

<https://doi.org/10.1038/s41535-026-00888-2>

Spin-dependent optical activity of the telecom range CIV center in SiC: a wavefunction theory analysis



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Recently, density functional theory-based high-throughput screening of point defects in 4H-SiC revealed the positively charged chlorine-vacancy (CIV) defect to be a promising quantum bit candidate emitting at telecom wavelengths, with an electronic structure analogous to the well-known NV center in diamond. Furthermore, recent infrared photoluminescence (PL) measurements on chlorine-implanted 4H-SiC have revealed new PL lines associated with the CIV defect. While the defect possesses a high-spin ground state, there is a lack of evidence of optically detected magnetic resonance (ODMR), a key ingredient for optical spin initialization and readout. In this article, we employ a multireference wavefunction-based quantum chemistry method, specifically, second-order perturbation theory (NEVPT2) on top of a defect-localized many-body wavefunction (CASSCF), to explore the many-body electronic structure of the CIV center. We estimate photoluminescence, internal conversion, and intersystem crossing rates to investigate the possibility of spin polarization and ODMR activity. Our findings establish the CIV center in 4H-SiC as an optically addressable spin qubit with fiber optics compatibility in the technologically mature 4H-SiC host material, enabling the development of large-scale quantum networks.

Color centers in wide-bandgap semiconductors have been studied for over two decades due to their potential in emerging quantum technologies, including spin-photon interfaces^{1–3}, single-photon emitters^{4,5}, spin qubits^{6–8}, and quantum sensors^{9–12}. Considerable attention has been paid to the negatively charged nitrogen vacancy (NV) center in diamond, demonstrating great versatility in applications^{13,14} thanks to its remarkable quantum properties, such as high-temperature coherence and strong visible emission^{15,16}. The success of the NV center inspired the search for NV-like defects in other host materials. For example, several recent works have focused on color centers in 4H silicon carbide (4H-SiC) with similar characteristics to harness the fabrication advantages of the technologically mature SiC host^{17–19}.

Automated computer simulation tools have accelerated the pace of defect search by performing density functional theory (DFT) on a large number of defect structures. As such, the high-throughput workflow implemented in the ADAQ code²⁰ revealed the positively charged CIV defect center in 4H-SiC, see Fig. 1a, as a near-C-band telecom emitter²¹, making it the most favorable spin qubit candidate in terms of compatibility with quantum communication networks utilizing modern fiber optic

technologies at minimal signal loss. The triplet ($S = 1$) ground spin state, the similarity to the NV center in electronic structure, and the predicted long coherence time²¹ of the CIV center could also enable its application as a qubit and quantum sensor²².

Importantly, very recent experiments have reported the observation of telecom S-band, O-band, and C-band spectral lines in 4H-SiC after chlorine implantation^{23,24}. Four previously unobserved zero-phonon lines (ZPLs) have been tentatively assigned to the four possible configurations of the CIV center in SiC by Astakhov et al.²³, based on the circumstances of their creation and the overall good agreement between the theoretical and experimental emission energies. Later, Shafizadeh et al. reported ODMR activity for the same spectral lines²⁴, which further emphasizes the importance of these new centers. Since the assignment of the CIV center to the new emitters is not certain, additional theoretical investigations of CIV are vital to resolve these discrepancies. Herein, we will focus on the simulation of spin-dependent optical activity^{25–28}, in other words, the description of the CIV-related ODMR sign.

Computationally demonstrating that a defect is ODMR active requires a comprehensive characterization of the system's optical cycle, including the

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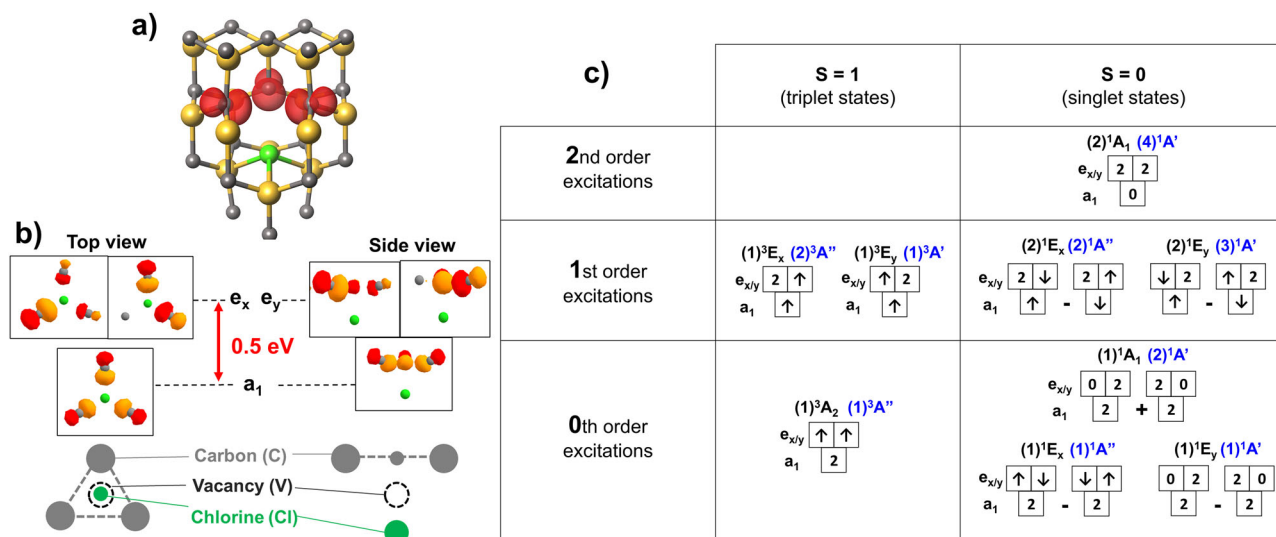


Fig. 1 | Summary of the considered defect system with regard to structure and electronic configuration. **a** Crystal structure and spin density of the CIV defect in 4H-SiC, in the ground state *kk* configuration (visualized in VESTA⁷⁵). **b** Shape of

frontier molecular orbitals. **c** Conceivable occupation patterns of *e_x*, *e_y*, and *a₁* orbitals according to group theory analysis. Black and blue signs indicate irreducible representations at *C_{3v}* and *C_s* symmetry, respectively.

optically excited spin-1 many-body state, the metastable spin-0 many-body shelving state(s), and radiative and non-radiative transitions among them. The electronic states often include open-shell states, which are not accurately modeled in DFT due to their multireference character^{29–31}. The ¹A₁ shelving state of the NV center is one such state notorious for its inaccuracy in DFT and other single-determinant methods^{30,32}. Due to the analogy between the NV center in diamond and the CIV center in 4H-SiC, similar hurdles can be expected in the theoretical analysis of the latter. To describe such states, higher-order multireference computational techniques must be employed. A cost-efficient example is CASSCF-NEVPT2 (i.e., *n*-electron valence state perturbation theory^{33–35} on top of a complete active space self-consistent field^{36–38} wavefunction), which has been demonstrated to accurately describe the excited states of NV[−] in diamond^{39,40}.

