.* **4**, eaar5492 (2018).
 - [12] J. Scheuer, I. Schwartz, S. Müller, Q. Chen, I. Dhand, M. B. Plenio, B. Naydenov, and F. Jelezko, Robust techniques for polarization and detection of nuclear spin ensembles, *Phys. Rev. B* **96**, 174436 (2017).
 - [13] J. Henshaw, D. Pagliero, P. R. Zangara, M. B. Franzoni, A. Ajoy, R. H. Acosta, J. A. Reimer, A. Pines, and C. A. Meriles, Carbon-13 dynamic nuclear polarization in diamond via a microwave-free integrated cross effect, *Proc. Natl. Acad. Sci. USA* **116**, 18334 (2019).
 - [14] R. Blinder, Y. Mindarava, M. Korzeczek, A. Marshall, F. Glöckler, S. Nothelfer, A. Kienle, C. Laube, W. Knolle, C. Jentgens, M. B. Plenio, and F. Jelezko, ^{13}C hyperpolarization with nitrogen-vacancy centers in micro- and nanodiamonds for sensitive magnetic resonance applications, *Sci. Adv.* **11**, eadq6836 (2025).
 - [15] B. Smeltzer, J. McIntyre, and L. Childress, Robust control of individual nuclear spins in diamond, *Phys. Rev. A* **80**, 050302(R) (2009).
 - [16] M. Steiner, P. Neumann, J. Beck, F. Jelezko, and J. Wrachtrup, Universal enhancement of the optical readout fidelity of single electron spins at nitrogen-vacancy centers in diamond, *Phys. Rev. B* **81**, 035205 (2010).
 - [17] A. Jarmola, I. Fescenko, V. M. Acosta, M. W. Doherty, F. K. Fatemi, T. Ivanov, D. Budker, and V. S. Malinovsky, Robust optical readout and characterization of nuclear spin transitions in nitrogen-vacancy ensembles in diamond, *Phys. Rev. Res.* **2**, 023094 (2020).
 - [18] L. Childress, M. V. G. Dutt, J. M. Taylor, A. S. Zibrov, F. Jelezko, J. Wrachtrup, P. R. Hemmer, and M. D. Lukin, Coherent dynamics of coupled electron and nuclear spin qubits in diamond, *Science* **314**, 281 (2006).
 - [19] A. Dréau, J.-R. Maze, M. Lesik, J.-F. Roch, and V. Jacques, High-resolution spectroscopy of single NV defects coupled with nearby ^{13}C nuclear spins in diamond, *Phys. Rev. B* **85**, 134107 (2012).

- [20] See Supplemental Material at <http://link.aps.org/supplemental/10.1103/g88t-fddb> for theoretical predictions and further experimental details, which includes Refs. [52–56].
- [21] B. Smeltzer, L. Childless, and A. Gali, ^{13}C hyperfine interactions in the nitrogen-vacancy centre in diamond, *New J. Phys.* **13** 025021 (2011).
- [22] M. W. Doherty, N. B. Manson, P. Delaney, F. Jelezko, J. Wrachtrup, and L. C. Hollenberg, The nitrogen-vacancy colour centre in diamond, *Phys. Rep.* **528**, 1 (2013).
- [23] V. Jacques, P. Neumann, J. Beck, M. Markham, D. Twitchen, J. Meijer, F. Kaiser, G. Balasubramanian, F. Jelezko, and J. Wrachtrup, Dynamic polarization of single nuclear spins by optical pumping of nitrogen-vacancy color centers in diamond at room temperature, *Phys. Rev. Lett.* **102**, 057403 (2009).
- [24] R. Fischer, A. Jarmola, P. Kehayias, and D. Budker, Optical polarization of nuclear ensembles in diamond, *Phys. Rev. B* **87**, 125207 (2013).
- [25] A. Schweiger and G. Jeschke, *Principles of Pulse Electron Paramagnetic Resonance* (Oxford Academic, Oxford, 2023).
- [26] S. Lourette, A. Jarmola, V. M. Acosta, A. G. Birdwell, D. Budker, M. W. Doherty, T. Ivanov, and V. S. Malinovsky, Temperature sensitivity of ^{14}N -V and ^{15}N -V ground-state manifolds, *Phys. Rev. Appl.* **19**, 064084 (2023).
- [27] S. Felton, A. M. Edmonds, M. E. Newton, P. M. Martineau, D. Fisher, and D. J. Twitchen, Electron paramagnetic resonance studies of the neutral nitrogen vacancy in diamond, *Phys. Rev. B* **77**, 081201(R) (2008).
