

Interaction between shallow NV^- centers and spin-active azafullerenes on hydrogenated and fluorinated diamond (001) surfaces

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The interaction between surface-lying nitrogen-substituted fullerenes (radical azafullerene, $C_{59}N^\bullet$) with subsurface negative nitrogen-vacancy complexes (NV^-) in diamond is investigated using first-principles calculations. We consider (2×1) reconstructed (001) oriented diamond surfaces with both H- and F-surface termination. The charge stability of NV^- when in close proximity to both the nearby surface and the spin active azafullerene is discussed, in the context of diamond band bending arising from surface-induced changes in electron affinity (EA). In the case of the hydrogenated surface, the system spin is quenched, yielding a negatively charged azafullerene ($C_{59}N^-$) and neutrally charged NV^0 as the most stable electronic configuration. In contrast, fluorinating the surface favors the negatively charged NV^- and conserves the $C_{59}N^\bullet$ neutrality and stabilizes uncompensated free spins. This opposing behaviour is attributed to surface charge doping emerging from different band bending effects associated with the surface EA. This study is consistent with experimentally observed photoluminescence quenching, and shows that surface passivation by fluorination could efficiently tackle the problem of charge transfer between adsorbed molecules and shallow NV centers.

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I. INTRODUCTION

Nanomaterials and molecular systems have successfully achieved important milestones in magnetism and quantum information processes (QIP) in recent years [1,2]. Semiconducting carbon-based nanomaterials such as epigraphene, nanotubes, and fullerenes are of interest for QIP since they are capable of exhibiting both localized long-lived coherent spin states, as well as high-mobility conductivity [3,4]. Notable among these are endohedral fullerenes, carbon cages containing trapped species within them, such as $N@C_{60}$. The nuclear spin states of the trapped nitrogen atom can serve as storage for quantum information, and a delocalized electron over the cage as a read/write probe [5]. $N@C_{60}$ shows competitive longitudinal (T_1) and dephasing (T_2) nuclear spin decoherence times already at room temperature, satisfying one of the important criteria for effective QIP candidates [6,7]. However, its low production yield and complicated purification procedures

are the two main limiting factors that hinder further development in that direction.

An alternative fullerene platform is the paramagnetic azafullerene $C_{59}N$, where substitution of a carbon by a nitrogen atom in Buckminsterfullerene, C_{60} , breaks a C–C π bond. This leaves a free valence electron which is predominantly localized in the vicinity of the C–N bond Fig. 1(b). This symmetry breaking splits the degenerate states of C_{60} (h_g , g_g , h_u etc.) into a spread of eigenstates energetically close to Buckminsterfullerene associated states. In particular, the triply degenerated t_{1u} lowest unoccupied molecular orbital (LUMO) state splits, trapping the radical electron and creating a semi-occupied molecular orbital (SOMO). Electron paramagnetic resonance (EPR) investigations of this SOMO, through photolysis in a CS_2 solvated liquid phase or by thermolysis in its dried solid state, corroborate the unpaired spin localization next to the N-site and report outstanding T_1 , T_2 , and an electronic spin lifetime [8–13]. These properties are a good starting point for any application, but effective spin control of such molecular systems requires good control over the system geometry in either one or two dimensions. Recent studies have shown how to engineer an assembly of such molecular radical entities by depositing $C_{59}N^\bullet$ directly onto an (111)Au surface or a [10]CPP molecular monolayer template, while still conserving the spin active character of the system [14,15].

To read-out locally the single molecular spin properties we could use a negatively charged nitrogen-vacancy (NV^-)

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defect in diamond. This impurity has been successfully used as a nanometric probe in magnetometry and biosensing as well as for single-photon generation for QIP [16–18]. NV^- consists of a substitutional nitrogen (N_s) impurity neighboring a carbon vacancy in the diamond lattice and an additional captured electron. Typically, N_s concentration control is performed through ion implantation and the vacancies are made mobile with an annealing process to create a stable NV defect structure. Electronically, the center consists of an N_s lone pair, the three electrons originating from the unpaired carbon orbitals neighboring the vacancy, and an electron captured from a nearby substitutional donor (usually P or N). This creates four electronic states ($\{a'_1, a_1, e_x, e_y\}$) containing six electrons. The a'_1 orbital lies in the diamond valence band, while the four remaining electrons populate the singlet a_1 and doublet e_x, e_y gap states. In the most stable $^3A_2$ symmetry, the defect has a total spin of $S = 1$. These highly localized states lying deep inside the wide diamond gap are well decoupled from the host lattice and can be treated as an isolated system. This enables the use of fluorescence to access the NV^- electron spin resonance (ESR) and to optically detected magnetic resonance (ODMR) response. Bringing this defect closer to a source of magnetic noise (spin active systems), one can perform magnetometry and/or relaxometry with high sensitivity and spatial resolution. Promising experimental studies have demonstrated that NV^- centres are indeed sensitive to surface spins [19,20]. Notably, Pinto *et al.* have successfully shown that the ODMR of NV^- in bulk diamond is capable of detecting multilayer surface deposited N@C₆₀ [21]. This result provides a working proof of principle that NV^- can indeed act as a read-write atomic-size element for fullerene-based QIP.

However, surface effects are important when performing measurements with shallow NV^- defects. The main property at play is the electron affinity (EA); it describes how much a system stabilises over an electron gain, here defined as the difference between the vacuum level and the conduction band minimum of the diamond. It is expressed through an electronic band bending effect at the surface interface. This has been extensively studied for both H- and F-terminated surfaces for a large variety of surface orientations and reconstructions [22–34]. The electron affinity is known to influence the interaction of the diamond with on-surface molecules, as it may promote charge transfer between the substrate and the adsorbent. In the case of NV charge states, it translates as a conversion between NV^- and NV^0 where only the former can be utilized in NV magnetometry measurements. As a possible mitigation approach to avoid charge quenching of shallow NV^- centers, wetting of the diamond surface has been suggested [35].