In this article, we employ a large-scale 151-atom SiC cluster-model implementation of the CASSCF-NEVPT2 methodology, as available in current quantum chemical codes^{41–43}, to achieve a complete and accurate description of the CIV center's many-body electronic structure. We utilize this model to address the open questions regarding the excitation dynamics of the defect and discuss the implications of the predicted transition rates. We conclude that the CIV center can be spin polarized by optical excitation, giving rise to ODMR signals when microwave irradiation is additionally applied. These results establish the CIV center as a telecom wavelength atomic-scale spin qubit.

Results and discussion

Many-body composition of electronic states

The main characteristics of the electronic states of the CIV defect can be described by the occupation pattern of three frontier molecular orbitals (*a₁*, *e_x*, *e_y*, shown in Fig. 1b), formed as linear combinations of the dangling sp³ orbitals of carbon atoms adjacent to the vacancy. We note that the fourth dangling sp³ orbital is strongly localized to the chlorine atom and is buried deeply in the valence band.

Accounting for four active electrons occupying *a₁*, *e_x* and *e_y* (which satisfies the overall charge of +1), group theory predicts nine conceivable electronic configurations, which are depicted in *C_{3v}* and *C_{1h}* point groups in Fig. 1c. These pure states are mixed to form the many-body eigenstates at the CASSCF level, which is visualized in Fig. 2. In the following, the six lowest-lying eigenstates, which are expected to be relevant for qubit applications, will be referred to according to the nomenclature shown in Fig. 2, i.e. ³A₂, ³E_x (³A'), ³E_y (³A''), ¹E_x (¹A'), ¹E_y (¹A'') in *C_{3v}* (*C_{1h}*), and ¹A₁, where the overline

emphasizes the distinction of the mixed many body states from the unmixed group-theory states.

The mixing of group-theory states, as provided by percentages in Fig. 2, can be attributed to two main factors. Firstly, the high-lying and low-lying states of equivalent *C_{3v}* irreducible representations are already intensively mixed at high-symmetry geometries: that is, ¹E and ¹A' states borrow Slater determinants from multiple group-theory configurations, (1)¹E and (2)¹E or (1)¹A₁ and (2)¹A₁, respectively. Green occupation diagrams show this type of mixing in Fig. 2. Secondly, the symmetry reduction to *C_{1h}* due to Jahn-Teller distortion of the *E* states, enables additional combinations within A' and A'' symmetry blocks. The electron configurations appearing due to the latter effect are shown in blue in Fig. 2. We recall that A₁ and A₂ irreducible representations are Jahn-Teller inactive according to group theory. Jahn-Teller distortion of the excited state, in particular ³E_x → ³A'', introduces the character of the ground triplet state (0.23% ³A₂). This JT-induced state mixing enables a non-radiative internal conversion (IC) between the optically excited triplet and the ground state, which competes with the desired telecom-band photoemission. The other Jahn-Teller unstable triplet, ³E_y → ³A', remains pure even after the distortion, as its A' irreducible representation is unique among the triplets.

In the case of singlets, the proportion of state mixing at *C_{3v}* symmetry is approximately 70%–30% between (1)¹E and (2)¹E, which appear in ¹E → ¹A'' and ¹E → ¹A', and a striking near-equal contribution between (1)¹A₁ and (2)¹A₁, which form the many-body state of ¹A₁. Upon symmetry reduction by Jahn-Teller distortion, ¹E → ¹A' also becomes mixed with (1)¹A₁ and (2)¹A₁. Conspicuously, these new contributions to ¹E → ¹A' (32% in total) are far more significant than the nearly undetectable mixing of A'' type triplet states, which can be traced back to the identical Slater determinants in (1)¹E_y and (1)¹A₁, see Fig. 1c.

Altogether, the composition of singlet and triplet states is analogous to the many-body picture of NV center³⁹, albeit the degree of multireference character of singlets is considerably higher, which has an important effect on the transition rates.

Energy levels of electronic states

The energy level positions of the studied electronic states on relaxed geometries, relative to the ground state of ³A₂, are shown in Fig. 2. We note that a detailed discussion of these relaxations, including *C_{3v}* symmetry conserving relaxation and symmetry breaking Jahn-Teller relaxation, can be found in Tab. S2–S3 of the Supplementary Information (SI). Based on our

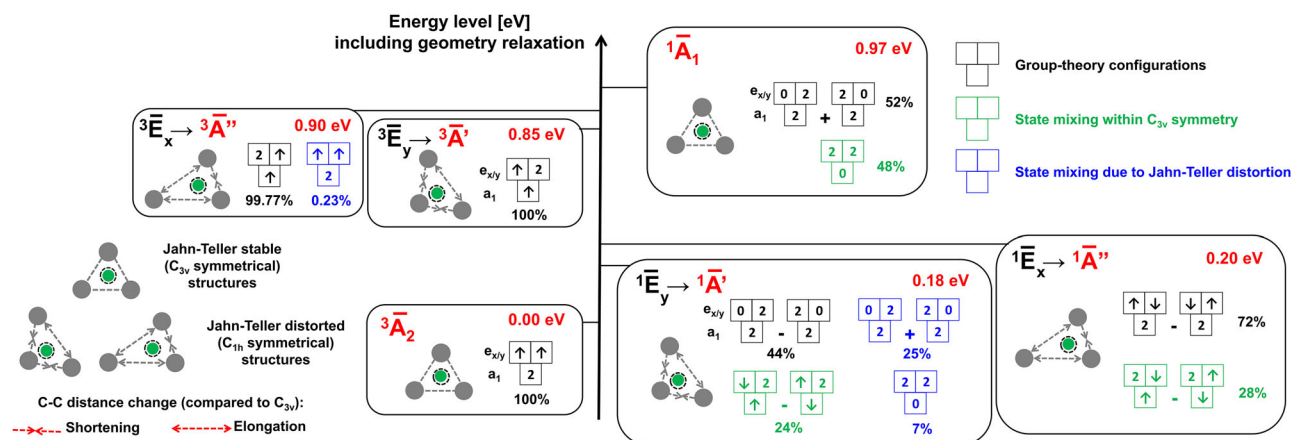


Fig. 2 | Many-body composition (on the basis of canonical $e_{x/y}$ and a_1 orbitals) and energy level of the lowest-lying electronic states of CIV in 4H-SiC, computed at CASSCF-NEVPT2 level of theory. Black, green, and blue color orbital

occupation patterns indicate group-theory configurations, state mixing within C_{3v} symmetry, and state mixing related to Jahn-Teller distortion, respectively.

wavefunction theory calculation, the lowest energy triplet excited state $^3\bar{A}'$ is located at 0.85 eV, giving rise to a ~ 1460 nm ZPL emission for the kk configuration of the CIV center. This value confirms S-band telecom emission and corresponds well to our previously reported DFT calculations²¹. Furthermore, the small difference (≈ 50 meV) between the two excited energy levels indicates dynamic Jahn-Teller behavior, analogously to the corresponding 3E state of NV center in diamond⁴⁴.

