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# Theoretical study of hyperfine interactions and optically detected magnetic resonance spectra by simulation of the $C_{291}[NV]^-H_{172}$ diamond cluster hosting nitrogen-vacancy center

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#### Abstract

Single nitrogen-vacancy (NV) centers in diamond coupled to neighboring nuclear spins are promising candidates for room-temperature applications in quantum information processing, quantum sensing and metrology. Here we report on a systematic density functional theory simulation of hyperfine coupling of the electronic spin of the NV center to individual <sup>13</sup>C nuclear spins arbitrarily disposed in the H-terminated  $C_{291}[NV]^{-}H_{172}$  cluster hosting the NV center. For the 'families' of equivalent positions of the <sup>13</sup>C atom in diamond lattices around the NV center we calculated hyperfine characteristics. For the first time the data are given for a system where the <sup>13</sup>C atom is located on the NV center symmetry axis. Electron paramagnetic resonance transitions in the coupled electron–nuclear spin system <sup>14</sup>NV-<sup>13</sup>C are analyzed as a function of the external magnetic field. Previously reported experimental data from Dréau *et al* (2012 *Phys. Rev.* B **85** 134107) are described using simulated hyperfine coupling parameters.

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#### 1. Introduction

The ability to create, control and measure coherence in multi-spin systems in solids is crucial for scalable applications of quantum information processing, quantum sensing and metrology. Coupled electron–nuclear spin systems where electrons act as fast processing qubits and, additionally, form an interface with photons, while nuclei can store quantum information for a long time owing to their exceptional isolation from the environment, are especially useful for these purposes.

The negatively charged nitrogen-vacancy (NV) color center in diamond (see, e.g. [1–4] for reviews) provides a unique opportunity to realize such a hybrid quantum register in a solid. Its ground-state electron spin (e-spin) S = 1 is coupled to the nuclear spin (n-spin)  $I^{(N)} = 1$  of its own <sup>14</sup>N atom and, potentially, to nearby n-spins  $I^{(C)} = 1/2$  of isotopic <sup>13</sup>C atoms that are distributed randomly in the diamond lattice substituting spinless <sup>12</sup>C atoms with 1.1% probability. A remarkable property of the NV center is its spin-projection-dependent triplet-singlet electronic transitions that allow one to initialize and read out the e-spin magnetic state using optical excitation [1, 5, 6]. Moreover, it exhibits a long coherence time ( $T_2 \sim a$  few ms [7–9] in isotopically purified diamond) at room temperature and can be coherently manipulated with high fidelity by microwaves [1] to implement one-qubit quantum gates. Hyperfine coupling of the e-spin to nearby n-spins leads directly to few-qubit gates which can be realized using a sequence of optical, microwave or radio frequency pulses to initialize, coherently manipulate and read out the electron-nuclear spin system states [10-21]. Initial work [11] was done on single NV centers strongly coupled to a <sup>13</sup>C n-spin located in one of three lattice sites being nearest neighbors (NN) to the vacancy of the NV center. Later [12-15, 18]. sensing of more distant <sup>13</sup>C nuclear spins located in the third coordination sphere of the vacancy was realized. Most recently the use of dynamical decoupling methods (see, e.g. [24, 25]) to suppress unwanted background spin noise has enabled detection of much more distant <sup>13</sup>C nuclear spins [26-30] followed by observation of nuclear spin dimers [31, 32]. The prospects of using such multi-e-n-spin systems to, for instance, implement a few-qubit quantum register [10–17, 21, 33–40], quantum repeater [41, 42] and quantum memory [12–14, 43–45], perform quantum algorithms or single-shot readout of both nuclear and electronic spins [15, 16, 19–23]. or realize entanglement-based sensitivity enhancement of single-spin quantum magnetometry and metrology [46–53], require full understanding of their spin properties and of hyperfine interactions in such systems. Additionally, these data are useful for developing deeper insight into the decoherence mechanisms of the NV center e-spin in the <sup>13</sup>C n-spin bath [18, 34, 54–62].

Along with experimental characterization of hyperfine interactions (HFIs) in different NV-<sup>13</sup>C spin systems, a complementary approach to getting the desired information is provided by quantum chemistry modeling, which has been shown [26, 35–37, 63–67] to be effective in calculating the characteristics of hyperfine interactions of NV centers with surrounding nuclear spins. In earlier works [63, 64] this was done using rather small supercells [63] and H-terminated carbon clusters [64] hosting the NV centers, while subsequent works, in which larger 512-atom supercells [65, 66] and  $C_{84}$ [NV]<sup>-</sup>H<sub>78</sub> clusters [35–37] were studied, were focused on the simulation of HFI characteristics for NV-<sup>13</sup>C spin systems wherein the <sup>13</sup>C atom

was located quite close to the NV center vacancy (in the first or third coordination sphere of the center) because these spin systems were being actively investigated experimentally at that time. Here, for the above reasons, we will mainly pay attention to the systematic computational chemistry simulation of HFI characteristics for NV-<sup>13</sup>C spin systems involving more distant <sup>13</sup>C nuclear spins. For this purpose, we will use the much larger NV-hosting H-terminated carbon cluster  $C_{291}[NV]^{-}H_{172}$  and calculate the  $A_{KL}^{(C)}$  matrices describing HFIs between the e-spin of a single NV center and <sup>13</sup>C n-spins taking all possible positions in the cluster. Further, the calculated HFI matrices are used in the ground-NV-state spin Hamiltonian of the NV center to simulate the signatures of these HFIs in optically detected magnetic resonance (ODMR) spectra of an arbitrary <sup>14</sup>NV-<sup>13</sup>C spin system. Numerical diagonalization of respective spin Hamiltonians are accompanied by simplified analytical consideration within the secular approximation. We also show how calculated HFI characteristics correlate with spatial positions of <sup>13</sup>C nuclei in the cluster. The HFI characteristics are presented for the 'families' [26, 27] of equivalent positions of the <sup>13</sup>C atom in the diamond lattice around the NV center. The effect of external magnetic field on the rates of 'allowed' and 'forbidden' EPR transitions in an arbitrary <sup>14</sup>NV-<sup>13</sup>C three-spin system is studied and shown to be different in the  $m_S = 0 \leftrightarrow m_S = -1$  and the  $m_S = 0 \leftrightarrow m_S = +1$  manifolds depending on the sign of the HFI matrix element  $A_{ZZ}^{(C)}$ . General consideration is illustrated by detailed analysis of the experimental data presented in the work [27].

#### 2. Model and methods

To model the NV center in bulk- or nano-sized diamond we chose the diamond cluster  $C_{291}[NV]$ <sup>-</sup>H<sub>172</sub> (figure 1(a)) which was constructed from a piece of ideal diamond lattice by removing one C atom in its central part, substituting the neighboring C atom with the N atom and saturating the surface C atoms' dangling bonds with H atoms. With the available computer resources the size of this cluster was optimal to ensure simulation of HFI characteristics for rather distant <sup>13</sup>C nuclear spins, in particular, for those disposed on the NV axis.

The geometric structure of the studied  $C_{291}[NV]^-H_{172}$  cluster was optimized by the total energy minimization using the density functional theory (DFT) method with the B3LYP hybrid functional [68, 69] and the MINI basis set [70]. In the cluster, atomic relaxation of the diamond lattice around the formed NV center results in increased distances between the three C atoms that are NNs of the vacancy (from 2.527 Å to 2.649 Å) and between these atoms and the N atom (from 2.527 Å to 2.764 Å), while the distances from the N atom to the three nearest C atoms are reduced from 1.547 Å to 1.512 Å. For the other C atoms in the relaxed cluster the C–C bond lengths range from 1.55 to 1.59 Å. These bond lengths reflect the overestimated bulk bond length obtained at this level of theory [71].