Probing the spin state of $\text{C}_{59}\text{N}^\bullet$, adsorbed on a diamond surface, requires two main conditions to be fulfilled: (1) the use of shallow NV^- centers to achieve suitable sensitivity while (2) maintaining the NV^- charge integrity intact. Because of the high electron affinity of fullerenes, it is not easy to satisfy both conditions at the same time. Moreover, the wetting of the diamond surface approach [35] is not applicable in such cases as fullerenes are poorly soluble in water.

In this density functional theory (DFT) study we investigate the coupling of $\text{C}_{59}\text{N}^\bullet$ to shallow NV^- centers when

the former are adsorbed on the surface of nanodiamonds. Such calculations are usually computationally prohibitive due to their complexity and low symmetry, requiring large cell sizes. In the current study we circumvent this problem by using smaller wave-function basis sets to describe (001)-oriented diamond surfaces in “slab” calculations. Notably, we model H- and F-terminated surfaces and explore the electronic stability of the surface deposited spin active molecule $\text{C}_{59}\text{N}^\bullet$, considering a shallow NV^- below.

II. METHOD

DFT investigations were carried out using the *aimpro* package, a localized orbital electronic structure code [36–38]. Exchange-correlation was described using the generalised-gradient approximation (GGA) via the Perdew-Burke-Ernzerhof (PBE) functional [39] coupled with D2-Grimme long-range dispersion corrections [40]. Relativistic Hartwigsen-Goedecker-Hutter (HGH) pseudopotentials were used to describe the core electrons [41]. Brillouin zone sampling was handled with the Monkhorst-Pack scheme using $n \times n \times n$ or $n \times n \times 1$ k -point grids [42].

A similar approach has been previously and successfully applied to model both $\text{C}_{59}\text{N}^\bullet$ [12–14] and NV^- in diamond [43–45]. The plane-wave energy cutoff for charge density was set to 175 Ha in all calculations. A Fermi distribution function is used to fill the levels to help with convergence, with an effective temperature of the electronic system of $k_B T = 0.025$ meV.

Calculations were considered self-consistent and converged when the self-consistent energy difference, total energy, and position change between two iterations was less than 10^{-6} Ha, 10^{-6} Ha, and 10^{-5} a.u., respectively.

Following this scheme, isolated $\text{C}_{59}\text{N}^\bullet$ was geometrically converged in a large cell ($a = c = 15.9$ Å) to avoid interaction between molecules in neighboring cells (eigenfrequencies were checked to ensure the minimum in energy was reached). In the case of three-dimensional (3D) bulk-like supercells, all atoms were allowed to move in the geometric optimization before any further analysis. For two-dimensional (2D) slabs, all atoms were allowed to move to optimize the slab structure. After this, all atoms were fixed when NV^- was introduced, except those directly associated with the defect, i.e., N_s and the vacancy neighbors. For the heterosystems with an azafullerene on the diamond surface, all atoms were fixed except the NV and $\text{C}_{59}\text{N}^\bullet$ related atoms. Multiple initial fullerene positions and orientations were optimized to find the overall global minimum.

Figure 2 shows the modeled slab unit cells (383 atoms). They measure 1.4 nm in the x and y directions and are about 1-nm thick, with a 1.8-nm vacuum to ensure no interaction between the top slab surface (or the C_{59}N molecule) and the bottom surface of the next repeating slab. In the combined structure (443 atoms) the NV lies 0.45 nm (0.47 nm) from the surface and 0.65 nm (0.73 nm) from the azafullerene base for the hydrogenated (fluorinated) surfaces, respectively.

To reduce the computational cost of such large systems we describe the diamond slab C atoms with a wave-function basis set of 22 Gaussian-based function of s , p , and d character. For the fullerene we use a larger 38 function set due to its higher

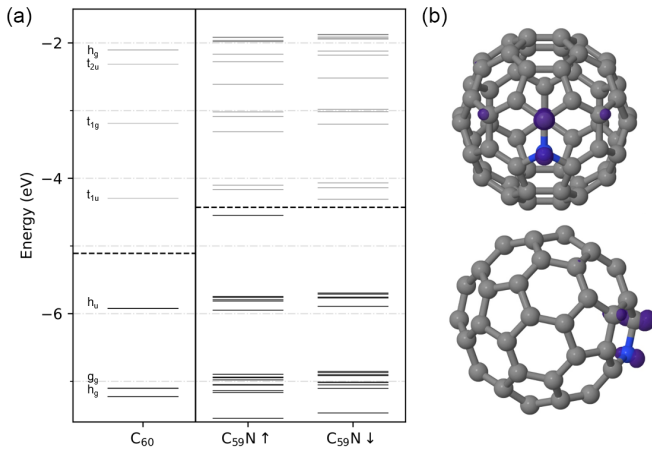


FIG. 1. The energies in (a) represent C₆₀ (left) and C₅₉N[•] (right) eigenstates with symmetries and spin orientation. Zero is set to the vacuum level of each molecule. Dashed lines correspond to respective Fermi levels. Full and faded bars show occupied and unoccupied states respectively. With (b) the C₅₉N[•] radical state wave function is shown: the visualization is done using jmol. Grey and blue spheres represent carbon and nitrogen atoms, respectively, while purple lobes show the wave-function isosurface with a 7.5 meV Å⁻³ cutoff.

degrees of freedom and the vacuum proximity. This basis set has previously been demonstrated to be reliable [12,13]

For periodic systems it is necessary to maintain overall charge neutrality in the cell. Therefore, to model a negatively charged NV defect, an equal and opposite uniform constant positive electric potential is applied throughout the cell. This approach is used for all negatively charged bulk and surface calculations, also when modeling C₅₉N, on both H- and F-terminated surfaces. No charge correction is applied on the charged systems, thus we take the relevant valence band maximum as reference to compare their energies. Mulliken analysis was used to generate density of states projected (pDoS) onto specific atoms or atom groups.