Our multireference calculations can be used to position the singlet states. The lowest-lying singlets, $^1\bar{E} \rightarrow ^1\bar{A}'$ and $^1\bar{E} \rightarrow ^1\bar{A}''$ are located 0.18 and 0.20 eV above the ground triplet, respectively. Similar to the triplet excited state, dynamic Jahn-Teller character was found at the CASSCF-NEVPT2 level of theory. The third singlet state, $^1\bar{A}_1$ lies at 0.97 eV, which is slightly (0.07–0.12 eV) above the level of $^3\bar{E}$ state. We emphasize that this energy difference is comparable to the expected error margin of our wavefunction theory calculations.

Transition rates between electronic states

Having all equilibrium geometries and energy levels at hand, we fitted 1D effective phonons to all possible transitions among the six identified low-lying electronic states. Applying Fermi's golden rule by the equations described in SI, section S1.5, we were able to estimate all photoluminescence, intersystem crossing, and internal conversion rates. These results are visualized in Fig. 3, with more details on numerical results, such as transition matrix elements, displacements, and effective phonon energies, in Tab. S4 of SI.

Firstly, let us discuss the spin conserving relaxations ($^3\bar{E} \rightarrow ^3\bar{A}_2$ for triplets, $^1\bar{A}_1 \rightarrow ^1\bar{E}$ for singlets). In the triplet sector, this process is radiation-dominated ($\tau_{PL} = 50$ ns). This can be traced back to the high transition dipole moment, ≈ 7 Debyes, facilitating PL as well as the negligible triplet wavefunction mixing, 0.23% 3A_2 in $^3A'$, see Fig. 2, which drives a slow nonradiative internal conversion with a half-life in the range of seconds. The singlet-to-singlet conversion, on the other hand, comes with a remarkably fast IC ($\tau_{IC} = 2$ ns). The vast deviation from the triplet IC rate can be explained by the intensive state mixing through the pseudo Jahn-Teller effect between $^1\bar{A}_1$ and $^1\bar{A}'$, as indicated by the large weight of Jahn-Teller distortion-related singlet configurations in Fig. 2. Here, the competing photoluminescence, which occurs at a comparable rate to triplet-triplet radiative transition, is about two orders of magnitude slower ($\tau_{PL} = 130$ ns). We further note here that Fermi's golden rule assumes weak coupling between the initial and final states, which might not hold for the closely related $^1\bar{A}_1$ and $^1\bar{A}'$ species; therefore, in our opinion, the obtained non-radiative lifetime of 2 ns should be considered as an upper limit.

Apart from photon emissions and the $^1\bar{A}_1 \rightarrow ^1\bar{E}$ internal conversion, intersystem crossings (ISC) connecting the singlet-triplet spin sectors can

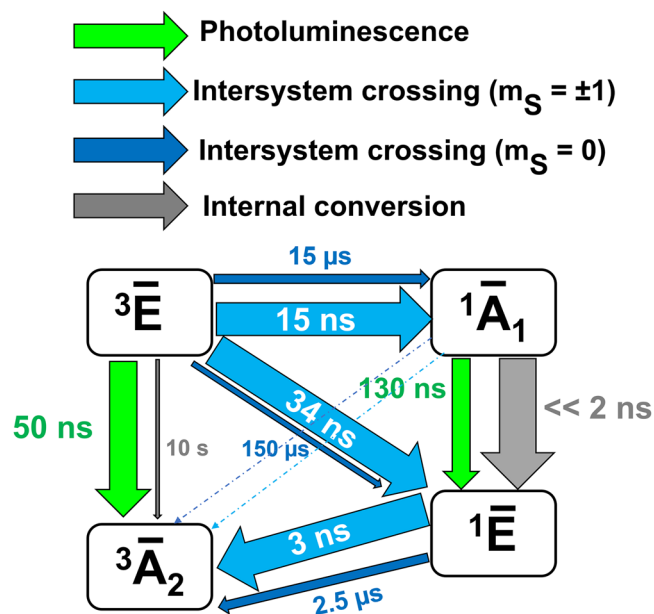


Fig. 3 | Calculated transition rates (given as half-lives) between the lowest-lying electronic states of CIV@4H-SiC.

also occur at a nanosecond timescale. The ISC processes of $^3\bar{E} \rightarrow ^1\bar{A}_1$, $^3\bar{E} \rightarrow ^1\bar{E}$ and $^1\bar{E} \rightarrow ^3\bar{A}_2$, which are driven by strong spin-orbit coupling matrix elements (10–40 GHz), proceed with half-lives of 15 ns, 34 ns, and 3 ns respectively. However, these fast rates only apply to the $m_S = \pm 1$ channel in the triplet state; the conversion to/from the $m_S = 0$ sublevel was calculated to be about three orders of magnitude slower in all three cases, owing primarily to the reduced parallel spin-orbit coupling matrix elements compared to the perpendicular $m_S = \pm 1$ case.

Emitter and qubit properties

For bright emission from the CIV defect, the $^3\bar{E} \rightarrow ^3\bar{A}_2$ transition should not be suppressed by alternative nonradiative relaxation routes. Based on our kinetic model, this requirement is fulfilled, i.e., the direct IC in the triplet sector has negligible rate, while ISC towards either $^1\bar{A}_1$ or $^1\bar{E}$ has at most similar rate to PL, even if we consider the kinetically favored ($m_S = \pm 1$) channel. This means that the photoemission is expected to be clearly detectable even from the $m_S = \pm 1$ sublevel of $^3\bar{E}$, albeit ISC might reduce the quantum yield to some extent. Furthermore, at $m_S = 0$ sublevel, PL is clearly

the dominant relaxation mechanism. In other words, $m_S = 0$ can be viewed as the “bright” state, in contrast to the “dark” $m_S = \pm 1$, which is more apt to relaxation via ISC.

Another important characteristic is the relative intensity of the ZPL in the emission spectrum, i.e., the Debye-Waller factor (DWF). Previous DFT work reported on a 1–3% DWF (depending on the configuration²¹), calculated for a single phonon connecting the geometry of the Jahn-Teller distorted excited state and that of the ground state. We hereby confirm this DWF range by CASSCF-NEVPT2 computations, see SI, Tab. S5, for details. Thus, the emission of phonons during PL also significantly reduces the quantum yield towards the desired narrow ZPL sign, but only to a similar extent to the case of NV center in diamond. However, we note that the DWF can be potentially increased by Purcell enhancement in SiC crystal cavities⁴⁵.