- [28] L. Razinkovas, M. Maciaszek, F. Reinhard, M. W. Doherty, and A. Alkauskas, Photoionization of negatively charged NV centers in diamond: Theory and *ab initio* calculations, *Phys. Rev. B* **104**, 235301 (2021).
- [29] M. Pfender, N. Aslam, P. Simon, D. Antonov, G. Thiering, S. Burk, F. F. de Oliveira, A. Denisenko, H. Fedder, J. Meijer, J. A. Garrido, A. Gali, T. Teraji, J. Isoya, M. W. Doherty, A. Alkauskas, A. Gallo, A. Grüneis, P. Neumann, and J. Wrachtrup, Protecting a diamond quantum memory by charge state control, *Nano Lett.* **17**, 5931 (2017).
- [30] G. Waldherr, J. Beck, M. Steiner, P. Neumann, A. Gali, T. Frauenheim, F. Jelezko, and J. Wrachtrup, Dark states of single nitrogen-vacancy centers in diamond unraveled by single shot NMR, *Phys. Rev. Lett.* **106**, 157601 (2011).
- [31] P. Siyushev, H. Pinto, M. Vörös, A. Gali, F. Jelezko, and J. Wrachtrup, Optically controlled switching of the charge state of a single nitrogen-vacancy center in diamond at cryogenic temperatures, *Phys. Rev. Lett.* **110**, 167402 (2013).
- [32] S. Sangtawesin, C. A. McLellan, B. A. Myers, A. C. Bleszynski Jayich, D. D. Awschalom, and J. R. Petta, Hyperfine-enhanced gyromagnetic ratio of a nuclear spin in diamond, *New J. Phys.* **18**, 083016 (2016).
- [33] M. Chen, M. Hirose, and P. Cappellaro, Measurement of transverse hyperfine interaction by forbidden transitions, *Phys. Rev. B* **92**, 020101(R) (2015).
- [34] H. Duarte, H. T. Dinani, V. Jacques, and J. R. Maze, Effect of intersystem crossing rates and optical illumination on the polarization of nuclear spins close to nitrogen-vacancy centers, *Phys. Rev. B* **103**, 195443 (2021).
- [35] A. Gali, Identification of individual ^{13}C isotopes of nitrogen-vacancy center in diamond by combining the polarization studies of nuclear spins and first-principles calculations, *Phys. Rev. B* **80**, 241204(R) (2009).
- [36] V. Ivády, K. Szász, A. L. Falk, P. V. Klimov, D. J. Christle, E. Janzén, I. A. Abrikosov, D. D. Awschalom, and A. Gali, Theoretical model of dynamic spin polarization of nuclei coupled to paramagnetic point defects in diamond and silicon carbide, *Phys. Rev. B* **92**, 115206 (2015).
- [37] I. Takács and V. Ivády, Accurate hyperfine tensors for solid state quantum applications: Case of the NV center in diamond, *Commun. Phys.* **7**, 178 (2024).
- [38] B. Bürgler, T. F. Sjolander, O. Brinza, A. Tallaire, J. Achard, and P. Maletinsky, All-optical nuclear quantum sensing using nitrogen-vacancy centers in diamond, *npj Quantum Inf.* **9**, 56 (2023).
- [39] T. H. Taminiau, J. Cramer, T. van der Sar, V. V. Dobrovitski, and R. Hanson, Universal control and error correction in multi-qubit spin registers in diamond, *Nat. Nanotechnol.* **9**, 171 (2014).
- [40] F. Shi, X. Kong, P. Wang, F. Kong, N. Zhao, R.-B. Liu, and J. Du, Sensing and atomic-scale structure analysis of single nuclear-spin clusters in diamond, *Nat. Phys.* **10**, 21 (2014).
- [41] K. Herb, T. F. Segawa, L. A. Völker, J. M. Abendroth, E. Janitz, T. Zhu, and C. L. Degen, Multidimensional spectroscopy of nuclear spin clusters in diamond, *Phys. Rev. Lett.* **132**, 133002 (2024).
- [42] H. P. Bartling, M. H. Abobeih, B. Pingault, M. J. Degen, S. J. H. Loenen, C. E. Bradley, J. Randall, M. Markham, D. J. Twitchen, and T. H. Taminiau, Entanglement of spin-pair qubits with intrinsic dephasing times exceeding a minute, *Phys. Rev. X* **12**, 011048 (2022).