Rotating the C₅₉N, from pointing to the diamond surface to facing the vacuum, we find the configuration with the radical pointing towards the surface to be the most stable orientation. We then varied the C₅₉N[•] position above a H or F atom and two different hollow sites. The total system energy varied by only a few 10 meV, while not affecting the electronic configuration regardless of the choice of site.

Discussion concerning choice of functional

We note that the HSE06 exchange-correlation functional has been found to capture electronic properties of NV⁻ defects in bulk diamond with high accuracy, namely, the electronic band gap, zero phonon line (ZPL), and ionization energy [46,47]. The approach has also been successfully used to study diamond surfaces and the impact of different orientations and terminations on the NV⁻-gap states [24,48,49]. In contrast, the GGA-PBE method used here gives qualitative accuracy of the same physical values (ZPL) and can show significant discrepancy for properties such as band gap, and may, therefore, not seem an obvious choice. There are, however, a number of reasons GGA-PBE is adopted here.

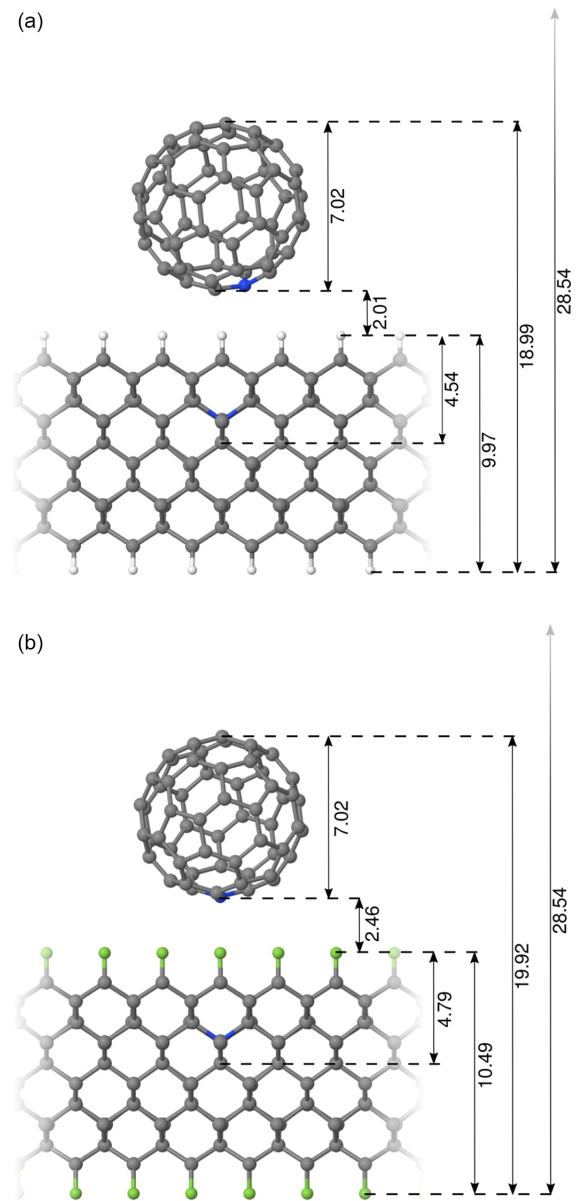


FIG. 2. Heterosystem geometries after complete structural optimisation for (a) hydrogenated and (b) fluorinated surface. Relevant *c*-axis lengths (Å): fullerene diameter and distance to the surface, slab thickness, NV defect distance to surface, total system width, and *c*-axis unit cell length (including vacuum).

The first is the prohibitive computational cost of HSE06 (typically from two to ten times slower than GGA-PBE depending on the basis-set type) which places such calculations beyond our available computational resources (the calculations already require a reduced basis-set size as mentioned above). The second concerns the choice of mixing and screening cutoff parameters within HSE which can be system dependent. In general for bulk systems the HSE06 functional works well. However, precautions have to be taken when describing systems with low dielectric constant, large surfaces, as well as for layered materials [50] and molecules. In these cases the screening lengths and resulting optimal parameters within the HSE functional are often quite different

TABLE I. Dispersion for a_1 (ω_a), e (ω_e) states and the splitting of the e states (E_{x-y}) for NV^- in different $n \times n \times n$ diamond supercells (meV). Bracketed literature values are calculated using LDA with large wave-function basis set for the carbon [43], rather than a smaller set used in our calculations.

Systems	ω_e	ω_a	E_{x-y}
$2 \times 2 \times 2$	760	233	387 (300)
$3 \times 3 \times 3$	86	146	86 (50)
$4 \times 4 \times 4$	18	33	14 (8)

from bulk. Unfortunately these are exactly the conditions in our current system, and it is not *a priori* clear how the mixing and screening parameter can be properly handled. Finding the appropriate computational parameters for different systems in this study to yield consistency and exactitude is far from trivial and beyond the scope of this work.

The GGA-PBE functional is sufficient for a qualitative exploration of this problem. It remains a highly used and versatile method, successfully applied to study point defects in bulk, layered, and slab systems: from the object of this study NV^- to metal impurities [51–54], different diamond orientations and surfaces, again with NV^- inside [55–57]. Related methods were previously successfully applied to determine molecular levels, hyperfine structure and geometry of C_{59}N radical molecules but using the local density approximation (LDA) [12,13,58,59]. While keeping in mind the gap underestimation and valid criticisms of GGA, it still nonetheless permits a broad range of study, geometric optimization, electronic band structure, hyperfine coupling [53,54], vibrational calculation [60], and formation energies while remaining consistent between those properties. For example, Neethirajan *et al.* used this methodology to successfully study diamond hydrogenated surface with NV^- inside, and the impact of water molecules on the NV charge under band bending considerations [35].