As for the singlet ($^1\bar{A}_1 \rightarrow ^1\bar{E}$) emission, our calculation suggests a similarly low DWF factor (0.7%). This PL is expected to be barely detectable, as IC is dominant, and even the remaining PL consists mainly of a broad phonon sideband.

As ISCs predicted for all triplet spin sublevels ($0, \pm 1$) with significant rates (ns- μ s timescale), we concluded from our results that an optical spin polarization cycle similar to that of the NV center in diamond is possible. Furthermore, the aforementioned dark and bright character of $m_S = \pm 1$ and $m_S = 0$ sublevels of $^3\bar{A}_2$, respectively, enable optical spin readout and also give rise to an ODMR signal.

In order to test the above hypotheses numerically, we calculated the time evolution of all electronic states by solving the kinetic master equation of the system, in the presence of continuous $^3\bar{A}_2 \rightarrow ^3\bar{E}$ laser pumping (see SI, section S7 for details). We found that the original Boltzmann distribution of ground-state spin sublevels is polarized towards a population of 90% $m_S = \pm 1$ after a time interval of 140 μ s. This relatively slow polarization rate can be traced back to the low transition rate from the $m_S = 0$ state to the singlet and the faster optical transition. These factors suppress the $m_S = 0 \rightarrow m_S = \pm 1$ transition, which allows little population transfer within a single optical cycle. Furthermore, high readout contrast (up to 40% brightness difference in $^3\bar{E} \rightarrow ^3\bar{A}_2$ photoluminescence) is expected in a microsecond-scale experiment where the distinction of pure $m_S = \pm 1$ and $m_S = 0$ is targeted. Finally, the continuous-wave ODMR contrast (i.e. the change of steady-state $^3\bar{E} \rightarrow ^3\bar{A}_2$ photoluminescence rate upon turning on a spin-resonant microwave (MW) field) is estimated to be 35%, with increased brightness in the presence of MW. We emphasize here that even though these numbers are directly comparable to experiments, the approximations applied in the rate calculations are only suitable for qualitative estimations regarding polarization, readout and ODMR behavior. We note that the kinetic model and its derived observables can be refined in the future based on single-defect measurements and/or higher-level ab-initio calculations.

Zero-field splitting parameters

Having shown evidence for the CIV in 4H-SiC to be ODMR active, its ODMR signal could be one of the most relevant characteristics for identification as it carries information on the unique fine and hyperfine structure of the ground state of the CIV center. To simulate the ODMR signal, we first calculate the ZFS of the CIV center. Even though D values on DFT level have been previously reported²¹, the calculations carried out in this work allow us to provide revised results. Indeed, the previous unrestricted DFT computations suffer from spin-contamination issues, which can be resolved by (i) CASSCF-NEVPT2 level zero-field splitting calculations, which also operate over restricted open-shell orbitals in quantum chemical programs, (ii) restricted open-shell (RO) Kohn-Sham formalism, (iii) spin decontamination corrections⁴⁶ on the previous unrestricted results. We recall that due to the single-reference character of $^3\bar{A}_2$, DFT is expected to be sufficiently accurate for this property.

For the cluster model with kk defect configuration, we obtain 1.34 GHz and 1.02 GHz at CASSCF-NEVPT2 and RO-DFT level, respectively. Similarly, the supercell model of Ref. 21 gives $D = 1.15$ GHz, taking into account spin decontamination, details on the revision of supercell DFT calculations can be found in section S5 of SI. While the methodologies differ

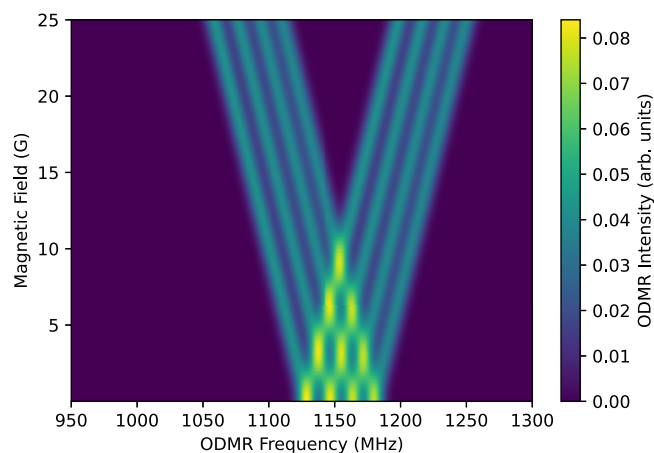


Fig. 4 | Microwave drive matrix element amplitudes of the CIV⁺ and Cl spin system for the kk configuration, incorporating ^{35}Cl . A Gaussian broadening term is applied in the frequency domain, using a smearing parameter of 5 MHz.

on the scale of 300 MHz, they fairly agree on a corrected range for the CIV ZFS parameters.

We present here a qualitative investigation into possible ODMR signatures for the CIV in 4H-SiC. With the spin parameters for the CIV center hyperfine coupling to the component Cl isotope from Ref. 21, which is dominantly a $I = 3/2$ nuclear spin, and updated ZFS tensors obtained in this work, an effective spin model of the CIV center electron spin and Cl nuclear spin can be constructed and diagonalized to reveal its possible microwave-driven transitions, see SI, section S6 for details.

Figure 4 shows our ODMR reconstruction for the kk configuration, in the given range showing the electron transition between $m_S = \pm 1$ and $m_S = 0$ levels of the CIV electron spin. We note that the Cl isotope spin quartet will contribute with a splitting of the signature origin by a multiple of its hyperfine, at ca. 15 MHz.

Finally, we comment on the comparison of Fig. 4 with the recently reported experimental ODMR sign of Ref. 24. Importantly, as Ref. 24 is an ensemble study, the obtained ODMR spectrum derives from multiple sources, which may include different configurations of the CIV center (if the proposed assignment²³ is correct) and/or any other defects with similar photoemission range. Still, it can be stated that some of the individual spectral features qualitatively resemble Fig. 4, except for the apparent absence of hyperfine splitting. In this regard, we note that it depends strongly on the experimental setup whether the hyperfine structure can be resolved. The reader is referred to Fig. S2 and Tables S6–S7 of SI for a more detailed discussion on the relation of the present theoretical results to ODMR experiments.

Summary

To summarize, we have investigated the lowest-energy electronic states of the CIV defect in 4H-SiC using multireference wavefunction theory. Our calculations strongly suggest that the defect is ODMR active and is therefore suitable for quantum computing and quantum sensing applications. In experiments, the defect can be identified based on its telecom-band ZPL (0.8–0.9 eV) and its ODMR sign corresponding to $D = 1.0$ –1.3 GHz zero-field splitting.

Methods

Wavefunction theory computations

We carried out wavefunction theory-level computations using the ORCA program⁴⁷, version 6.0.1. Sample input files are available in section S1 of SI.