For the relaxed cluster the spin density distribution was calculated using the same method and the 3–21G basis set [72]. Calculations have been performed for singly negatively charged clusters in the triplet ground state (S = 1) using the unrestricted Kohn–Sham (UKS) procedure for open shell structures. We have used the PC GAMESS (US) software package [73] for geometry optimization of the cluster and the ORCA software package [74] to calculate the spin characteristics, in particular for full HFI matrices  $A_k^{(C)}$  for all possible positions  $k = 1 \div 291$  of the <sup>13</sup>C atom in the cluster. These calculations have been done in the principle axes system (PAS) of the NV center where the *z*-axis coincides with the C<sub>3V</sub> symmetry axis of the center



**Figure 1.** (a) Illustration of the simulated  $C_{291}[NV]^-H_{172}$  cluster hosting the e-spin of the NV center disposed in the central part and the n-spin of the nucleus <sup>13</sup>C located somewhere in the cluster, (b) simulated ODMR spectrum of the exemplary <sup>14</sup>NV-<sup>13</sup>C three-spin system, having the <sup>13</sup>C atom located on the NV symmetry axis and exhibiting the six-line hyperfine structure of the  $m_S = 0 \leftrightarrow m_S = -1$  transition in the presence of the magnetic field BllOZ = 50 gauss, (c) energy levels of the typical <sup>14</sup>NV-<sup>13</sup>C system in low external magnetic field Bll OZ numerated from 1 to 18 in accordance with the increase in their energy and transitions between them (right part) shown along with simplified fine-structure energy levels of the NV center without and with external magnetic field Bl.

while the *x*- and *y*-axes are chosen arbitrarily. Various <sup>13</sup>C lattice sites exhibit different and generally anisotropic hyperfine interactions with the NV e-spin, leading to different spin (and optically detected) properties of various NV-<sup>13</sup>C spin systems. The calculated HFI  $A_k^{(C)}$  matrices can be converted into their respective diagonal ones  $\tilde{A}_k^{(C)} = U_k^{-1}A_k^{(C)}U_k$  by unitary transformations  $U_k$  from the NV PAS to the <sup>13</sup>C PAS with elements of the  $U_k$  matrix being the direction cosines between various axes of both PASs.

In this article we are going to present not only the results of our calculations of the HFI matrices  $A_k^{(C)}$  for all possible positions of the <sup>13</sup>C atom in the studied cluster, but also show how DFT calculations can be employed for the quantitative description of experimental data. Here we will focus on ground-state ODMR spectra of different <sup>14</sup>NV-<sup>13</sup>C spin systems. To model the NV center we introduce the standard spin Hamiltonian  $H_k$  of an arbitrary <sup>14</sup>NV-<sup>13</sup>C system

comprising the e-spin S = 1 of the ground-state NV center coupled to the internal n-spin  $I^{(N)} = 1$  of the <sup>14</sup>N atom of the center (<sup>14</sup>N is the most common nitrogen isotope having 99.63% natural abundance) and to the additional n-spin  $I_k^{(C)} = 1/2$  of a <sup>13</sup>C atom disposed in the *k*th lattice position in the cluster. These spin Hamiltonians are of the form

$$H_k = H_0^{(NV)} + \mathbf{S} \cdot A_k^{(C)} \cdot \mathbf{I}_k^{(C)} + \beta_e g^{(NV)} \mathbf{S} \cdot \mathbf{B} - \beta_n g^{(N)} \mathbf{I}^{(N)} \cdot \mathbf{B} - \beta_n g^{(C)} \mathbf{I}_k^{(C)} \cdot \mathbf{B}.$$
(1)

Here the first term is the common zero-field spin Hamiltonian of the ground-state NV center

$$H_0^{(NV)} = D\left[S_Z^2 - S(S+1)/3\right] + S \cdot A^{(N)} \cdot I^{(N)} + Q\left[\left(I_Z^{(N)}\right)^2 - I^{(N)}\left(I^{(N)} + 1\right)/3\right],$$
(2)

taking into account the zero-field splitting of the  $m_S = 0$  and  $m_S = \pm 1$  e-spin substates due to dipole–dipole interaction of two unpaired electrons of the center (D=2870 MHz [74]), the intrinsic HFI within the center [75–77] ( $A^{(N)}$  is the tensor of HFI between S and  $I^{(N)}$  spins, being diagonal with elements  $A_{XX}^{(N)} = A_{YY}^{(N)} = -2.14$  MHz and  $A_{ZZ}^{(N)} = -2.70$  MHz [75] in the NV PAS) and the quadrupole moment of the 14N nucleus (Q=-5.01 MHz [73]). The second term in (1) accounts for the HFI between S and  $I_k^{(C)}$  spins described by the matrix  $A_k^{(C)}$  which in the general case is not diagonal in the NV PAS. Finally, the last three terms in (1) describe interactions of the three spins S,  $I^{(N)}$  and  $I_k^{(C)}$  with external magnetic field B( $\beta_e = 1.399$  64 MHz G<sup>-1</sup> and  $\beta_n = 0.76226$  kHz G<sup>-1</sup> are the Bohr and the nuclear magnetons,  $g^{(NV)} = 2.0028$ ,  $g^{(N)} = 0.4037607$  and  $g^{(C)} = 1.40483$  are the NV center, <sup>14</sup>N and <sup>13</sup>C g-factors, respectively [78, 79]).

The dimensionality of the Hilbert space of the Hamiltonian (1) is  $(2S + 1)(2I^{(N)} + 1)(2I^{(C)} + 1) = 18$ . Its diagonalization provides 18 energies  $E_{\alpha}$  of the threespin system (at B=0 some of them can be degenerated) and coefficients  $c_{\alpha}^{m_s, m_I^{(N)}, m_I^{(C)}}$  in respective spin wave-functions  $|\Psi_{\alpha}\rangle$  presented as the decomposition

$$\left|\Psi_{\alpha}\right\rangle = \sum_{m_{S}=-S}^{S} \sum_{m_{I}^{(N)}=-I}^{I^{(N)}} \sum_{m_{I}^{(C)}=-I^{(C)}}^{I} c_{\alpha}^{m_{S}, m_{I}^{(N)}, m_{I}^{(C)}} \left|m_{S}, m_{I}^{(N)}, m_{I}^{(C)}\right\rangle,$$
(3)

over the basis formed by the spin states  $|m_S, m_I^{(N)}, m_I^{(C)}\rangle$  corresponding to the magnetic quantum numbers  $m_S$  and  $m_I^{(N)}, m_I^{(C)}$  of the e-spin and n-spin projections to the z-axis. Having these eigenenergies and eigenstates one can find frequencies  $\omega_{\alpha\beta}$  and matrix elements  $\mu_{\alpha\beta}$  of possible EPR and NMR transitions within the considered <sup>14</sup>NV-<sup>13</sup>C spin systems and further simulate ODMR spectra replacing delta-shaped lines  $|\mu_{\alpha\beta}|^2 \delta(\omega - \omega_{\alpha\beta})$  on the Lorentzians  $|\mu_{\alpha\beta}|^2 \Gamma/\pi/[(\omega - \omega_{\alpha\beta})^2 + \Gamma^2]$  of equal area and using the halfwidth  $\Gamma$  as a fitting parameter.

#### 3. Arbitrary <sup>14</sup>NV-<sup>13</sup>C spin system: analytical consideration in the secular approximation

#### 3.1. ODMR spectra, energy levels and eigenstates

Typical HFI structure of an ODMR spectrum of an arbitrary <sup>14</sup>NV-<sup>13</sup>C system in low magnetic field is shown in figure 1(b) for the case of rather distant <sup>13</sup>C n-spin for which the HFI with the NV center e-spin is weaker than that with the <sup>14</sup>N n-spin. Both  $m_S = 0 \leftrightarrow m_S = -1$  and  $m_S = 0 \leftrightarrow m_S = +1$  manifolds of the spectrum exhibit three characteristic pairs of lines corresponding to possible EPR transitions in the system with their frequencies determined by

the HFI with both <sup>14</sup>N and <sup>13</sup>C n-spins, and also by the interaction of these spins with the external magnetic field. Note that the respective ODMR spectrum of the <sup>14</sup>NV center, having no nearby <sup>13</sup>C n-spin, consisted of just three lines with HFI splitting of ~2.16 MHz between them [75–77]. It is the HFI with additional distant <sup>13</sup>C n-spin splitting each of these three lines into pairs of lines, with each pair corresponding to definite projection  $m_I^{(N)} = -1$ , 0, 1 of the <sup>14</sup>N n-spin, as shown in figure 1(c).