III. RESULTS

The computational model is initially benchmarked using an NV^- defect in bulk diamond and quantified in Table I, before creating 1-nm-thick (001) hydrogenated and fluorinated diamond slabs with lateral cell dimension choice based on the bulk system results. The electron affinity of the constructed surfaces is evaluated as well as the spin population over the system eigenstates through Mulliken analysis. Finally, the spin active $\text{C}_{59}\text{N}^\bullet$ is added to the surface, evaluating its stability and interaction with the NV^- centre. Calculated slab band gap, eigenstates energies of all NV^- electronic states for bulk diamond, H- and F- terminated surfaces, and heterogenous systems (with added C_{59}N) are summarized in Table II, with full details given in Table S4 of the Supplemental Material [61].

A. NV^- in bulk diamond

In all cases, we find NV^- defect with $S = 1$ in bulk diamond as the most stable configuration, see Fig. 3 where the

TABLE II. Calculated band gap (bulk) and slab band gaps E_g (eV), the maximum $e_\uparrow$ ($e_\downarrow$) splitting (meV) for bulk diamond as reference, followed by the NV^- with hydrogenated and fluorinated surfaces, and the combined system with $\text{C}_{59}\text{N}^\bullet$ molecule on the slab surface.

System	E_g	E_{x-y}
Bulk diamond	4.210	14(14)
NV^- H-terminated	4.347	97(146)
NV^- F-terminated	4.184	72(147)
$\text{C}_{59}\text{N}^- \perp \text{NV}^0$ H-terminated	4.463	13(125)
$\text{C}_{59}\text{N}^\bullet \perp \text{NV}^-$ F-terminated	4.134	74(172)

$4 \times 4 \times 4$ supercell (512 atoms) electronic band structure is shown together with associated NV molecular orbitals.

The maximum observed lifting of the e doublet (in both spin up and down) state degeneracy at a specific k -point, $E_{x-y} = 14$ meV, and the sizable dispersion of these electronic bands, $\omega(k)$ Table I, emerge due to the coupling between the NV^- defects in neighboring cells.

Typically interested in commercially available nanodiamonds in the ppm range, in this study we are well above that value (~ 2000 ppm). Additionally, those diamonds contain additional anisotropy sources that affect NV^- such as vacancies, substitutional atoms, or surface strains. Modifying the defect density can significantly alter E_{x-y} and ω .

Next, we study the impact of the defect-defect distance, i.e., the NV density, on the dispersion ω of the a and e states,

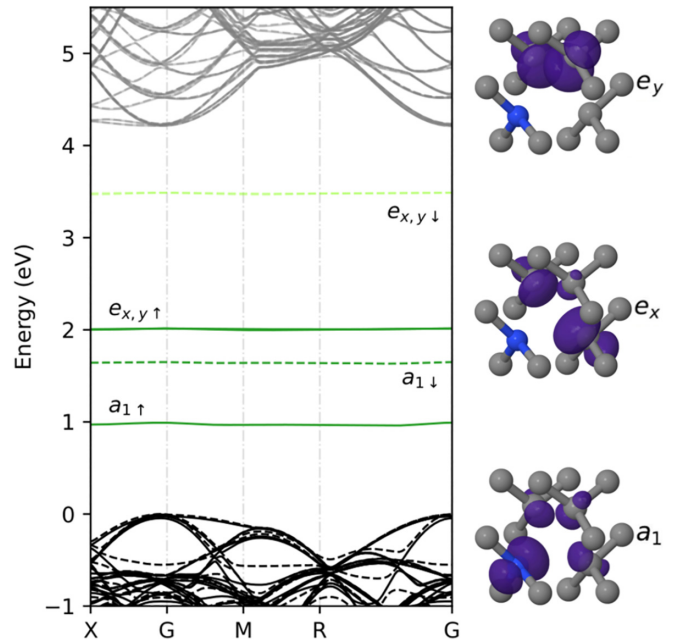


FIG. 3. Electronic band structure of NV^- within a $4 \times 4 \times 4$ diamond supercell. Zero is set to the top of the diamond valence band. Solid/dashed lines represent spin-up/-down electrons, respectively, while dark/faded lines showing filled/empty states, respectively. Black and green colors indicate bulk diamond and NV defect-related eigenstates. The wave-function isosurfaces of the a_1 and e states are shown with a $20 \text{ meV}/\text{\AA}^{-3}$ cutoff.

where ω_e is the largest dispersion between e_x and e_y Table I. As expected, we observe a decrease of both the dispersion and the splitting as the system size and defect spacing increase. Notably, the band splitting E_{x-y} follows closely the trends obtained with a larger wave-function basis-set-type of calculation [43], with only a negligible 6-meV difference between our calculations and the literature, for the largest comparable supercell (512 atoms). This agreement validates our choice of smaller carbon basis set to describe the diamond by reducing the computational cost while conserving the same accuracy. We note that in all bulk supercells the degeneracy is reduced to 0 in the Γ symmetry point.

Figure 3 shows the molecular orbital of each defect state, where the influence of the electronic bands dispersion is already included. The a_1 state shows its expected orbital composition, made of both the N lone-pair and the C- sp^3 orbitals. The e state should have purely C- sp^3 orbital character with e_x composed of two carbon orbitals, and e_y of three [62,63]. This description is also verified in our calculation when integrating the Kohn-Sham functions at Γ point. The slight asymmetry visible in the e_x state is due to dispersion caused by the finite cell size. The asymmetry is further exacerbated by the strain effects due to the defect-defect interactions.