For the time being, wavefunction-based quantum chemical calculations are mostly available for molecular models. Therefore, we modeled the structure of CIV⁺@4H-SiC defects by hydrogen terminated clusters, which were prepared as follows. In the first step, an Si atom was replaced by a

vacancy in a large 4H-SiC cell, the atomic positions in which were determined according to experiments. Then, we selected Si and C atoms in the order of the distance from the vacancy. Atoms within 3 chemical bond distance relative to the vacancy, along with the terminating H atoms and after a carbon $\rightarrow$ chlorine replacement, give our MODEL-1 (chemical formula: $\text{Si}_{12}\text{C}_{28}\text{H}_{64}\text{Cl}^+$; see SI, Fig. S1, left). This small cluster, which contains one layer of C and one layer of Si atoms around the innermost shell (i.e. C_3Cl), is only suitable for qualitative investigations (which were performed for the purpose of method development). Upon the expansion of the model by another layer of Si and another layer of C atoms, we arrive to MODEL-2 (chemical formula: $\text{Si}_{56}\text{C}_{95}\text{H}_{156}\text{Cl}^+$; see SI, Fig. S1, right), the size of which is, according to our previous works^{39,40}, sufficiently large to provide quantitatively correct results.

In 4H-SiC, the CIV defect can be constructed in four different configurations, i.e. kk , hh , kh , and hk ²¹. For computational efficiency and to convey the main message of this article, we only discuss the electronic structure of the kk configuration in detail. The quantitative description of other configurations will be presented elsewhere. We demonstrate, however, that the electronic structures of the hh , kh , and hk configurations are qualitatively the same, see Tab. S1 of SI.

We calculated the many-body wavefunctions for the electronic states of CIV^+ at state-average (SA) complete active space self-consistent field (CASSCF)^{48–50} level of theory, with NEVPT2 perturbation^{33,35,41,42} accounting for dynamic correlation.

Within CASSCF, we take all possible electron configuration patterns within a selected molecular orbital subspace into account. During the SA-CASSCF calculation, a two-step cycle of full configuration interaction (FCI) solution and orbital optimization (i.e. mixing active and external orbitals to minimize the average energy of the considered electronic states) is repeated until convergence. For the SA-CASSCF procedure, one needs to choose (i) the number of electronic states to be involved, (ii) the active orbitals, (iii) the number of electrons that occupy the latter orbitals in various patterns. Our considerations on these input parameters are detailed below.

As for the number of electronic states, we selected 3 triplet and 3 singlet roots. Namely, based on our initial density functional theory results²¹, we expected CIV^+ @4H-SiC to form analogous electronic structures to NV^- @diamond, where the spin polarization and spin-selective readout is realized via 3 triplet and 3 singlet low-lying states (3A_2 , $^3E_{x/y}$, $^1E_{x/y}$, 1A_1).

Next, let us consider the number of relevant orbitals. Upon the formation of a CIV^+ vacancy in the 4H-SiC lattice, 4 dangling orbitals are formed as linear combinations of partially occupied sp^3 orbitals of C and Cl atoms surrounding the vacancy. Nevertheless, it is not evident that this “chemically motivated” active space is the best suited for CASSCF-based methods. For example, the “dangling” sp^3 orbital of chlorine is deeply buried in the valence band, and is therefore expected to be inert in CASSCF calculations. Furthermore, non-dangling orbitals might also contribute to static correlation significantly.

For these reasons, we performed approximate CASSCF calculations on the full valence space of the atoms surrounding the CIV^+ defect (i.e. 2s and 2p shells of the innermost three C and three Si atoms, as well as the Cl atom), in order to rationally select the active space. We utilized the recently introduced iterative configuration expansion (ICE) method^{51,52} as an approximate CI solver, and ran the calculation on the atomic valence active space (AVAS)⁵³, prepared for the aforementioned atoms and atomic orbitals. This ICE-SCF calculation (48 electrons, 28 orbitals, 3 triplet and 3 singlet electronic states) revealed that only the a_1 , e_x and e_y orbitals possess significant fractional occupation numbers ($1.97 > \text{occ.} > 0.03$) in natural orbital basis. This result implies the reliability of a three-orbital active space.

On these three carbon-centered orbitals, 4 valence electrons of the innermost atoms are distributed; these are the “free” electrons that are not involved in covalent C-Si and Cl-Si bonds or in the chlorine localized $a_1^{(\text{low})}$ orbital (1 free electron from each of the three C atoms adjacent to the vacancy; 2 free electrons from Cl; 1 electron is subtracted due to the net positive charge). Altogether, we arrive at 4-electron (4e) 3-orbital (3e) CASSCF.

The SA-CASSCF(4e,3o) energy of the electronic states was corrected by dynamic correlation using 2nd order N-electron valence perturbation theory (NEVPT2). Among the different NEVPT2 implementations³⁴, we applied the so-called strongly contracted (SC) NEVPT2 method. The CASSCF-NEVPT2 results, especially the relative energy levels of electronic states, are known to be basis set dependent. Nevertheless, in our previous CASSCF-NEVPT2 study on the NV^- defect in diamond³⁹, we found that the use of the moderate basis set size of cc-pVDZ⁵⁴ is reasonable, as it practically recovers the basis set limit at cluster sizes comparable to MODEL-2. Therefore, we also kept the use of cc-pVDZ in this work.

If density fitting approximations are applied, which considerably accelerate the computation presented in this work at a negligible loss in accuracy, it is also mandatory to choose appropriate auxiliary basis sets. In our calculations, the construction of Coulomb- and exchange integrals during self-consistent field (SCF) procedures was carried out in the RIJCOSX⁵⁵ framework, with def2/J⁵⁶ auxiliary basis set. To speed up integral transformations from the atomic to the molecular orbital basis, which can be rate-determining in post-SCF quantum chemical calculations, density fitting was introduced with the cc-pVDZ/C⁵⁷ auxiliary basis set.

The geometry of the cluster model was optimized for each electronic state separately, at state-specific (SS) CASSCF(4e,3o) level. That is, the orbital optimization of the CASSCF procedure was performed exclusively for one selected electron configuration. C_s symmetry was assumed, at which the E_x and E_y states can be conveniently distinguished by setting two different irreducible representations (A' and A'' , respectively). We note that the SS-CASSCF energy minimization results in Jahn-Teller distorted C_s symmetrical minima for E states, while we obtain C_{3v} symmetrical geometries for A states, in line with group theory considerations. The coordinates of the optimized geometries of the clusters at each electronic state can be found in section S8.