In many practical cases (excluding those at  $B \sim 1027$  gauss where avoided-crossing of sublevels with  $m_S = 0$  and  $m_S = -1$  takes place) good approximation for energy levels, eigenstates and transition rates for the <sup>14</sup>NV-<sup>13</sup>C spin system is provided by the secular approximation where only the terms with  $S_Z$  are kept in the Hamiltonian (1). In particular, using the approximation one can find that, at fixed  $m_I^{(N)}$  projection (for definiteness, we choose here the case  $m_I^{(N)} = +1$  [19] and use below the state numeration adopted in figure 1(c)), the energy levels of an arbitrary three-spin system <sup>14</sup>NV-<sup>13</sup>C in a magnetic field B, aligned along the z-axis, are

$$E_{13,14} \simeq D/3 + \gamma_e^{(NV)} B \pm \Delta^+/2 \quad (m_S = +1),$$
  

$$E_{9,10} \simeq D/3 - \gamma_e^{(NV)} B \pm \Delta^-/2, \quad (m_S = -1),$$
  

$$E_{1,3} \simeq -2D/3 \pm \gamma_n^{(C)} B/2, \quad (m_S = 0),$$
(4)

where  $\Delta^{\pm} = \sqrt{A_{nd}^2 + (A_{ZZ} \mp \gamma_n^{(C)} B)^2}$ ,  $A_{nd}^2 = A_{ZX}^2 + A_{ZY}^2$  and  $\gamma_e^{(NV)} = \beta_e g^{(NV)} = 2.803 \text{ MHz/}$ gauss and  $\gamma_n^{(C)} = \beta_n g^{(C)} = 1.071 \text{ kHz/gauss}$  are the NV center e-spin and <sup>13</sup>C n-spin gyromagnetic ratios. It follows from (4) that the splitting of the substates 1 and 3 in the  $m_S = 0$  manifold is only due to the Zeeman effect on the <sup>13</sup>C n-spin:  $E_3 - E_1 = \delta = \gamma_n^{(C)} B$ , while those for the  $m_S = \pm 1$  substates  $(E_{10} - E_9 = \Delta^- \text{ and } E_{14} - E_{13} = \Delta^+)$  are determined by the parameters  $\Delta^{\pm}$  that describe the combined effect of the HFI and the external magnetic field on the <sup>13</sup>C n-spin being conditioned on the electronic spin projection  $m_S = \pm 1$  [60]. The same is valid for the sublevels corresponding to other  $m_I^{(N)}$  projections. Note the different dependence of the splittings  $\Delta^{\pm}$  on B which can be used to determine the sign of the HFI matrix element  $A_{ZZ}$ , as will be discussed in more detail later. At zero B field both splittings  $\Delta^{\pm}$  are reduced to  $\Delta^{(0)} = \sqrt{A_{nd}^2 + A_{ZZ}^2}$ .

The eigenfunctions  $|\Psi_{\alpha}\rangle$ , corresponding to the eigenvalues (4), can be written in the secular approximation as

$$\begin{aligned} |\Psi_{1}\rangle &= |0\uparrow \nearrow\rangle, \\ |\Psi_{3}\rangle &= |0\uparrow \swarrow\rangle, \\ |\Psi_{9}\rangle &= \cos\left(\theta^{-}/2\right)|\Downarrow\uparrow \nearrow\rangle + exp\left(i\varphi\right)\sin\left(\theta^{-}/2\right)|\Downarrow\uparrow \checkmark\rangle, \\ |\Psi_{10}\rangle &= -\sin\left(\theta^{-}/2\right)|\Downarrow\uparrow \nearrow\rangle + exp\left(i\varphi\right)\cos\left(\theta^{-}/2\right)|\Downarrow\uparrow \checkmark\rangle, \\ |\Psi_{13}\rangle &= -\sin\left(\theta^{+}/2\right)|\Uparrow\uparrow \nearrow\rangle + exp\left(i\varphi\right)\cos\left(\theta^{+}/2\right)|\Uparrow\uparrow \checkmark\rangle, \\ |\Psi_{14}\rangle &= \cos\left(\theta^{+}/2\right)|\Uparrow\uparrow \nearrow\rangle + exp\left(i\varphi\right)\sin\left(\theta^{+}/2\right)|\Uparrow\uparrow \checkmark\rangle, \end{aligned}$$
(5)

where the states  $|\Uparrow\uparrow \uparrow \nearrow \rangle = |I\rangle$ ,  $|\Uparrow\uparrow \downarrow \swarrow \rangle = |II\rangle$ ,  $|0\uparrow \nearrow \rangle = |III\rangle$ ,  $|0\uparrow \swarrow \rangle = |III\rangle$ ,  $|0\uparrow \checkmark \rangle = |IV\rangle$ ,  $|\Uparrow\uparrow \uparrow \nearrow \rangle = |V\rangle$  and  $|\Downarrow\uparrow \checkmark \rangle = |VI\rangle$  are the basis states of type  $|m_S, m_I^{(N)}, m_I^{(C)}\rangle$  for the considered spin system. The first double arrows  $\uparrow$ ,  $\Downarrow$  or 0 depict the NV e-spin projections  $m_S = -1, +1, 0$ , respectively, the second straight arrows  $\uparrow$ ,  $\downarrow$  or 0 exhibit the  $m_I^{(N)} = +1, -1, 0$  projections of the <sup>14</sup>N n-spin and, finally, the third oblique arrows  $\nearrow$ ,  $\checkmark$  indicate the  $m_I^{(C)} = \frac{1}{2}, -\frac{1}{2}$  projections of the <sup>13</sup>C n-spin. Coefficients in (5) are determined by relations  $tan(\theta^{\pm}) = A_{nd}/(A_{ZZ} \mp \gamma_n^{(C)}B)$  and  $tan\varphi = A_{ZY}/A_{ZX}$  where the angles  $\theta^{\pm}$  and  $\varphi$  are chosen on account of the signs of  $A_{ZY}, A_{ZX}$  and  $A_{ZZ} \mp \gamma_n^{(C)}B$ . For example, assuming  $A_{nd} > 0$ , at  $A_{ZZ} \mp \gamma_n^{(C)}B > 0$  one needs to take the angles  $\theta^{\pm}$  within the first quarter [0,  $\pi/2$ ], while at  $A_{ZZ} \mp \gamma_n^{(C)}B < 0$  the angles must be taken from the second quarter  $[\pi/2, \pi]$ .