B. NV⁻ and (2 × 1)-(001) hydrogenated diamond surface

Keeping the same defect-defect distance from the 4 × 4 × 4 bulk supercell (xy plane), we next construct a hydrogenated (2 × 1)-(001) diamond surface. The shallow defect is placed in the middle of the slab at a distance of 0.45 nm from the surface. Mulliken analysis demonstrates that the negative charge and unpaired electron population localize on the nitrogen and the vacancy neighbors (> 90%), respectively, similar to the bulk case discussed above. Figure 4 shows an E_{x-y} splitting increase to a maximum of 97 meV for the up and 146 meV for the down configurations. We note that the dispersion does not change, showing it comes solely from the defect density. The e states degeneracy is of a similar order of magnitude to the bulk 3 × 3 × 3 supercell. The surface strain induces an additional degeneracy lift of the e doublet over the entire Brillouin zone, even at the Γ point, which is in contrast to the impurity density related strain present and discussed for the bulk supercell.

To clarify the discussion we define a slab band gap which describes the band gap of the slab system or heterosystem. The difference between the bulk and slab band gap lies in the appearance of surface states when modeling diamond slabs. Studying these states are important and extended studies of hydrogenated and fluorinated slab surface states as been done using a different methodology [49,64]. Following the discussion in Sec. II, we do not make a detailed quantitative analysis of our results here, focusing instead on describing the electronic stability of our systems.

Hydrogenation of the surface does not introduce surface states deep into the slab band gap, as seen in other study (Rydberg states), which can be understood through our use of localised Gaussian based orbitals rather than plane waves. Nonetheless Mulliken analysis and pDoS on the first H layer confirms the presence of surface states at the bottom of the conduction band, consistent with the literature (see Fig. S5)

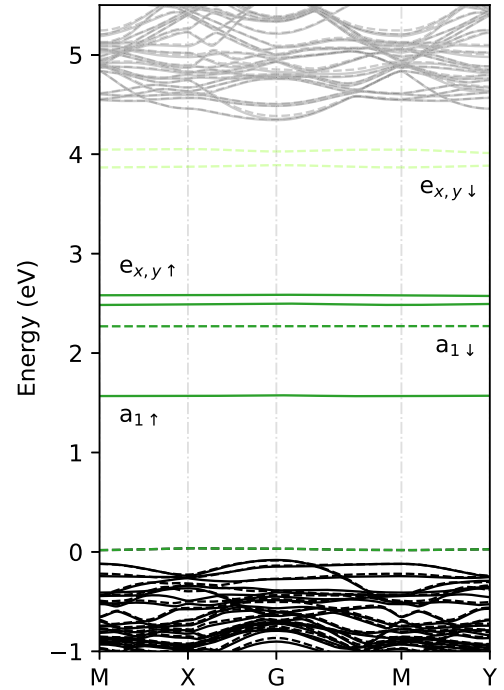


FIG. 4. Electronic band structure of (2 × 1)-(001) hydrogenated diamond surface with a single NV⁻ embedded in the center of the diamond slab. Zero is set to the top of the valence band. Solid/dashed lines represent spin-up/-down electrons respectively, while dark/faded lines showing filled/empty states, respectively. Black and green colors indicate diamond slab and NV defect-related eigenstates, respectively.

[61]. In our case they are not overlapping with the high-lying NV⁻ electronic states.

The proximity to the hydrogenated surface shifts the NV⁻ defect levels up in the gap by 0.5 to 0.6 eV (zero of energy set at the top of the valence band). Notably, while the a'_1 down state lies deep inside the valence band in bulk diamond, it emerges from the diamond valence band in this case.

The standard definition of the electronic affinity, $EA = E_{\text{vacuum}} - E_{\text{CBM}}$, where E_{vacuum} is the vacuum energy of the system and E_{CBM} is the conduction band minimum. Since GGA-PBE underestimates band gap values, for the hydrogenated slab we multiply E_{CBM} by 1.23, scaling the gap to the experimental diamond band gap, $E_g = 5.46$ eV. This gives a negative electron affinity (NEA) for the hydrogenated slab of -1.66 eV, which agrees well with literature [22–24,45]. We note that the slab band gap is 0.14-eV higher than the bulk value, which is another demonstration of the importance of hydrogenated surfaces for shallow NV⁻ centres in nanodiamonds. The upward shifts of the NV⁻ defect states as well as the increased band gap are closely linked to the NEA. This may have important consequences for potential charge transfer behavior at the surface when it is in contact with an adsorbed species. The NV⁻ proximity to the (2 × 1)-(001) hydrogenated surface influences the degeneracy but leaves the NV⁻ electronic configuration itself intact Fig. 4. We note that these variations have to be moderated by the quantum confinement imposed by these finite slabs.

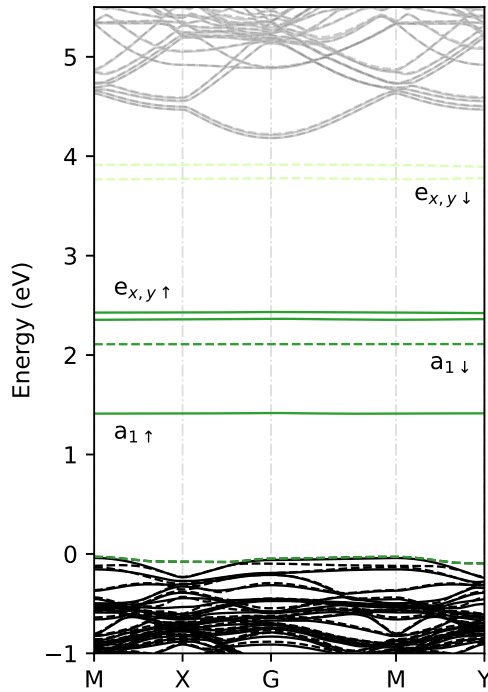


FIG. 5. Electronic band structure of (2×1) -(001) fluorinated diamond surface with a single NV^- embedded in the center of the diamond slab. Zero is set to the top of the valence band. Solid/dashed lines represent spin-up/-down electrons, respectively, while dark/faded lines showing filled/empty states, respectively. Black and green colours indicate diamond slab and NV defect-related eigenstates, respectively.