The energy levels relative to the ground state ($(1)^3\bar{A}_2$) presented in Fig. 2 of the main text were determined as follows. In the first step, the energy levels at $(1)^3\bar{A}_2$ geometry were calculated, using NEVPT2 on top of a state-averaged CASSCF(4e,3o) wavefunction (3 singlet, 3 triplet roots). Secondly, relaxation within C_{3v} symmetry was calculated at state-specific CASSCF level. While the SS-CASSCF equilibrium geometry of A states has C_{3v} symmetry by construction, additional geometry optimization is required for E states to gain a C_{3v} symmetrical energy minimum. In the case of $(1)^3\bar{E}$ and $(1)^1\bar{E}$, we managed to locate the minimum-energy crossing point (MECP) of $\bar{E}_x$ and $\bar{E}_y$ by geometry optimization with 50–50% weighing, and the relaxation within C_{3v} symmetry constraint was studied on these structures. Thirdly, the energy contribution of Jahn-Teller distortion of E states was calculated, which is given by the energy difference between A'/A'' and MECP geometries at SS-CASSCF level. Tab. S3 of SI summarizes the results of relaxation-corrected CASSCF-NEVPT2 calculations, which altogether describe the relative energy levels comparably to experimental ZPLs.

The calculation of zero-field splitting parameters (D tensor, E tensor) requires spin-orbit coupled (SOC) and spin-spin coupled (SSC) states and their energy levels. In wavefunction theory, the SOC and SSC effects are introduced in a post-process manner, within the framework of the quasi-degenerate perturbation theory (QDPT)⁵⁸. The QDPT treatment assembles a SOC + SSC matrix from the non-relativistic CASSCF eigenstates (Ψ_I^{SM}) as

$$\langle \Psi_I^{SM} | \hat{H}_{\text{CASSCF}} + \hat{H}_{\text{SOC}} + \hat{H}_{\text{SSC}} | \Psi_J^{SM'} \rangle = \delta_{IJ} \delta_{SS'} \delta_{MM'} E_I^S + \langle \Psi_I^{SM} | \hat{H}_{\text{SOC}} + \hat{H}_{\text{SSC}} | \Psi_J^{SM'} \rangle \quad (1)$$

where the indices I/J , S/S' , and M/M' refer to the number of the CASSCF root, its spin state, and spin sublevel, respectively. Even though the spin sublevel dependence does not appear explicitly in non-relativistic CASSCF wavefunctions, it can be introduced by means of the Clebsch-Gordan coefficients, in accordance with the Wigner-Eckart theorem⁵⁹. In our study, the $\langle \Psi_I^{SM} | \hat{H}_{\text{SOC}} + \hat{H}_{\text{SSC}} | \Psi_J^{SM'} \rangle$ matrix elements are calculated between the previously obtained CASSCF roots using the spin-orbit mean-field (SOMF)

approximation⁶⁰. Finally, E_f^S in the above equation refers to the (non-relativistic) electronic energy at CASSCF-NEVPT2 level.

The diagonalization of the QDPT matrix yields the coupled states as eigenvectors and the respective energy levels as eigenvalues, from which the ZFS parameters can be extracted as energy differences. Importantly, since CASSCF implementations work in the restricted open-shell formalism (that is, the orbitals of α and β spin channels are equal), the spin-contamination issues of ZFS calculations, commonly observed for DFT⁴⁶, are avoided by construction.

Density functional theory computations

Supporting density functional theory (DFT) calculations were performed in the Vienna Ab-initio Simulation Package^{61,62} which implements Kohn-Sham DFT based on the projector-augmented wave method^{63,64}, starting from optimized geometries from Ref. 21, consisting of 576 atom 4H-SiC supercells. Calculations using the PBE functional⁶⁵ were performed on cells with dimensions of 18.56 Å along *ab* lattice directions and 20.25 Å along the *c*-direction. These calculations were performed with a 420 eV energy cutoff for the plane-wave basis set, with electron density and forces optimized with thresholds of 10^{-6} eV and 0.01 eV/Å, respectively, and using a $2 \times 2 \times 2$ Γ -centered *k*-point grid.

Revised ZFS values (summarized also in Tab. S6 of SI) were calculated at PBE-level with the spin de-contamination procedure of the unrestricted DFT⁴⁶. This technique involves eliminating the spin contamination by *D*-tensor subtraction by an average of the *D*-tensor of $S - 1$ states corresponding to the target spin *S* state, believed to cancel the spin-contamination present in all these states. We note, however, that the technique requires converging several singlet states using the constrained-occupation approach and calculating their (non-spin-scaled) ZFS parameters, which can be challenging at the risk of switching the orbital order, as DFT inherently tries to find the lowest-energy state. Therefore, the ZFS parameters for the singlet states, with the exception of the *kk* configuration, were instead obtained using the frozen wavefunctions in the 3A_2 ground state. We also note that non-spin-scaled ZFS tensors were calculated via a modified binary, allowing for such calculations even in the singlet-spin case.

Transition rate estimation

The relaxation pathways, initiated by the photonic excitation of the CIV⁺ defect, involve the combination of PL, IC and ISC. Fermi's golden rule can be applied to all three transitions⁶⁶, according to which the rate of transition, *k*, which occurs as a jump between two energetically close phonon levels (*n, m*) of the initial (*i*) and final (*f*) electronic states, is proportional to i) the overlap of the phonon wavefunctions (ψ_n, ψ_m), ii) the strength of coupling between the electronic wavefunctions (Ψ_i, Ψ_f).

$$k_{in \rightarrow fm} = \frac{2\pi}{\hbar} |\langle \Psi_i \Psi_n | \hat{H}_c | \Psi_f \Psi_m \rangle|^2 \delta(E_{in} - E_{fm}), \quad (2)$$

In the expression above, $\hat{H}_c$ represents the Hamiltonian that couples the initial electron-phonon product wavefunction (*in*) to the final state (*fm*), while the Dirac delta of $\delta(E_{in} - E_{fm})$ stands for the energy conservation law between these states.

Taking into account that the transition process involves all possible phonon state transitions, the full rate arises as

$$k_{i \rightarrow f} = \sum_{n,m} p_n(k_{in \rightarrow fm}), \quad (3)$$

where p_n is the temperature-dependent Boltzmann factor of the *n*th phonon level. However, at low temperatures, the sum over *n* can be neglected and it is a reasonable assumption that practically all transitions occur from the zero-point vibrational level of *i*.

In this work, we apply the 1D effective phonon approximation⁶⁷, where the transition occurs on the reaction coordinate connecting the equilibrium geometries of the initial and final state. Consequently both *i* and *f* possess

only one vibrational mode, along which the coupling was assumed to change linearly (Herzberg-Teller formalism). An advantage of this approach is that computation of rate constants requires only two single-point calculations, i.e. one at the initial and one at the final geometry.

We note here that dynamic Jahn-Teller systems ($^3\bar{E}, ^1\bar{E}$) require additional treatment as they continuously rotate around the high-symmetry point via their $\bar{A}'$ and $\bar{A}''$ states and therefore do not possess a well-defined equilibrium geometry; in these cases, we calculated all conceivable single-phonon routes involving the previously optimized Jahn-Teller distorted geometries, and searched for the maximal possible rate.