#### 3.2. HFI-induced dynamics of a single <sup>13</sup>C nuclear spin in a <sup>14</sup>NV-<sup>13</sup>C spin system

One can see from (5) that in the general case of an arbitrary spin system NV-<sup>13</sup>C in the external magnetic field BllOZ the substates  $|\Psi_1\rangle$  and  $|\Psi_3\rangle$  of the  $m_s = 0$ ,  $m_I^{(N)} = +1$  manifold are the basis states  $|III\rangle \equiv |0\uparrow \rangle$ ,  $|IV\rangle \equiv |0\uparrow \rangle$ . For these states the n-spin of the <sup>13</sup>C atom is quantized along the NV symmetry axis and has nuclear spin projections  $m_1^{(C)} = \frac{1}{2}, -\frac{1}{2}$  while all four of the other involved substates corresponding to  $m_s = \pm 1$ ,  $m_I^{(N)} = \pm 1$  projections are mixtures of the basis states  $|I\rangle = |\uparrow\uparrow \uparrow \nearrow\rangle$ ,  $|II\rangle = |\uparrow\uparrow \downarrow \rangle$  and  $|V\rangle = |\Downarrow\uparrow \uparrow \nearrow\rangle$ ,  $|VI\rangle = |\Downarrow \uparrow \swarrow\rangle$  with coefficients depending on the HFI matrix elements and on the magnetic field. From this it follows that the <sup>13</sup>C n-spin does not change its projection when the NV e-spin is in the  $m_S = 0$  state while it will oscillate between the basis states  $|V\rangle = |\Downarrow \uparrow \rangle$ ,  $|VI\rangle = |\Downarrow \uparrow \swarrow\rangle$  or the states  $|I\rangle = |\Uparrow \uparrow \nearrow\rangle$ ,  $|II\rangle = |\Uparrow \uparrow \checkmark\rangle$  due to the HFI with the NV espin having  $m_S = -1$  or  $m_S = +1$  projections, respectively. One can show within the secular approximation that in the case of the  $m_S = -1$  e-spin state, for example, the <sup>13</sup>C n-spin prepared in the  $|V\rangle = |\Downarrow \uparrow \nearrow\rangle$  state at the moment t=0 can be found in the state  $|VI\rangle = |\Downarrow \uparrow \checkmark\rangle$  at time *t* with the probability  $W_{VI,V}(t) = \left[A_{nd}^2/(\Delta^-)^2\right] \left[1 - \cos(\Delta^- t)\right]/2$ . Analogously, in the  $m_S = +1$  manifold the probability of the <sup>13</sup>C n-spin flip from the initial state  $|II\rangle = |\Uparrow \uparrow \swarrow\rangle$  to the state  $|I\rangle = |\Uparrow \uparrow \nearrow\rangle$  is  $W_{I,II}(t) = [A_{nd}^2/(\Delta^+)^2][1 - \cos(\Delta^+ t)]/2$ . Therefore, the parameters  $\Delta^-$  and  $\Delta^+$  determine the rate of n-spin flips for <sup>13</sup>C induced by its HFI with the NV e-spin in  $m_s = -1$ and  $m_s = +1$  states.

From the above it follows that the HFI-induced <sup>13</sup>C n-spin flipping will be absent if the respective HFI matrix is diagonal. This case is realized for the NV-<sup>13</sup>C spin system with the <sup>13</sup>C atom located at the NV's symmetry axis. The quantization axis of such a <sup>13</sup>C n-spin is always parallel to the NV axis and therefore it can be completely polarized using the technique demonstrated in [77, 80, 81] for the <sup>14</sup>N nuclear spin belonging to the NV center. Looking ahead, we would like to point out here that in the simulated C<sub>291</sub>[NV]<sup>-</sup>H<sub>172</sub> cluster there are three such 'on-NV-axis' positions for the <sup>13</sup>C n-spin, with two of them disposed on the edge of the cluster while the third one (which is the fifth neighbor of the vacancy) is rather well inside the cluster so that its HFI characteristics are barely influenced by passivating H-atoms. In fact, it is this last position which was chosen for the simulation at B = 50 gauss of the ODMR spectrum, shown in figure 1(b). The calculated  $A_{XX}^{(C)} = -0.2705$  MHz,  $A_{YY}^{(C)} = -0.2707$  MHz, and

 $A_{ZZ}^{(C)} = 0.1874$  MHz. The splittings  $\Delta^{\pm}$  calculated for this case in the secular approximation are  $\Delta^{\pm} = A_{ZZ} \mp \gamma_n^{(C)} B$ . Using analytical expressions for the zero-field splitting  $\Delta^{(0)}$  in terms of elements of an arbitrary HFI matrix  $A^{(C)}$  obtained in [82, 83] up to the second order on  $A_{KL}^{(C)}/D$ , one can get for the on-NV-axis <sup>13</sup>C atom the estimation  $\Delta^{(0)} \simeq A_{ZZ}^{(C)} - A_{XX}^{(C)} A_{YY}^{(C)}/2D$  giving the result  $\approx 187.387$  kHz, which is very close to the value  $\Delta^{(0)} = 187.380$  kHz obtained by direct computer diagonalization of the spin Hamiltonian (1) with the above diagonal  $A^{(C)}$  matrix. Calculated numerically spin wave functions in this special case practically coincided with the basis states  $|m_S, m_I^{(N)}, m_I^{(C)}\rangle$  (in particular, for functions (5) one got  $|\Psi_1\rangle = |0 \uparrow \nearrow\rangle$ ,  $|\Psi_3\rangle = |0 \uparrow \swarrow\rangle$ ,  $|\Psi_9\rangle = |\downarrow \uparrow \nearrow\rangle$ ,  $|\Psi_{10}\rangle = |\downarrow \uparrow \swarrow\rangle$ ,  $|\Psi_{13}\rangle = |\uparrow \uparrow \checkmark\rangle$  and  $|\Psi_{14}\rangle = |\uparrow \uparrow \nearrow\rangle$ ), so that the allowed EPR transitions with selection rules  $\Delta m_S = 1$ ,  $\Delta m_I^{(C)} = 0$  and  $\Delta m_I^{(N)} = 0$  result in 12 vertical lines in the ODMR spectrum shown in figure 1(c). As was explained above, the only fitting parameter for figure 1(b) was the halfwidth of Lorentzians which was taken to be  $\Gamma = 20$  kHz. One can check that in this special case the splitting of paired lines in ODMR spectra both in the  $m_S = -1$  and  $m_S = +1$  states is equal to  $\Delta^{(0)} = 187.38$  kHz. Thus, the <sup>14</sup>NV-<sup>13</sup>C spin system with the <sup>13</sup>C atom in the on-NV-axis position can be identified experimentally by monitoring the above characteristic splitting in its ODMR spectrum.

#### 3.3. Allowed and forbidden transitions

Along with HFI-induced <sup>13</sup>C n-spin flipping, mixed eigenstates (5) of the  $m_S = \pm 1$  manifolds make EPR transitions possible from each of the  $m_S = 0$  substates to all four  $m_S = \pm 1$  substates. In terms of figure 1(c) and with fixed  $m_I^{(N)} = +1$  projection the probabilities of respective transitions are proportional to  $W_{1,10} = W_{3,9} = |\sin(\theta^-/2)|^2$ ,  $W_{1,9} = W_{3,10} = |\cos(\theta^-/2)|^2$ ,  $W_{1,13} = W_{3,14} = |\sin(\theta^+/2)|^2$  and  $W_{1,14} = W_{3,13} = |\cos(\theta^+/2)|^2$ . Which of these are 'allowed' or 'forbidden' (i.e. have high or low probabilities) depends not only on the absolute values of the HFI matrix elements  $A_{ZY}$ ,  $A_{ZX}$ ,  $A_{ZZ}$  and on magnetic field B, but also on the sign of  $A_{ZZ} \equiv \gamma_n^{(C)} B$ .

At low magnetic field  $\gamma_n^{(C)} B < \langle |A_{ZZ}|$  and in the typical situation when  $|A_{ZZ}| > A_{nd}$  (see below table 1) one can find that the angles  $\theta^{\pm} \simeq \theta^{(0)} = \operatorname{atan}(A_{nd}/A_{ZZ})$  are close to  $\pi$  at  $A_{ZZ} < 0$ and to zero at  $A_{ZZ} > 0$ , so that  $\left|\sin\left(\theta^{(0)}/2\right)\right|^2 \sim 1$ ,  $\left|\cos\left(\theta^{(0)}/2\right)\right|^2 \sim 0$  in the first case while  $\left|\sin\left(\theta^{(0)}/2\right)\right|^2 \sim 0$ ,  $\left|\cos\left(\theta^{(0)}/2\right)\right|^2 \sim 1$  in the second one. As a result, at low magnetic field and at  $A_{ZZ} > 0$  the EPR transitions 1–9, 3–10, 1–14 and 3–13 at energy levels (4) will be allowed with the probabilities proportional to  $W_a^{(0)} \simeq 1/(1 + A_{nd}^2/4A_{ZZ}^2) \sim 1$  while the other transitions 1–10, 3–9, 1–13, 3–14 will be forbidden as they have low probabilities proportional to  $W_f^{(0)} \simeq 1/(1+4A_{ZZ}^2/A_{nd}^2) \ll 1$ . The frequency difference of the pairs of allowed lines at low magnetic field is  $\Delta^{(0)}$ . In particular, the above case is realized for the considered special case of the on-NV-axis <sup>13</sup>C atom and respective allowed transitions are shown in figure 1(c). At  $A_{ZZ} < 0$ 