- [43] L. Nicolas, T. Delord, P. Jamonneau, R. Coto, J. Maze, V. Jacques, and G. Hétet, Coherent population trapping with a controlled dissipation: Applications in optical metrology, *New J. Phys.* **20**, 033007 (2018).
- [44] P. Jamonneau, G. Hétet, A. Dréau, J.-F. Roch, and V. Jacques, Coherent population trapping of a single nuclear spin under ambient conditions, *Phys. Rev. Lett.* **116**, 043603 (2016).
- [45] P. Jamonneau, A. Dréau, G. Hétet, J. F. Roch, J. R. Maze, and V. Jacques, Room-temperature polarization of individual nuclear spins in diamond via anisotropic hyperfine coupling and coherent population trapping, *Eur. Phys. J. D* **76**, 228 (2022).
- [46] P. Huillery, J. Leibold, T. Delord, L. Nicolas, J. Achard, A. Tallaire, and G. Hétet, Coherent microwave control of a nuclear spin ensemble at room temperature, *Phys. Rev. B* **103**, L140102 (2021).
- [47] S. Xu, M. Liu, T. Xie, Z. Zhao, Q. Shi, P. Yu, C.-K. Duan, F. Shi, and J. Du, High-precision measurements and first-principles explanation of the temperature-dependent ^{13}C and ^{14}N hyperfine interactions of single NV^- centers in diamond at room temperature, *Phys. Rev. B* **107**, L140101 (2023).
- [48] V. V. Soshenko, V. V. Vorobyov, S. V. Bolshedvorski, O. Rubinas, I. Cojocar, B. Kudlatsky, A. I. Zeleneev, V. N. Sorokin, A. N. Smolyaninov, and A. V. Akimov, Temperature drift rate for nuclear terms of the NV-center ground-state Hamiltonian, *Phys. Rev. B* **102**, 125133 (2020).
- [49] M. S. J. Barson, P. Reddy, S. Yang, N. B. Manson, J. Wrachtrup, and M. W. Doherty, Temperature dependence of the ^{13}C hyperfine structure of the negatively charged nitrogen-vacancy center in diamond, *Phys. Rev. B* **99**, 094101 (2019).
- [50] H. Wang, S. Wu, K. Jacobs, Y. Duan, D. R. Englund, and M. E. Trusheim, Cavity-enhanced solid-state

- nuclear spin gyroscope, *Phys. Rev. Lett.* **134**, 183603 (2025).
- [51] V. V. Soshenko, S. V. Bolshedvorskii, O. Rubinas, V. N. Sorokin, A. N. Smolyaninov, V. V. Vorobyov, and A. V. Akimov, Nuclear spin gyroscope based on the nitrogen vacancy center in diamond, *Phys. Rev. Lett.* **126**, 197702 (2021).
- [52] C. Findler, R. Blinder, K. Schüle, P. Balasubramanian, C. Osterkamp, and F. Jelezko, Detecting nitrogen-vacancy-hydrogen centers on the nanoscale using nitrogen-vacancy centers in diamond, *Phys. Rev. Mater.* **8**, 026203 (2024).
- [53] C. Pellet-Mary, M. Perdriat, P. Huillery, and G. Hétet, Relaxation processes in dipole-coupled nitrogen-vacancy centers in zero field: Application in magnetometry, *Phys. Rev. Appl.* **20**, 034050 (2023).
- [54] D. Pagliero, K. R. K. Rao, P. R. Zangara, S. Dhomkar, H. H. Wong, A. Abril, N. Aslam, A. Parker, J. King, C. E. Avalos, A. Ajoy, J. Wrachtrup, A. Pines, and C. A. Meriles, Multispin-assisted optical pumping of bulk ^{13}C nuclear spin polarization in diamond, *Phys. Rev. B* **97**, 024422 (2018).
- [55] R. Wunderlich, J. Kohlrautz, B. Abel, J. Haase, and J. Meijer, Optically induced cross relaxation via nitrogen-related defects for bulk diamond ^{13}C hyperpolarization, *Phys. Rev. B* **96**, 220407(R) (2017).
- [56] D. Shimon, K. A. Cantwell, L. Joseph, E. Q. Williams, Z. Peng, S. Takahashi, and C. Ramanathan, Large room temperature bulk DNP of ^{13}C via P1 centers in diamond, *J. Phys. Chem. C* **126**, 17777 (2022).