C. NV^- and (2×1) -(001) fluorinated diamond surface

We next examine a comparable (2×1) -(001) diamond slab, but this time with a fluorinated surface. The NV^- defect is positioned at ~ 0.48 nm depth. The excess charge and spin population localises mostly on the NV^- defect ($\sim 90\%$), similarly to both the hydrogenated surface and bulk diamond cases. This demonstrates that the shallow NV^- defect survives as a spin active NV^- center when the surface is fluorinated. Changes in the electronic band structure Fig. 5 show either weaker or opposing trends to those of the hydrogenated surface.

In this case, the slab band gap only slightly decreases by 0.03 eV compared to bulk diamond, related to the absence of surface states in the conduction band giving instead looping states inside the slab. Unlike the H-terminated surface, surface states can be found in the valence band as seen in Fig. S4 [61].

All NV^- defect-related states shift upward in energy compared to the bulk, but the effects are less pronounced than with the hydrogenated surface. Specifically, the shifts are now in the range of 0.3 to 0.4 eV.

The degeneracy lifting between the e up-levels is comparable, as E_{x-y} decreases from 97 meV to 72 meV. Applying the same scaling method as for the hydrogenated case, this time with a scaling factor of 1.30 the fluorination makes the surface electron affinity positive (PEA) at about +1.89 eV, which is smaller than expected from the literature data but still can be considered as a high PEA [22,24].

In summary, shallow NV^- beneath a fluorinated surface shows the same reconstruction and similar surface proximity effects to the hydrogenated surface case. However the system presents a PEA, in direct opposition to the hydrogenated surface case.

We see in the next section that this important difference between the surface functionalities profoundly affects the behavior of adsorbed spin-active radical, $\text{C}_{59}\text{N}^\bullet$, with both NEA and PEA surface systems sheltering a shallow NV^- defect.

D. Spin-active molecule on (001) diamond surfaces

We next bring the radical azafullerene into the proximity of diamond surfaces. Fullerenes are known as very good electron acceptors. The spin active fullerene, while charge neutral, has a SOMO making $\text{C}_{59}\text{N}^\bullet$ a radical species, when the SUMO can potentially trap an additional charge [12,13]. Both the radical and the extended π -states on the cage are highly sensitive to environmental perturbation, including the proximity of a negatively charged NV inside the slab and the EA at play on the surface. All these factors may compromise the computational convergence, when starting with the neutral atom electronic distribution before redistributing the electrons during the self-consistency cycle. We report here the most stable electronic configuration for the two EA cases, namely the adsorbent radical $\text{C}_{59}\text{N}^\bullet$ on either H- and F-terminated (001) diamond surfaces with an underlying subsurface NV^- center.

1. C_{59}N on a (2×1) -(001) H-terminated diamond surface with a subsurface NV^- defect

We first investigate the hydrogenated surface with a C_{59}N adsorbed on the surface just above the subsurface NV defect. After structural and electronic relaxation, Mulliken analysis of the charge, spin, and eigenstates in this combined system demonstrate a negatively charged azafullerene C_{59}N^- , and a neutral nitrogen vacancy, NV^0 . Compared to the initially isolated stable $\text{C}_{59}\text{N}^\bullet$ and NV^- , the final state suggests a one-electron charge transfer to the fullerene cage. In this new charge state, C_{59}N^- loses its spin, and the magnetic field sensing capability of the NV center is completely quenched.

The electronic band structures and the pDoS for both up- and down-spins are shown in Fig. 6. Due to the large number of gap states, the pDoS is also included as a guide to the eye. The calculated surface band gap increases by 116 meV when compared to the bare structure with a NV^- beneath a clean H-terminated surface, reaching 4.46 eV. For comparison, we find the slab band gap getting closer to a hydrogenated slab with subsurface NV^0 without C_{59}N present (see Supplemental Material [61]). Therefore, the increase in slab band gap is mainly due to charge transfer that changes the charge state of NV^- to NV^0 and affects the slab band gap at the same time by moving the surface states in the conduction band.

Interestingly, the splitting of the e doublet for the up and down configuration are not equivalent; without C_{59}N present, E_{x-y} is 97 and 146 meV for spin-up and -down, but when the azafullerene is in the vicinity of the defect $e_\uparrow$ states (populated by one electron) are split by only 13 meV, while the empty $e_\downarrow$ states are separated by 172 meV.