		$\bar{A}_{ZZ}$	$\bar{A}_{nd}$	$ar{\varDelta}_k^{(0)}$				
Family	$N_C$	(MHz)	(MHz)	(MHz)	$\cos(Zz)$	$\bar{Z}(\text{\AA})$	$\bar{r}_{XY}(\text{\AA})$	$\bar{r}_{NC}(\text{\AA})$
A	6	12.451	1.166	12.471	0.288	-0.522	3.937	4.536
В	3	11.386	1.434	11.451	0.412	-2.655	2.972	5.298
С	3	-8.379	0.827	8.437	0.907	-2.109	1.487	4.118
D	6	-6.450	0.931	6.521	0.296	-0.010	2.552	3.089
E	3	4.055	0.826	4.136	0.848	-2.643	1.491	4.621
F	6	3.609	0.738	3.682	0.829	1.577	2.562	2.566
G	6	2.281	0.240	2.292	0.247	0.008	5.166	5.446
Н	3	1.884	0.208	1.895	0.956	-4.242	2.976	6.673
Ι	3	-1.386	0.130	1.392	0.167	0.005	4.458	4.780
J	6	-1.145	0.328	1.191	0.488	-2.110	3.932	5.497
K1	3	-0.886	0.510	1.022	0.555	-2.118	2.985	4.871
K2	3	-1.011	0.014	1.012	0.029	-0.002	4.460	4.785
L	3	0.980	0.121	0.986	0.069	-0.535	2.972	3.737
М	3	0.602	0.557	0.819	0.865	2.127	1.460	1.513
Ν	6	0.725	0.095	0.731	0.219	-0.541	6.467	6.855
01	3	0.673	0.171	0.694	0.528	-4.712	4.479	7.847
O2	3	0.655	0.166	0.676	0.902	3.707	2.983	3.578
Р	6	0.474	0.190	0.510	0.402	-2.635	5.355	6.909
Q	6	0.391	0.273	0.477	0.524	-2.645	3.953	5.897
R	3	-0.226	0.393	0.453	0.759	2.115	2.985	3.009
S	3	0.412	0.060	0.417	0.119	-0.511	5.942	6.351
Т	3	0.366	0.149	0.395	0.955	3.709	1.504	2.485
U	3	0.286	0.225	0.364	0.624	1.578	4.481	4.484
V	6	-0.209	0.232	0.312	0.639	2.105	3.927	3.945
W	3	-0.200	0.171	0.266	0.941	-4.220	1.489	6.135
Х	6	0.211	0.152	0.259	0.899	-4.768	2.573	6.990
Y	6	-0.228	0.001	0.227	0.002	-0.522	5.381	5.834
Z1	3	0.158	0.131	0.205	0.857	4.226	3.001	3.903
Z2	3	0.086	0.184	0.203	0.464	1.576	4.447	4.447
on-	1	0.187	0.001	0.187	1.000	-4.734	0.009	6.465
NV-								
axis								

**Table 1.** Simulated HFI and spatial characteristics for the families of equivalent positions of  ${}^{13}C$  n-spin in the  $C_{291}[NV]$ - $H_{172}$  cluster.

The increase of a magnetic field BllOZ acting on a given NV-<sup>13</sup>C spin system results in a modification of both probabilities and frequencies of EPR transitions in the spin system, which is different for the  $m_S = 0 \leftrightarrow m_S = -1$  and  $m_S = 0 \leftrightarrow m_S = +1$  manifolds depending on the  $A_{ZZ}$  sign. Indeed, as follows from (4), (5), the formulae for the frequencies and amplitudes of EPR transitions belonging to the two manifolds contain quantities  $\Delta^-$  and  $\Delta^+$ , which change in a different way with magnetic field B. In particular, at  $A_{ZZ} > 0$  the quantity  $\Delta^-$  increases constantly with the B growth while the quantity  $\Delta^+$  first decreases up to  $A_{nd}$  at  $B = A_{ZZ}/\gamma_n^{(C)}$ , and only then starts to increase. As a result, at  $A_{ZZ} > 0$  the quantities  $W_{1,9} = W_{3,10} = \left|\cos(\theta^-/2)\right|^2$  for the transitions 1–9 and 3–10 in the  $m_S = 0 \leftrightarrow m_S = -1$  manifold which are allowed at low field will further increase with the B growth from the

low-field value  $W_a^{(0)}$  to 1 so that these transitions continue to be allowed. Conversely, the quantities  $W_{1,14} = W_{3,13} = \left|\cos\left(\theta^{+}/2\right)\right|^2$  for the analogous initially allowed transitions 1–14 and 3-13 in the  $m_S = 0 \leftrightarrow m_S = +1$  manifold will constantly decrease from  $W_a^{(0)}$  up to zero with the B growth thus resulting in the transformation of the respective transition from the allowed to the forbidden. Moreover, from (4) it follows that the difference of frequencies  $\Delta \omega \ (m_S = -1 \rightarrow m_S = 0) = (E_{10} - E_3) - (E_9 - E_1) = \Delta^- - \gamma_n^{(C)} B$  of the allowed EPR transitions 10-3 and 9-1 in the  $m_S = 0 \leftrightarrow m_S = -1$  manifold will only slightly decrease with the B growth from  $\Delta^{(0)}$  to  $A_{ZZ}$  while for the transitions 14-1 and 13-3 of the  $m_S = 0 \leftrightarrow m_S = +1$  manifold their frequency difference  $\Delta \omega \ (m_S = +1 \rightarrow m_S = 0) =$  $(E_{14} - E_1) - (E_{13} - E_3) = \Delta^+ + \gamma_n^{(C)} B$  will increase constantly up to linear dependence  $\sim 2\gamma_n^{(C)} B$ . In turn, at  $A_{ZZ} > 0$ , among the initially forbidden transitions 1–10, 3–9, 1–13 and 3–14 the transitions 1–10 and 3–9 in the  $m_s = 0 \leftrightarrow m_s = -1$  manifold will further decrease in probability with the B growth up to zero, while for the transitions 1-13 and 3-14 in the  $m_S = 0 \leftrightarrow m_S = +1$  manifold their probabilities will grow with an increase of W from  $W_f^{(0)}$  up to 1, thus transforming the last transitions from forbidden to allowed. In the second case the frequency difference of the transitions 14-3 and 13-1 will change from  $\Delta^{(0)}$  at low B up to  $-A_{ZZ}$ at high B with the two respective lines getting coincident frequencies at  $B = \Delta^{(0)2} / (2A_{ZZ} \gamma_n^{(C)})$ . Obviously, at  $A_{ZZ} < 0$  the situation with the modification of transition probabilities with B growth will be reversed for the forbidden and allowed transitions. Note that in all cases the threshold magnetic field B at which forbidden transitions become allowed and vice versa is  $B = A_{ZZ} / \gamma_n^{(C)}$ .

