Electronic structures and spectroscopic signatures of silicon-vacancy containing nanodiamonds

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The presence of midgap states introduced by localized defects in wide-band-gap-doped semiconductors can strongly affect the electronic structure and optical properties of materials, generating a wide range of applications. Silicon-divacancy defects in diamond have been recently proposed for probing high-resolution pressure changes and performing quantum cryptography, making them good candidates to substitute for the more common nitrogen-vacancy centers. Using group-theory and *ab initio* electronic structure methods, the molecular origin of midgap states, zero-phonon line splitting, and size dependence of the electronic transitions involving the silicon-vacancy center is investigated in this paper. The effects of localized defects on the Raman vibrational and carbon K-edge x-ray absorption spectra are also explored for nanodiamonds. This paper presents an important analysis of the electronic and vibrational structures of nanosized semiconductors in the presence of midgap states due to localized defects, providing insight into possible mechanisms for modulating their optical properties.

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I. INTRODUCTION

Wide-band-gap-doped semiconductors are promising candidates for use in many technological applications since the controlled implantation of localized defects can introduce new electronic levels within the band gap, strongly modifying the material interactions with electromagnetic radiation [1–6]. Diamond presents a large optical band gap for bulk (∼5.5 eV) [7] and has a very dense lattice that both restricts defect diffusion and restricts phase transitions at high temperatures. Thus, the manipulation and the characterization of isolated defects in diamonds have generated a wide range of applications, such as quantum computing, sensing, and cryptography [8–14].

When the crystal size approaches the nanodimension (∼5 nm), diamonds no longer express bulk properties. A band-gap opening is observed, and discrete electronic levels (typical of molecules) emerge at the band edges. These are all consequences of the quantum confinement effect [15–18]. Therefore, the interaction between doped diamonds and light may be further modulated by adjusting the host nanocrystal size. Substitutional nitrogen and nitrogen-vacancy (NV) centers are common defects in diamond and have received attention for their sensitive optical and spin properties [8–11,19–21]. The peculiar low diffusion rate of NV centers enables the optical probing of local variations in time, which can affect the spin precession rate of the defects, making them suitable for quantum sensing applications [14]. Doping introduces new sub-band-gap levels, and it has been shown that NV centers in diamond give rise to new dopant-centered $sp^3$ $sp^3$ midgap electronic transitions and charge-transfer ("photoionization") excited states [22]. Similar applications in quantum information processing [23] have been shown for the negatively charged silicon-vacancy ($SiV^−$) center due to its short fluorescent lifetime, narrow emission linewidth, and high percentage of photons (∼70–80%) emitted through its zero-phonon line (ZPL) [24,25]. This defect has also been shown to be useful as a high-resolution high-pressure sensor [26]. Doped diamond-based pressure probes can function at higher pressures than the currently used ruby sensors as the rigid diamond lattice is still present above 100 GPa, whereas ruby undergoes a phase transition.

The $SiV$ center can exist as either a neutral triplet in its ground state, neutral SiV, or as an anionic doublet state, anionic SiV$^−$ [27–31]. The latter is the most common stable ground-state electronic configuration [32]. Experimentally, the ZPL measured in doped diamonds in the bulk limit is 1.31 and 1.68 eV for the neutral SiV and anionic SiV$^−$, respectively. Additionally, in SiV$^−$ a blueshift in the zero-phonon line as a function of the decreasing crystal size has been observed for nanodiamonds [33]. For the reduced systems the ZPL splits into a four-line fine-structure at helium temperature [34,35]. The origin of this fine-structure splitting in the ground and excited states has been explained by dynamic Jahn-Teller and/or by spin-orbit effects [27,34,36,37].

Vibrational spectroscopy can also be used to probe the presence of these defects since the changes in the dipole and the polarizability induced by the dopant can strongly modify the selection rules for the infrared and Raman active modes, respectively. In addition to UV-visible (vis), the K-edge x-ray absorption spectrum in diamonds has been proposed to be sensitive to the introduction of dopants [38]. Moreover, carbon K-edge spectra in nanodiamonds exhibit unidentified pre-edge features that have been either attributed to the presence
of sp² carbon atoms lying on the surface as a consequence of the surface reconstruction, or to the introduction of new empty levels within the band gap resulting from impurities [38]. Despite their importance, carbon K-edge x-ray and vibrational transitions for the characterization of SiV centers in nanodiamond along with the effects of the SiV center location in the crystal lattice (i.e., surface effects and symmetry breaking) and system size (i.e., quantum confinement) on the electronic and vibrational excitations have not been well studied. In this paper, theoretical investigations with a finite cluster approach of both the electronic and the vibrational properties are carried out using hybrid density functional theory (DFT) and linear-response time-dependent density functional theory (TDDFT) for a reduced SiV° center in nanodiamond systems of different sizes. TDDFT, combined with a cluster approach, has shown very promising results for the theoretical characterization of excited states in doped semiconductor quantum dots (in particular, NV-doped nanodiamonds) [22,39–48] and the vibrational/dynamical properties of molecules [49–53]. The work presented herein focuses on the quantum confinement effects on the electronic (UV-vis and x-ray) and vibrational (Raman) spectroscopies on several SiV-doped diamond nanoclusters. The effect of the defect symmetry (or the lack of) as a function of the size is also analyzed.