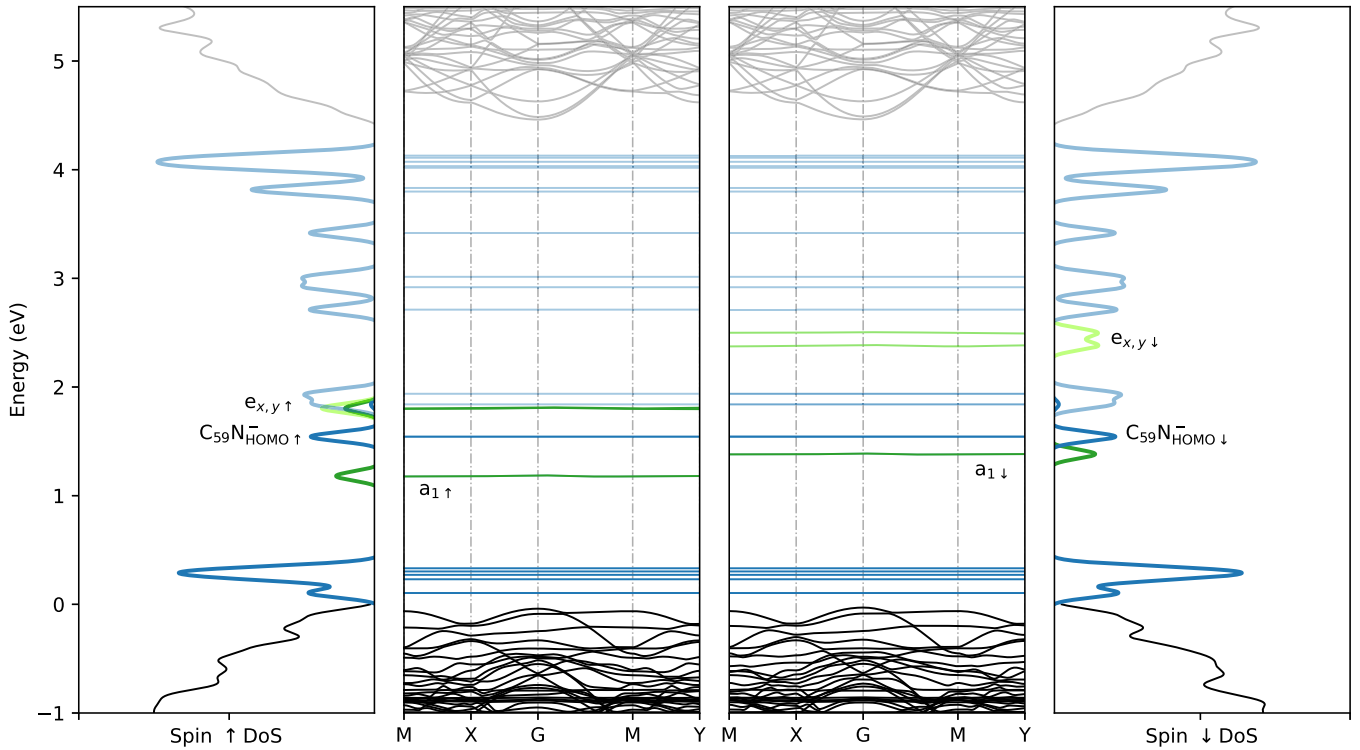


FIG. 6. Electronic band structure and projected density of states (pDoS) of $C_{59}N^-$ on top of $(2 \times 1)-(001)$ hydrogenated diamond surface system with a single neutral NV defect (NV^0). Left and right half sides correspond to the spin up- and down-states, respectively. Zero is set to the top of the diamond slab valence band. Dark/faded lines show filled/empty states respectively. Black, green, and blue colours indicate slab diamond, NV defect and $C_{59}N^0$ related eigenstates, respectively, which is identified by the pDoS.

Due to the charge transfer associated with the adsorption of $C_{59}N$, the former SOMO of the $C_{59}N^\bullet$ becomes a fully occupied HOMO of $C_{59}N^-$, with both the up- and down-states aligned in energy. This state is lying lower in energy than the highest occupied e state of the NV defect. These e up-states are also nearly degenerate with the first LUMO $C_{59}N^-$ states, raising the intriguing possibility that the small local electronic excitations could give rise to further charge transfer from the NV center to the $C_{59}N$, creating NV^+ centres. Indeed, when we run the same calculation starting from neutral NV^0 the final stable configuration is NV^+ and $C_{59}N^-$.

2. $C_{59}N$ on a $(2 \times 1)-(001)$ F-terminated diamond surface with a subsurface NV^- defect

As discussed above, surface passivation by fluorination gives PEA character to the surface. Adding a $C_{59}N$ to the surface thus results in very different behavior compared to the hydrogenated surface. In the fluorinated case the charge, spin and eigenstate population show that the most stable electronic distribution involves a neutral radical $C_{59}N^\bullet$, and a negatively charged NV center, NV^- , i.e., both species maintain their electronic spin and charge states in the heterosystem. Figure 7 shows the electronic band structure and the pDoS for the case of fluorinated surface. In the presence of $C_{59}N^\bullet$, the diamond slab band gap decreases further (50 meV) relatively to the pristine F-terminated surface and the bulk system, similarly the populated NV^- defect states energetically shift down (by 50 to 70 meV) relatively to their positions without the presence of azafullerene.

The azafullerene SOMO contains a single up-electron, matching the isolated neutral species Fig. 1. The pDoS shows that the $a_{1\uparrow}$ state lies above the fullerene h_u states, which slightly splits due to the symmetry lowering. There is an upward shift of all the $C_{59}N^\bullet$ levels compared to the hydrogenated surface system, allowing identification of the symmetrically broken azafullerene g_g and h_g states (in total nine eigenstates) just above the diamond valence band.

We note that both the conduction and valence bands demonstrate crossing and anticrossing with the $C_{59}N^\bullet$ states. However, their position in the bulk electronic structure makes precise assignment difficult.

IV. DISCUSSION AND SUMMARY

In this study we explored shallow NV^- centers beneath both hydrogenated and fluorinated (001) diamond surfaces using density functional methods, both with and without surface adsorbed azafullerene $C_{59}N$ species.

The hydrogenated (001) diamond surface has a calculated NEA of -1.66 eV. Such a strongly negative value is known to facilitate band bending at the diamond surface region, with the potential to aid charge transfer between an adsorbent and the surface [22–24]. In contrast, the fluorinated surface has a calculated PEA of $+1.89$ eV, which shows the least modifying behavior of the NV^- , bulk diamond electronic band structure.