The above approximate analytical consideration of an arbitrary spin system  $NV^{-13}C$ indicates that, in experimentally recording ODMR spectra for various individual NV centers, one can not just discover the presence of the <sup>13</sup>C atom in the vicinity of the NV center but also, measuring the HFI splittings  $\Delta \omega$  ( $m_S = +1 \rightarrow m_S = 0$ ) and  $\Delta \omega$  ( $m_S = -1 \rightarrow m_S = 0$ ) of paired ODMR lines for the spin system and their modification with an applied external magnetic field, extract HFI parameters  $\Delta^{(0)}$ ,  $A_{ZZ}$  and  $A_{nd}$ , and, moreover, determine the sign of the most essential element  $A_{ZZ}$  of the HFI matrix for the specific kth position of the <sup>13</sup>C n-spin in a diamond lattice. Such experimental work was systematically performed recently in the studies [26, 27], in which the ODMR spectra of hundreds of NV centers were studied for their HFI structures. Many of them proved to be coupled with single nearby or distant <sup>13</sup>C n-spins. systems exhibited discrete possible values of HFI splittings Such spin  $\Delta \omega$  ( $m_S = -1 \rightarrow m_S = 0$ ). Evidently, if we compare such experimental data with those calculated for all possible <sup>14</sup>NV-<sup>13</sup>C systems by diagonalization of their spin Hamiltonians (1) we will be able to distinguish the position of the specific <sup>13</sup>C nucleus among others.

#### 4. Simulation of the HFI characteristics for the C<sub>291</sub>[NV]<sup>-</sup>H<sub>172</sub> cluster

Calculated data obtained by the simulation for 121 possible positions of the <sup>13</sup>C n-spin in the  $C_{291}[NV]$ <sup>-</sup>H<sub>172</sub> cluster are summarized in table 1. Calculations show that owing to the  $C_{3V}$  symmetry of the NV center there are few positions of <sup>13</sup>C nuclei in the cluster that exhibit



**Figure 2.** Calculated values of the HFI splittings  $\Delta_k^{(0)}$  for families A–N (a) versus those measured in [27] (b). 2(b) is reproduced with permission from [27]. Copyright 2012 by the American Physical Society.

practically equal values of calculated HFI parameters (see also [26]). These sets of nearequivalent lattice sites can be termed as 'families' [27]. In table 1, we present data for 26 such families labeled by letters of the English alphabet, indicated in the first column. The second column contains the number  $N_C$ (=3 or 6) of equivalent members for each family. The third, fourth and fifth columns of the table show the values of  $\bar{A}_{ZZ}$ ,  $\bar{A}_{nd}$  and zero-field splitting  $\bar{\Delta}_k^{(0)}$ being the averages of respective quantities  $A_{ZZ}$ ,  $A_{nd}$  and  $\Delta_k^{(0)}$  calculated for all members of each family. These data are characteristic for each family. Moreover, the next characteristic property of the above families is the absolute value of the cosine between the z-axis in the NV PAS and the z-axis of the <sup>13</sup>C PAS given by the element  $(U_k)_{Zz}$  of the respective unitary matrix  $U_k$  that transforms the DFT simulated HFI  $A_k^{(C)}$  matrix into the diagonal matrix  $\tilde{A}_k^{(C)} = U_k^{-1}A_k^{(C)} U_k$ . The averages of these directional cosines over family members are shown in the sixth column of table 1. One can see from these data that only the on-NV-axis <sup>13</sup>C position exhibits exactly  $(U_k)_{Zz} = \cos(Zz_k) = 1$  indicating that this <sup>13</sup>C n-spin has a quantization axis coinciding with that of the e-spin of the NV center. It should, however, be noted that our cluster simulation predicts that there are also few families (e.g. C, H, T) for which the principle  $z_k$  axes of <sup>13</sup>C nuclear spins are aligned very closely to the NV symmetry z-axis.

Analysis of the spatial locations of <sup>13</sup>C positions belonging to specific families showed that all of them have near equal Z coordinates and are also situated in the plane near perpendicular to the z-axis, so that they are near equidistant from it. These calculated Z coordinates and distances from the z-axis averaged over family members are given in the seventh and eighth columns of table 1, respectively. Note that the coordinate origin for the NV PAS was set by computer after relaxation of the cluster and was disposed approximately at the position of the vacancy of the NV center. The N atom of the NV center in this PAS has the coordinates  $X_N = 0.001$  Å,  $Y_N = 0.002$  Å and  $Z_N = 1.731$  Å. In turn, the coordinates of the nearest on-NV-axis <sup>13</sup>C atom are as follows:  $X_C = -0.006$  Å,  $Y_C = -0.006$  Å and  $Z_C = -4.734$  Å. Finally, the ninth column in table 1 shows the averaged distances from the N atom to the positions of family members which are also characteristic of each family. Note that columns 6–9 of table 1 give the data for specification of 'shells' and 'cones' used recently in [84] to discuss the contribution to FID dynamics of various <sup>13</sup>C n-spins disposed differently with respect to the NV e-spin. Additionally, to demonstrate situations when a few families exhibit very close values of  $\overline{A}_k^{(0)}$ 



**Figure 3.** Distribution of numbers of possible positions of a <sup>13</sup>C nuclear spin in a diamond lattice exhibiting calculated HFI splittings  $\Delta_k^{(0)}$  falling into different frequency intervals of constant width h: (a) low-resolution case (h = 300 kHz), (b), (c) high-resolution cases (h = 10 kHz).

but have different positions with respect to the NV center, we single out in table 1 three pairs of families K1-K2, O1-O2 and Z1-Z2 that have such properties. Also, we do not show the largest HFI splittings of  $\sim$ 130 MHz for the three sites that are NNs of the vacancy, as they are well known from the literature.

#### 5. Comparison with experiment

In figure 2 we compare the calculated values of HFI splittings  $\Delta_k^{(0)}$  shown in table 1 with those experimentally measured in [27]. Both figures clearly demonstrate discrete values of possible HFI splittings  $\Delta_k^{(0)}$ , corresponding to different families. Typically, the calculated values of HFI splittings were slightly lower than those experimentally measured. As it was pointed out in section 2 (see also [71]) the basic reason for that is the level of theory used here to simulate the HFI characteristics for the studied cluster. It should also be noted that the accord of the theoretical predictions with the experimental data could be partially improved if we took into account that the experimental data were obtained at a low magnetic field of B ~ 20 gauss which gave a small additional contribution ~0.04 MHz to the measured splitting.

From figure 2 one can see also that experimentally obtained values for <sup>14</sup>NV-<sup>13</sup>C spin systems, attributed to a specific family in some cases (e.g. those of the families D, G and I), deviate from theoretical predictions, probably due to a short experimental data set in [27]. Nevertheless, qualitative near-coincidence of the two figures demonstrates that the HFI parameters simulated by DFT for the  $C_{291}[NV]$ - $H_{172}$  cluster in conjunction with subsequent spin Hamiltonian calculations provide a reasonable fit with the experimental HFI splittings, allowing one also to identify possible positions of the <sup>13</sup>C atom in the diamond lattice as belonging to a definite family.

Evidently, achieving this last goal would depend on the experimental frequency resolution. Therefore, in figure 3 we show the distribution of calculated possible values of  $\Delta_k^{(0)}$  in another way. We introduce the sequence of frequency intervals, [0–h] [h-2h],...,[nh-(n+1)h],... of the constant width h and count the number  $N_n$  of possible locations of <sup>13</sup>C



**Figure 4.** Summary of simulations for the specific <sup>14</sup>NV-<sup>13</sup>C spin system belonging to the K1 family in comparison with experimental data from [27]. (a) Side and top views showing spatial positions (10, 12 and 20) of <sup>13</sup>C atoms belonging to the K1 family with respect to the NV center. (b) Energy levels (for the  $m_I^{(N)} = +1$  case) of the spin system and possible allowed and forbidden transitions between them shown with vertical thick solid and inclined thin dotted lines. (c) Simulated magnetic field dependences of relative probabilities of the allowed transitions  $W_{13,1}=W_{14,3}$ ,  $W_{10,1}=W_{9,3}$  and of the forbidden transitions  $W_{14,1}=W_{13,3}$ ,  $W_{9,1}=W_{10,3}$  in the upper  $m_S = 0 \leftrightarrow m_S = +1$ 