II. METHODOLOGY

Nearly spherical diamond quantum dots, C_{44}H_{42} (diameter ~0.8 nm), C_{121}H_{104} (diameter ~1.2 nm), C_{182}H_{142} (diameter ~1.4 nm), and C_{487}H_{310} (diameter ~2.1 nm) were used as starting models for the SiV-doped systems. They were constructed using the bulk face-centered cubic lattice parameter [7] \( a_0 = 0.357 \) nm, and hydrogen atoms were used to passivate the surface dangling bonds, according to the procedure presented in Ref. [22]. The sizes of these quantum dots are similar to the smallest nanodiamonds obtainable by detonation or laser-heated diamond-anvil cell synthesis [12,54–56]. As the diamond excitonic (EXC) Bohr radius is estimated to be ~1.6 nm [57], electronic properties of these small diamond quantum dots will exhibit quantum confinement effects.

The SiV center in diamond consists of a silicon atom and a vacancy in a split-vacancy configuration [28,30,58]. The SiV center was created by removing two carbon atoms near the center of the nanodiamonds along the (1, 1, 1) axis of the models and positioning the silicon at the center of the resulting divacancy in a local \( D_{3d} \) environment (namely, SiV \textit{frozen}) as observed in previous computational studies [27,31,59,60]. To evaluate the lattice distortion due to the presence of the SiV center itself, the SiV center and the nearest-neighbor six carbon atoms were fully optimized while maintaining the rest of the diamond structure at the crystal lattice (namely, SiV \textit{relaxed}). These optimization schemes have shown accurate results for describing the lattice distortion of nitrogen-vacancy-doped diamonds of similar sizes [22]. In this paper, we focus on the reduced SiV° center, whose ground state has been shown to be a doublet [32]. The ~1.2-nm reduced SiV°-C_{119}SiH_{104} was used to estimate the excited-state structural reorganization and relaxation energy. This system was further optimized according the first bright excited-state energy gradient provided by TDDFT and using the SiV° \textit{relaxed} optimization scheme, described above. The relaxation energy in the excited state was computed as the energy difference between the vertical excitation energy using the ground-state and the excited-state optimized geometries. The ~1.2-nm-diameter pure C_{121}H_{104} and the reduced SiV°-C_{119}SiH_{104} were also further fully optimized in the ground state by relaxing all atoms to perform the vibrational analysis. Geometries were considered fully optimized when both the forces [maximum and root-mean-square (rms) force 0.000 450 and 0.000 300 Hartree/bohr, respectively] and displacement (maximum and rms displacement 0.0018 and 0.0012 bohr, respectively) values for all free atoms were below the threshold criteria.

All calculations were performed using the development version of the GAUSSIAN software package [61]. The ground-state electronic structures were obtained by solving the Kohn-Sham equation using the range-separated version of the hybrid Becke three-parameter Lee-Yang-Parr (B3LYP) density functional [62–64] with the Coulomb-attenuating approach (CAM-B3LYP) [65]. The necessity for using basis sets with large spatial extent (i.e., diffuse functions) has been demonstrated to be important in nanodiamonds since C-H bonds create low-energy empty states that are Rydberg-like, that may reduce the band gap [66,67]. These states can play an important role for shallow implanted NV centers in diamond [68]. On the other hand, diffuse functions have been previously shown to be less important for localized defects located far from the surface [33,69,70]. CAM-B3LYP is known to outperform the canonical hybrid (i.e., B3LYP, Perdew-Burke-Ernzerhof-0 functional, etc.) for the description of the Rydberg-like and charge-transfer states due to their high sensitivity to the treatment of exact exchange [71–73]. Since the presence of these Rydberg-like states can influence the predicted quantum confinement effects, CAM-B3LYP/6 – 31 + +G(d, p) was used for this paper. The electronic structures of excited states were calculated using TDDFT within the linear-response framework [74–76] and its energy specific implementation for the high-energy states [77,78].