Positioning NV^- in proximity to either surface increases the splitting between its occupied $e_\uparrow$ or unoccupied $e_\downarrow$ states. This splitting is expected to broaden the photoluminescence of

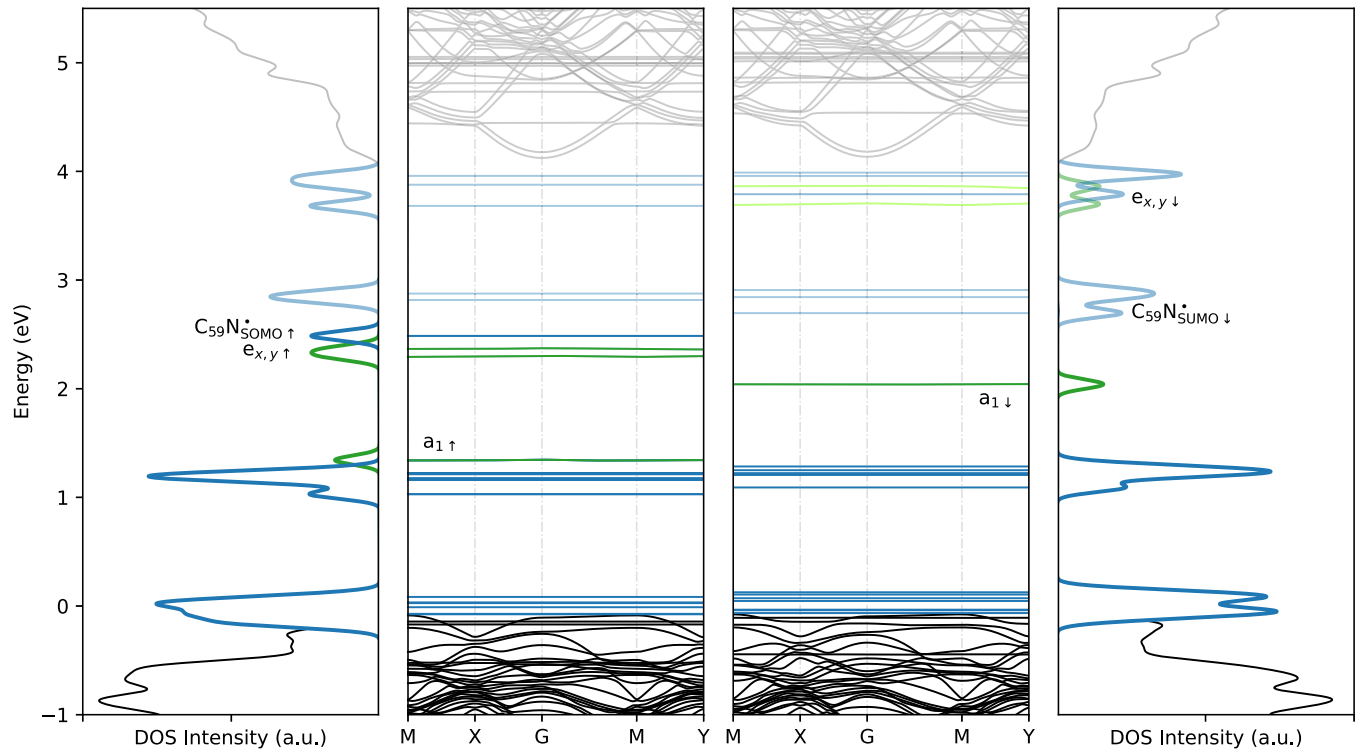


FIG. 7. Electronic band structure and the pDoS of $C_{59}N$ on top of (2×1) -(001) fluorinated diamond surface system with a single negatively charged NV^- defect embedded inside. Left and right half sides correspond to the spin up- and down-states, respectively. Zero is set to the top of the diamond slab valence band. Dark/faded lines show filled/empty states, respectively. Black, green, and blue colors indicate slab diamond, NV defect, and $C_{59}N^0$ related eigenstates, respectively, which is identified by the pDoS.

such shallow defects and could be experimentally detectable [43,65]. We note that the calculations show the energetic depth of the NV^- states in the gap is linked to the physical depth of the defect center below the surface, which may provide a useful spectroscopic probe for NV^- center depth profiling.

Adding the neutral spin active molecule $C_{59}N^\bullet$ to these systems provides insight into the charge doping effect. In the case of the hydrogenated surface the most stable electronic configuration is a negatively charged azafullerene, $C_{59}N^-$, on the surface with a subsurface neutral NV^0 center, NV^0 , beneath it. This is consistent with a charge doping effect induced by the NEA, where the negative charge of the defect can easily migrate to the surface due to its electron affinity, which is afterwards captured by the acceptor-like behavior of the fullerene. Our results suggest that even very small electronic excitations may result in even further charge redistribution and possible formation of NV^+ . However, our ground-state calculations are not capable to reveal the details of such transient electron dynamics.

We conclude that azafullerene in the vicinity of a hydrogenated (001) diamond surface with subsurface NV^- will undergo charge transfer from the defect to the $C_{59}N$, killing its radical state and spin activity. Such charge transfer effects may not occur when the NV^- center is sufficiently deep beneath the surface. Although computational resources preclude a complete investigation of NV^- stability as a function of depth, single point energy calculations of a thicker slab show

that even at a depth of 1.1 nm, the NV^- defect still loses one electron to the $C_{59}N$. This is consistent with quenching of NV^- photoluminescence we observe experimentally when mixing $C_{59}N$ with hydrogenated nanodiamonds, with a mean volumetric size of 40 nm.

We note that the EA for hydrogen- and fluorine-terminated surfaces is largely independent of surface orientation and reconstruction (± 1 eV) [22–34], showing the effects calculated here should equally apply to other surface orientations and diamond nanoparticles.

In contrast, surface fluorination may provide a useful route to block unwanted charge transfer processes. When passivated with fluoroine, subsurface NV maintains its negative charge state in the presence of surface azafullerene, which remains a neutral radical, $C_{59}N^\bullet$. This conserves both the spin activity of the molecule and the important photoluminescence properties of the defect. We associate this stability to the down band bending effect from the PEA of the F-terminated surface that prevents the additional electron on the NV transferring to the adsorbent. To investigate the spin dynamics of the $C_{59}N^\bullet$ or other similar spin-active molecules through the photoluminescence of the shallow NV^- defects, fluorination of the (nano)diamond surface may be a key first step.

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DATA AVAILABILITY

The data that support the findings of this article are openly available [66].

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