#### Figure 4. (Continued.)

and lower  $m_S = 0 \leftrightarrow m_S = -1$  manifolds. Red dotted curves show the ratio of simulated probabilities of forbidden transitions to 'allowed' ones in comparison with experimental points of [27]. (d) The central part of the figure shows simulated magnetic field dependences of relative frequencies of allowed transitions 10-1 (curve 1) and 9-3 (curve 2) and forbidden transitions 9-1 (curve 3) and 10-3 (curve 4) belonging to the  $m_S = 0 \leftrightarrow m_S = -1$  manifold of the studied <sup>14</sup>NV-<sup>13</sup>C spin system, in comparison with the experimental data of [27]. Curves 5 and 6 correspond to the allowed transitions 14-3 and 13-1 in the  $m_S = 0 \leftrightarrow m_S = +1$  manifold, which were not studied in [27]. Left and right parts of (d) exhibit, respectively, the experimental and simulated ODMR spectra for the studied <sup>14</sup>NV-<sup>13</sup>C spin system undergoing magnetic field BllOZ of three different strengths, with the lines indicating the theoretical parts of the transitions. See more details in text. Experimental data in (d) are courtesy of Vincent Jacques, ENS de Cachan.

atoms in the simulated cluster for which the calculated values of HFI splitting  $\Delta_k^{(0)}$  fall into definite intervals [nh-(n+1)h] having characteristic number n. Again, for obvious reasons we exclude from the figures the largest HFI splittings  $\Delta_k^{(0)} \sim 130$  MHz, characterizing the <sup>13</sup>C location in the three lattice sites that are NNs of the vacancy. To compare cases of low and high resolution we show in figure 3(a) the distribution for the case of a relatively wide frequency interval h = 300 kHz which approximately corresponds to the experiments of [27] while figures 3(b) and (c) demonstrate the distributions for the case of much higher resolution, h = 10 kHz. One can see from figure 3 that in the low-resolution case a measured value of  $\Delta_k^{(0)}$  only allows the assignment of the respective <sup>14</sup>NV-<sup>13</sup>C system to a definite family for rather large values of HFI splittings  $\Delta_k^{(0)}$  ( $\Delta_k^{(0)} > 1$  MHz). In turn, high-resolution experiments distinguishing values of  $\Delta_k^{(0)}$  with an accuracy of 10 kHz provide much more detailed information regarding the location of the <sup>13</sup>C atom in the diamond lattice with respect to the NV center. For example, one can see from figure 3(c) that in the case of the specific <sup>13</sup>C atom located on the NV axis and characterized by the value  $\Delta_k^{(0)} = 187.4 \text{ kHz}$ which falls within the frequency interval [180-190 kHz], there are three other positions providing HFI splittings  $\Delta_k^{(0)}$  that also fall into the above interval. Evidently, in these cases additional experiments are needed to differentiate the <sup>13</sup>C atom within a definite frequency interval and determine the family it belongs to. Figure 3(c), which differs from figure 3(b) by the x-axis scale, shows that in the case of the distant  ${}^{13}C$  atoms weakly coupled to the e-spin of the NV center there are typically rather many (10-20) different positions for the <sup>13</sup>C atom, demonstrating HFI splittings  $\Delta_k^{(0)}$  from the same frequency interval, and making it difficult to identify their positions in the diamond lattice solely by measuring the value of HFI splitting  $\Delta_k^{(0)}$  at zero magnetic field. Experiments in diamond samples with a lower <sup>13</sup>C density than natural samples where  $T_2^*$  can be high enough to resolve the hyperfine structure with high accuracy will be ideal for spectroscopy of <sup>14</sup>NV-<sup>13</sup>C systems. It should be noted, however, that in such samples the probability of finding an NV with <sup>13</sup>C spin in a specific position is reduced and time-consuming systematic work is required to find the desired system <sup>14</sup>NV-<sup>13</sup>C among others.

It would be instructive to demonstrate the ability to identify the position of a <sup>13</sup>C n-spin in a diamond lattice having measured the six-line ODMR spectrum of the <sup>14</sup>NV-<sup>13</sup>C spin system. In particular, available experimental data can be found in the work [27] where the magnetic-

field-dependent ODMR spectra of some specific <sup>14</sup>NV-<sup>13</sup>C systems were carefully studied in the  $m_S = 0 \leftrightarrow m_S = -1$  manifold. The low-field (20 gauss) HFI splitting for the studied spin system was 1.12 MHz. According to table 1, one can attribute the <sup>14</sup>NV-<sup>13</sup>C system to the families K1 or K2, each having three equivalent positions. Additional data for the attribution gave the studied B-field dependence of the ODMR spectra, presented in figures 3 and 4 of article [27], which made it possible to determine experimentally the values of  $A_{ZZ}^{(C)} = 1.02$  MHz and  $A_{nd}^{(C)} = (A_{ZX}^{(C)2} + A_{ZY}^{(C)2})^{1/2} = 0.51$  MHz. According to table 1, the finding  $A_{nd}^{(C)} = 0.51$  MHz is in agreement with the K1 family but not with the K2 one. Therefore, we conclude that the center <sup>14</sup>NV-<sup>13</sup>C that was carefully investigated experimentally in [27] belongs to the K1 family.

In more detail, for one representative member of the K1 family our simulation gave the following HFI matrix  $A_k^{(C)}$  (in the NV PAS)

$$A_{KI}^{(C)} = \begin{pmatrix} -0.4628 & -0.0356 & 0.5088 \\ -0.0356 & -1.0093 & -0.0335 \\ 0.5088 & -0.0335 & -0.8880 \end{pmatrix},$$
(6)

while the HFI matrices simulated for the other two members of the family were close to those obtained from (6) by unitary transformations of the rotation on the angles ±120° about the z-axis. From the simulated HFI matrices one can get the values  $A_{ZZ}^{(C)} = -0.8880, -0.8848$ and -0.8849 MHz and  $A_{nd} = 0.5099, 0.5097$  and 0.5110 MHz for the three possible positions of the K1 family which are close to the experimental findings. Note the negative sign of the element  $A_{ZZ}^{(C)}$ , which is important for the interpretation of ODMR spectra of the spin system in the presence of an external magnetic field. Substituting (6) into the spin Hamiltonian (1) one can straightforwardly find exact eigenvalues (energy levels)  $E_{\alpha}$  and eigenfunctions  $|\Psi_{\alpha}\rangle$  of the analyzed <sup>14</sup>NV-<sup>13</sup>C spin system in the presence of an arbitrary magnetic field. Comparing them with those obtained using simple approximate analytical expressions (4), (5) one can make sure that these expressions work very well for the studied spin system. Further, we have simulated ODMR spectra and studied their modification with an applied magnetic field. The results of our simulations for the above specific <sup>14</sup>NV-<sup>13</sup>C spin system are summarized in figure 4 in comparison with the available experimental data from [27].

Spatially, three equivalent <sup>13</sup>C n-spin positions belonging to the K1 family are fourth neighbors of the vacancy of the NV center. Their positions in the diamond lattice with respect to the NV center are illustrated by figure 4(a), which relates to the studied relaxed cluster  $C_{291}[NV]^{-}H_{172}$  and shows side (upper figure 4(a)) and top (lower figure 4(a)) views of essential carbon atoms around the NV center. Here, numeration of the atoms is as follows: 1 is the N atom of the NV center; 2, 3 and 4 are NNs of the N atom; 5, 6 and 7 are NNs of the vacancy of the NV center; 8, 14, 17, 18, 21, 23, 24 and 25 are the second neighbors of the vacancy; 9, 11, 13, 16, 19 and 22 are the third neighbors of the vacancy; and finally, 10, 12 and 20 are the three positions are near-equidistant from the  $C_{3V}$  symmetry axis of the NV center ( $\bar{r}_{XY} = 2.985$  Å according to table 1) which passes through the N atom to the plane wherein lie the K1 family members is 3.849 Å.