III. RESULTS AND DISCUSSION

A. Structural reorganization and electronic configurations

The models used in this paper support local symmetry, but they do not preserve a global inversion symmetry operation, therefore the SiV \textit{frozen} conformation has an overall \( C_{3v} \) symmetry, given the asymmetry on the nanodiamond surface. Effects of the SiV location in nanodiamonds (i.e., the position of the defect with respect to the surface) can also influence the electronic and optical properties of the systems, and they are separately investigated in detail in the next sections for one of the larger models. Despite this, the models can retain, in the SiV \textit{frozen} conformation, a local symmetric arrangement where all Si-C distances are 1.944 Å and the C-Si-C angles are either 80.9° or 99.1°. The local symmetry of the defect may still be described as \( C_{3v} \), plus inversion, retaining a local \( D_{3d} \) symmetry [see Fig. 1, panels (a) and (a')].
excited-state centers. There are also six dangling electrons from the six silicon atoms contribute their four valence electrons to the SiV ground state in

The lattice structural reorganization in the electronic ground state in a ~1.2-nm SiV-doped nanodiamond is summarized in Fig. 1 [panels (b) and (b')]. A uniform expansion of the Si pocket can be clearly seen from the elongation of all Si-C distances. Upon relaxation on the ground electronic state, the local $D_{3d}$ symmetry is broken, although a pseudo-$C_s$ symmetry can be still observed by inspecting the Si-C distances. When the system is further allowed to relax on the first bright excited state, a nonuniform bond change is observed. Half of the Si-C distances undergo an expansion of the bond length, and the other half undergo a compression [see panel (c) in Fig. 1] compared to the previously examined ground-state system). The local $D_{3d}$ symmetry splits the four $sp^3$ atomic orbitals of Si to $a_{2u}$, $e_u$, $a_1g$, and the six $p$ atomic orbitals of nearby C atoms to $e_g$, $e_u$, $a_2u$, and $a_1g$ symmetry groups. The symmetry rules dictate that the set of orbitals of $e_g$ symmetry has almost zero overlap with the Si atomic orbitals, resulting in a set of high-energy (and mostly energetically “pinned” in the band gap) MOs with significant contributions from the carbon $p$ orbitals surrounding the silicon (see the colored PDOS in Fig. 2); all other atomic orbitals previously listed ($e_g$, $e_u$, $a_2u$, and $a_1g$) can hybridize and form MOs surrounding the defect [depicted in Fig. 3(a)]. The resulting $\sigma$ bonding and antibonding MOs of $a_{2u}$ and $a_{1g}$ symmetries are energetically buried in the VB and CB, respectively (not shown).

On the other hand, the hybridized bonding MOs of $e_u$ symmetry are the most interesting ones because they are likely responsible for the peculiar optical properties of SiV centers. These molecular orbitals lie at the VB edge (the antibonding ones are energetically located at the CB edge, not represented) and show a reasonable contribution from both the carbon $p$ and the silicon $sp^3$ orbitals. The resulting MOs show a nonzero overlap with the VB edge of the nanodiamonds, forming a set of three molecular orbitals at the VB edge. Only in the 0.8-nm nanodiamond the MOs of $e_u$ symmetry are energetically well separated from the VB. In this paper, the negatively charged SiV defect ground-state electronic state is $^2E_g$ (in a $D_{3d}$ perfect symmetry), and its electronic configuration can be described as $e_u^4e_g^3$, where the $e_g$ level is partially filled, in agreement with previous DFT calculations [27,30,80].
FIG. 2. CAM-B3LYP/6-31 + +G(d, p) total and partial densities of states (PDOS) [this last visualized only for Si and its first-neighboring C atom levels within the band gap and the conduction band (CB)]. The red and light blue colored regions show the C 2p and Si (magnified by 5 ×) 3s and 3p contributions to the PDOS diagrams, respectively. Spin up, positive density values; spin down, negative density values. The DOS diagrams are calculated for the pure C\text{X}H\text{Y} and the reduced frozen C\text{X}−2SiH\text{Y} (left and right, respectively) nanodiamonds of increasing sizes (d ∼ 0.8, 1.2, 1.4, and 2.1 nm from top to bottom).

B. Midgap optical transitions

As the size of nanodiamond decreases, the quantum confinement effect \cite{18,81} leads to an increase in the band gap [5.21 eV for C_{487}, 5.78 eV for C_{182}, 6.07 eV for C_{121}, and 7.77 eV for C_{4d}; reported as the highest occupied molecular orbital/lowest unoccupied molecular orbital (HOMO/LUMO) differences] as observed in other semiconducting nanocrystals \cite{39,82}. The previously presented electronic structures for anionic SiV− defects in a nanodiamond give rise to several characteristic sets of optical transitions exhibited in the spectroscopic measurement of SiV-containing nanodiamonds. Optical spectra for different-sized SiV− containing nanodiamonds using linear-response TDDFT are reported in Fig. 4. The energy levels of these SiV centers in the diamond lattice are illustrated in Fig. 3(a). This energetic layout leads to unique midgap optical transitions in SiV-containing nanodiamonds.