For practical considerations, the δ function, which corresponds to a Dirac delta in Fermi's original formulation, was replaced by a Gaussian function.

$$\delta(E_{in} - E_{fm}) \approx (\sqrt{2\pi}\eta)^{-1} e^{-\frac{(E_{in} - E_{fm})^2}{2\eta^2}}, \quad (4)$$

Herein, the square root of variance is represented by a "linewidth" η , which we set to be equal to the effective phonon energy of the final state, in accordance with the general recommendations for Fermi's golden rule⁶⁸.

The formulation of ISC, IC and PL rates under these constraints^{69–72} is detailed below.

Considering the rate of intersystem crossing, corresponding to the relaxation of an excited state towards a state of another multiplicity (triplet-to-singlet conversion, or vice versa), Fermi's golden rule is obtained as

$$k_{ISC, i \rightarrow f} = \sum_m \frac{2\pi}{\hbar} \delta(E_{i0} - E_{fm}) \cdot \left| \int_{Q=-\infty}^{Q=+\infty} \psi_{i0}(Q) \psi_{fm}(Q) \lambda_{if}(Q, m_S) dQ \right|^2. \quad (5)$$

ψ here becomes explicitly dependent on the reaction coordinate (*Q*), and can be analytically calculated assuming the harmonic movement of the nuclei. The spin-orbit coupling matrix element, λ_{if} , which is to be determined between the electronic wavefunctions of excited and ground states, characterizes the probability of transition. In general, this is also a reaction coordinate dependent parameter. Furthermore, λ also depends on the spin sublevel (m_S) of the triplet state: $m_S = \pm 1$ and $m_S = 0$ behave as two competing channels of ISC, the relative rate of which gives rise to the spin polarization cycle and the ODMR sign. Accordingly, the matrix elements are often distinguished in the literature as $\lambda_{\perp}$ and $\lambda_{\parallel}$ for ± 1 and 0 sublevels, respectively.

Fermi's golden rule for photoluminescence is somewhat analogous to that for ISC, but additional terms appear due to account for the photon emission,

$$k(\hbar\omega)_{PL, i \rightarrow f} = \sum_m \frac{1}{4\pi\epsilon_0} \frac{4\omega^3 n}{3\hbar c^3} \delta(E_{i0} - (E_{fm} + \hbar\omega)) \cdot \left| \int_{Q=-\infty}^{Q=+\infty} \psi_{i0}(Q) \psi_{fm}(Q) \mu_{if}(Q) dQ \right|^2, \quad (6)$$

where $\hbar\omega$ refers to the energy of the emitted photon, and μ_{if} is the electric transition dipole moment, which determines the probability of transition in the case of PL. Among the constants in the prefactor, *n* stands for the refractive index of the environment ($n = 2.56$ for 4H-SiC at ≈ 1550 nm wavelength), while ϵ_0 and *c* are familiar universal constants (vacuum permittivity, speed of light).

The above phonon energy dependent partial rate (the dimension of which is $\frac{1}{\text{energy} \times \text{time}}$) is integrated over the full spectrum to obtain the final PL rate. Thus, the overall rate of photoluminescence is

$$k_{PL, i \rightarrow f} = \int_0^\infty k(\hbar\omega)_{PL, i \rightarrow f} d(\hbar\omega). \quad (7)$$

The rate of internal conversion is determined by the nonadiabatic coupling matrix elements, but Fermi's golden rule can also be rewritten based on the overlap (S) of electronic wavefunctions (Ψ):

$$S_{if}(Q) = \langle \Psi_i(Q=0) | \Psi_f(Q) \rangle, \quad (8)$$

In the expression above, $Q = 0$ corresponds to a reference nuclear configuration, which is typically chosen as the initial or final equilibrium geometry. Using S_{if} and the electronic energy change of the IC process (ΔE_{if}), the rate can be expressed as^{71,73}

$$k_{IC,i \rightarrow f} = \sum_m \frac{2\pi}{\hbar} \Delta E_{if}^2 \delta(E_{i0} - E_{fm}) \left| \int_{Q=-\infty}^{Q=+\infty} \Psi_{i0}(Q) \Psi_{fm}(Q) S_{if}(Q) dQ \right|^2. \quad (9)$$

We note that the overlap was estimated based on the coefficients of individual determinants in the CASSCF wavefunction. Both the initial and the final wavefunction was requested in canonical orbital basis, for the sake of compatibility across different geometries.

ODMR matrix elements

Evaluation of the microwave drive matrix elements for a qualitative estimation of the ODMR signal, shown in Fig. 4, was done as follows. The Hamiltonian of the CIV⁺ and Cl spins is constructed as

$$H = g_e \mu_B \vec{S} \cdot \vec{B} + g_{Cl} \mu_N \vec{I} \cdot \vec{B} + \vec{S} \vec{D} \vec{S} + \vec{S} \vec{A} \vec{I}, \quad (10)$$

containing, in order, the electron and nuclear Zeeman contributions with the electron and Cl nuclear spin g -factors, the ZFS and the hyperfine interactions, involving electron $S = 1$ spin operators, $\vec{S} = (S_x, S_y, S_z)$ and nuclear Cl $I = 3/2$ spin operators, $\vec{I} = (I_x, I_y, I_z)$. We used the ZFS parameters calculated in this work, while hyperfine parameters were taken from Ref. 21. We assume a spin defect g -factor equal to the Landé g -factor. While the Cl species in the defect is either ³⁵Cl or ³⁷Cl, both exhibiting an $I = 3/2$ nuclear spin, the results in these works were produced for ³⁵Cl. These chlorine species differ mainly in the nuclear g -factor ($g_{35} = 0.5479162$ and $g_{37} = 0.4560824$) which enters into the nuclear Zeeman contribution and as a scaling factor to the DFT hyperfine tensor obtained from the electron density⁷⁴. We therefore note that switching from the more abundant ³⁵Cl (ca. 76%) to ³⁷Cl (ca. 24%), the hyperfine and the size of the Zeeman splitting is expected to decrease by ca. 20%.

The Hamiltonian of eq. (10) is diagonalized at several magnetic field vectors, and the eigenvalue difference for states ϕ_i and ϕ_j are weighted by the matrix element of these states for the exchange operator

$$O_{ij}(\vec{B}) = \langle \phi_i(\vec{B}) | S_x \otimes I + I \otimes I_x | \phi_j(\vec{B}) \rangle. \quad (11)$$

Gaussian smearing was incorporated in the ODMR frequency to describe experimental precision and quantum-enforced uncertainty, giving a qualitative ODMR estimate, $\mathcal{I}$, as

$$\mathcal{I}(\vec{B}, \omega) = \sum_{i>j} |O_{ij}(\vec{B})| e^{-(\omega - |E_i(\vec{B}) - E_j(\vec{B})|)^2 / 2\sigma^2}, \quad (12)$$

with smearing parameter σ .