As follows from the above general analytical consideration of eigenvalues and eigenstates (see equations (4), (5)) for the chosen <sup>14</sup>NV-<sup>13</sup>C spin system belonging to the K1 family and exhibiting negative element  $A_{ZZ}^{(C)} = -0888$  MHz, at low magnetic field the transitions 10-1, 9-3, 14-3 and 13-1 will be allowed while the transitions 9-1, 10-3, 14-1 and 13-3 will be forbidden. In figure 4(b), which shows part of the simulated energy levels (those with the  $m_I^{(N)} = +1$  nitrogen atom nuclear spin projection) of the studied <sup>14</sup>NV-<sup>13</sup>C spin, these transitions are shown with thick solid vertical and thin dotted inclined lines. Note the difference between these transitions and those shown in figure 1(c) for the opposite case  $A_{ZZ}^{(C)} > 0$ . Numerical simulation with complete Hamiltonian (1) at B = 20 gauss and fixed nitrogen atom n-spin projection  $m_I^{(N)} = +1$  gave the values  $W_a \simeq 0.9302$  and  $W_f \simeq 0.0690$  for allowed and forbidden EPR transitions (see figure 4(c) at low magnetic field B) both in  $m_S = 0 \leftrightarrow m_S = -1$  and  $m_S = 0 \leftrightarrow m_S = +1$  manifolds. Note that the simple analytical expressions obtained for these quantities at zero magnetic field,  $W_a^{(0)} \simeq 1/(1 + A_{nd}^2/4A_{ZZ}^2)$  and  $W_f^{(0)} \simeq 1/(1 + 4A_{ZZ}^2/A_{nd}^2)$ , gave values ~0.9238 and ~0.0762 that are close to the above simulated low-field values.

At increased magnetic fields BllOZ the above consideration predicts that in the  $A_{ZZ}^{(C)} < 0$  case, the probabilities of the initially allowed transitions 10-1 and 9-3 belonging to the lower  $m_S = 0 \leftrightarrow m_S = -1$  manifold will reduce, while those of the forbidden transitions 9-1 and 10-3 will increase as shown in the lower part of figure 4(c) with solid and dotted blue curves. At  $B = |A_{ZZ}|/\gamma_n^{(C)} \approx 829$  gauss all four transitions will have equal probabilities with W = 1/2. The red curve in this figure shows the ratio of simulated forbidden and allowed transition probabilities in comparison with the respective experimentally measured values (red points). In turn, the upper part of figure 4(c) shows the B-field dependences of probabilities of transitions belonging to the upper  $m_S = 0 \leftrightarrow m_S = +1$  manifold. One can see from this figure that in this manifold the initially allowed transitions 14-3 and 13-1 remained bright while the initially forbidden transitions 14-1 and 13-3 further lost intensity at magnetic field growth.

Simultaneously, with increasing magnetic field strength the frequencies of all EPR transitions will modify. This is illustrated by the central part of figure 4(d) where solid blue curves 1 and 2 and dotted blue curves 3 and 4 show the simulated relative frequencies of allowed transitions 10-1 and 9-3 and forbidden transitions 9-1 and 10-3, belonging to the  $m_S = 0 \leftrightarrow m_S = -1$  manifold of the studied <sup>14</sup>NV-<sup>13</sup>C spin system, in comparison with the respective experimental data from [27], while black solid lines 5 and 6 show the relative frequencies of the allowed transitions 14-3 and 13-1 of the  $m_S = 0 \leftrightarrow m_S = +1$  manifold. One can see from the figure that, in accordance with the above theoretical consideration, at  $A_{ZZ} = -0.888 \text{ MHz} < 0$  in the lower  $m_S = 0 \leftrightarrow m_S = -1$  manifold the lines associated with the transitions 10-1 and 9-3 will diverge with the magnetic field growth while those with the transitions 9-1 and 10-3 will converge up to their crossing at  $B = \Delta^{(0)2} / (2 |A_{ZZ}| \gamma_n^{(C)}) \approx 551$ gauss and then further diverge so that finally the frequency distance between the respective two lines will approach  $|A_{ZZ}| = 0.888$  MHz. In turn, in the upper  $m_S = 0 \leftrightarrow m_S = + 1$  manifold one will observe at increased magnetic field BIIOZ only two lines of the HFI structure associated with the allowed transitions 14-3 and 13-1 whose frequency difference is changed only slightly from  $\Delta^{(0)}$  at low B field to  $|A_{ZZ}|$  at high B.

Finally, the left and right parts of figure 4(d) show a comparison of experimental ODMR spectra obtained in [27] for the  $m_S = 0 \leftrightarrow m_S = -1$  manifold with fixed  $m_I^{(N)} = +1$  nuclear spin projection at three different magnetic fields BllOZ=363, 598 and 785 gauss with respective spectra simulated for the chosen representative of the K1 family. In theoretical spectra the only fitting parameter was the width of Lorentzians  $\Gamma$  which was taken to be equal to 0.12 MHz. One can see that the simulated spectra are in good coincidence with the experimental ones. Concluding this section, it should also be noted that analogous analysis done for the system <sup>14</sup>NV-<sup>13</sup>C consisting of the <sup>13</sup>C atom in the on-NV-axis position reveals no forbidden transitions at any magnetic fields BllOZ, as should be clear from figure 1 which shows that, for this system, all combining substates are pure states with definite spin projections  $m_I^{(C)}$ .

#### Summary

In summary, we have systematically studied HFI and ODMR spectra of three-spin systems <sup>14</sup>NV-<sup>13</sup>C including the NV electronic spin S = 1, the intrinsic nuclear spin  $I^{(N)} = 1$  of the <sup>14</sup>N nuclei belonging to the center and the nuclear spin  $I^{(C)} = 1/2$  of the isotopic <sup>13</sup>C atom disposed in any possible position in the relaxed H-terminated C<sub>291</sub>[NV]<sup>-</sup>H<sub>172</sub> cluster, hosting the NV center. Using DFT we have calculated full HFI matrices  $A_{KL}^{(C)}$  (in the NV PAS for coordinates) for the <sup>14</sup>NV-<sup>13</sup>C spin systems which were substituted into a standard ground-electronic-state spin Hamiltonian to calculate energy levels and eigenstates of the systems and further simulate ODMR spectra using ODMR linewidths as the only fitting parameters. In particular, HFIinduced splittings of the  $m_s = \pm 1$  states at zero magnetic field were calculated for all positions of the <sup>13</sup>C nuclear spin in the cluster, along with the values of the most essential HFI parameters  $A_{ZZ}^{(C)}$  and  $A_{nd}^{(C)} = \left(A_{ZX}^{(C)2} + A_{ZY}^{(C)2}\right)^{1/2}$ . We tabulated these data for 30 families of equivalent positions of the <sup>13</sup>C atom in a diamond lattice around the NV center, each consisting of three or six members due to the C<sub>3V</sub> symmetry of the NV center. It was shown that the members of each family are disposed symmetrically on cones, each of which has its vertex at the N atom of the NV center (the axis coinciding with the NV symmetry axis) and is equidistant from the N atom of the NV center. For the first time HFI data are obtained for the specific system <sup>14</sup>NV-<sup>13</sup>C in which the <sup>13</sup>C atom is disposed on the NV center symmetry axis in the nearest-to-the-vacancy position. At zero field the HFI splitting of the  $m_S = \pm 1$  states for this specific spin system was found to be 187.38 kHz. Simple analysis of an arbitrary <sup>14</sup>NV-<sup>13</sup>C spin system in the axial magnetic field B||OZ done within the secular approximation showed that the effect of an external magnetic field on the rates of EPR transitions in the system is different in the  $m_S = 0 \leftrightarrow m_S = -1$  and the  $m_S = 0 \leftrightarrow m_S = +1$  manifolds depending on the sign of the HFI matrix element  $A_{ZZ}^{(C)}$ . General consideration is illustrated by analysis of available experimental data from the previous work [27] which is described well using simulated HFI parameters. Our results may contribute to the general understanding of NV-<sup>13</sup>C interactions in diamond, to the realization of multipartite entangled states in multi-nuclear spin systems, to the implementation of single-shot read-out measurements and to the understanding of details of the NV electron spin decoherence under a fluctuating <sup>13</sup>C nuclear spin bath, especially in the presence of an external magnetic field.

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