CIV kinetic model

The kinetic spin model of the CIV⁺ is obtained by constructing a master equation on the form

$$\begin{aligned} \frac{d\rho}{dt} = & -\frac{i}{\hbar} [H, \rho] + \sum_i \gamma_{ABS} \mathcal{L}_{ABS}^i + \sum_i \gamma_{PL}^i \mathcal{L}_{PL}^i \\ & + \sum_i \gamma_{IC}^i \mathcal{L}_{IC}^i + \sum_{ij} \gamma_{ISC}^{ij} \mathcal{L}_{ISC}^{ij}, \end{aligned} \quad (13)$$

which incorporates the predicted interstate transition rates γ_{PL}^i , γ_{IC}^i , γ_{ISC}^i as Lindbladian terms

$$\mathcal{L}^i(\rho) = L_i \rho L_i^\dagger - \{\rho, L_i^\dagger L_i\}, \quad (14)$$

with corresponding jump operators L_i between the spin-energy states of the transition. The effect of the laser applied to excite the defect is treated similarly with an artificial photon absorption rate γ_{ABS} , facilitating transitions from the ³A₂ ground state to the excited ³E states. The defect spin system is represented as a single quantum object incorporating each energy level, writing the density matrix on the form

$$\begin{aligned} \text{diag}(\rho) = & \underbrace{(\rho_{g,+1}, \rho_{g,0}, \rho_{g,-1})}_{S=1, {}^3\bar{A}_2}, \underbrace{(\rho_{e1,+1}, \rho_{e1,0}, \rho_{e1,-1})}_{S=1, {}^3\bar{A}''}, \\ & \underbrace{(\rho_{e2,+1}, \rho_{e2,0}, \rho_{e2,-1})}_{S=1, {}^3\bar{A}'}, \underbrace{(\rho_{se,0})}_{S=0, {}^1\bar{A}_1}, \underbrace{(\rho_{sg1,0})}_{S=0, {}^1\bar{A}''}, \underbrace{(\rho_{sg2,0})}_{S=0, {}^1\bar{A}'}, \end{aligned} \quad (15)$$

forming a 12-level quantum system with the triplet ground state (g), excited and JT-split triplet states ($e1, e2$), the singlet excited (se) and singlet JT-split metastable states ($sg1, sg2$). The Hamiltonian is also described as

$$\begin{aligned} H = & D_g(|g, -1\rangle\langle g, -1| + |g, +1\rangle\langle g, +1|) \\ & + \Omega \cos(\omega t)(|g, -1\rangle\langle g, 0| + |g, 0\rangle\langle g, +1| \\ & + |e, -1\rangle\langle e, 0| + |e, 0\rangle\langle e, +1| + c.c.), \end{aligned} \quad (16)$$

including the zero-field splitting of the ground state, D_g , determined from the kk ZFS result from Table S6, and a variable microwave drive with amplitude Ω and frequency ω acting on the ground state.

For PL simulations, the total emission rate is calculated as

$$I_{PL} = \sum_i \gamma_{PL}^i \rho_{e1,i} + \gamma_{PL}^i \rho_{e2,i}. \quad (17)$$

This model was used in this work to simulate the defect polarization process starting from a fully mixed state, spin state readout when starting fully polarized in either the $m_s = 0$ or equal mix of $m_s = \pm 1$, and finally the ODMR when applying the microwave drive in the PL process, defining the ODMR contrast as $C_{ODMR} = (R_w(t) - R_{wo}(t)) / (R_w(t) + R_{wo}(t))$, where $R_{w/wo}$ is the emission rate with, and without, a microwave drive added to the model, respectively. For the free parameters of absorption rate and microwave drive amplitude, we used $\gamma_{ABS} = 5$ MHz and $\Omega = 4$ MHz, for which the result was saturated with respect to each parameter, as well as $\omega_i = D_g$ for fully resonant ODMR signal. The reader is referred to Section S7 of the SI for further details on simulation results.

Data availability

The main data supporting the findings of this study are available within the paper and its Supplementary Information. Further numerical data are available from the authors upon reasonable request.

Code availability

The self-developed scripts for evaluation of harmonic oscillator overlaps, integration and evaluation of Fermi rule rates are made available at <https://github.com/oscarlindbul/Defect-Rate-Estimator> for the interest of the reader.

Received: 19 December 2025; Accepted: 21 April 2026;

Published online: 07 May 2026

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Acknowledgements

We thank Danial Shafizadeh, Ivan G. Ivanov, and Tien Son Nguyen for the fruitful discussions. Z.B. acknowledges the financial support of Janos Bolyai Research Fellowship of the Hungarian Academy of Sciences. J.D. acknowledges support from the Swedish Research Council (VR) Grant No. 2022-00276. We acknowledge support from the Knut and Alice Wallenberg Foundation (Grant No. 2018.0071 and 2025.0264). I.A.A. is a Wallenberg Scholar (Grant No KAW 2023.0309). This research was supported by the National Research, Development, and Innovation Office of Hungary within the Quantum Information National Laboratory of Hungary (Grant No. 2022-2.1.1-NL-2022-00004) and within grant FK 145395. This project is funded by the European Commission within Horizon Europe projects (Grant Nos. 101156088 and 101129663). We acknowledge the support of the European Union under Horizon Europe for the QRC-4-ESP project (Grant Agreement 101129663) and the QUEST project (Grant Agreement 101156088). The computations were enabled by resources provided by the National Academic Infrastructure for Supercomputing in Sweden (NAISS), partially funded by the Swedish Research Council through grant agreement no. 2022-06725. The computations were enabled by resources provided by the National Academic Infrastructure for Supercomputing in Sweden (NAISS) and the Swedish National Infrastructure for Computing (SNIC) at NSC, partially funded by the Swedish Research Council through grant agreement no. 2022-06725 and no. 2018-05973. We also acknowledge the Digital Government Development and Project Management Ltd. for awarding us access to the Komondor HPC facility based in Hungary.

Author contributions

Z.B. and O. B.-L. carried out the calculations, prepared the figures and wrote the main manuscript text. J.D., V.I. and I.A supervised the work. All authors reviewed the manuscript.

Funding

Open access funding provided by Linköping University.

Competing interests

J.D. and I. A. A. declare a potential conflict of interest in relation to the intellectual property associated with this research and a pending patent application. The manuscript investigates the CIV defect, which be the cause of the general effect described in the patent application titled: “A quantum information processing device, a quantum communications network and a quantum computer” (patent pending; appl. no. 2550928-2; inventors: Joel Davidsson, Danial Shafizadeh, Ivan Ivanov, Igor Abrikosov). The other authors declare no competing interests.

Additional information

Supplementary information The online version contains supplementary material available at <https://doi.org/10.1038/s41535-026-00888-2>.

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