The optical spectra in Fig. 4 shows a spectroscopic feature between 1.70 and 2.10 eV consisting of two transitions from the two filled MOs of \( e_u (\beta) \) symmetry to the empty \( e_g (\beta) \). Table I lists their vertical excitation energies in various SiV− containing nanodiamonds. These transitions give rise to the

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<tr>
<th>SiV\text{relaxed}</th>
<th>SiV\text{frozen}</th>
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<tr>
<td>SiV−C_{4d}SiH_{14}</td>
<td>1.70(0.077) 1.63(0.068)</td>
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<td>2.06(0.028) 1.81(0.014)</td>
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<tr>
<td>SiV−C_{119}SiH_{184}</td>
<td>1.67(0.070) 1.59(0.061)</td>
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<tr>
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<td>2.09(0.019) 1.82(0.014)</td>
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<tr>
<td>SiV−C_{180}SiH_{142}</td>
<td>1.59(0.064) 1.51(0.056)</td>
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<td>1.99(0.021) 1.90(0.015)</td>
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FIG. 3. Schematic of the SiV center electronic layout according to the \( D_{3d} \) point-group symmetry. Panel (a) SiV in the center of the nanodiamond and panel (b) where the SiV defect is close to the surface and partially breaks the group symmetry (positions 1 and 4 in Fig. 6, respectively). The zoomed-in \( C_{180}SiH_{142} \) CAM-B3LYP/6-31 + +G(d, p) \( \beta \) MO contour plots with the pseudo-C\text{3v} axis parallel to the \( z \) axis (entering the figure) are represented. The isodensity values of 0.05, 0.05, and 0.03 are used for the \( e_u, e_g \) and VB MO contour plots, respectively. The energetic layout presents an uneven alignment between the \( \alpha/\beta \) filled \( e_u \) with respect to the \( \beta e_g \) LUMO, please see Fig. 2 for a more detailed analysis.
FIG. 5. TD-CAM-B3LYP/6-31 + +G(d, p) SiV $^{2} E_{u}(e_{u}^{3}e_{g}^{1}) \rightarrow^{2} E_{u}(e_{u}^{3}e_{g}^{1})$ ZPL excitations as a function of the band-to-band-excitonic transition for the anionic SiV− systems. Extrapolation of the ZPL energies gives a value of 1.38 eV for the bulk and the ratio between $\Delta E_{ZPL}$ and $\Delta E_{EXC}$ as the slope of the linear fit is 0.04 [the reported EXC energy (band gap) is reported as a HOMO/LUMO difference, which can underestimate the experimentally observed optical band gap as it has not been computed at the TDDFT level of theory and can be affected by the presence of surface defects in the experiment].

The quantum confinement effect on the spectral shift of the ZPL ($\Delta E_{ZPL}$) as a function of the band-to-band-excitonic transition ($\Delta E_{EXC}$) has the approximate relationship, according to the effective-mass approximation for a spherical nanocrystal [17,39,42],

$$\Delta E_{ZPL} \approx \frac{m_{e}^{*}}{m_{e} + m_{h}^{*}} \Delta E_{EXC},$$

where $m_{e}^{*}$ and $m_{h}^{*}$ are the effective masses (in units of electron mass) of the electron and hole in the SiV-containing nanodiamond. The $^{2} E_{e}(e_{u}^{3}e_{g}^{1}) \rightarrow^{2} E_{e}(e_{u}^{3}e_{g}^{1})$ excitations (as a weighted average of the first two excitations in Table I) as a function of the band-to-band-excitonic transition for the different dot sizes is plotted in Fig. 5. The $\Delta E_{ZPL}/\Delta E_{EXC}$ value is 0.04, less than that in NV-doped nanodiamonds [22] and is significantly smaller than those for the free CB electron in diamond quantum dots. The observed size dependence of the ZPL is comparable with the one predicted using similar dimensions and level of theory [33]. Moreover, the quantitative analysis presented here suggests that the photoexcited electrons in the SiV ZPL excited states of diamonds are “heavier” than those in the pure diamond excitonic states.

C. Symmetry (or the lack of)

The two MOs of $e_{u}$ symmetry have different spatial extents [i.e., different symmetries along the $x$ and $y$ directions, see Fig. 3(a)] and subsequently different overlaps with the empty MOs of $e_{g}$ symmetry, showing different relative intensities in their transitions as can be inferred by inspecting computed oscillator strength values reported for the different sized SiV-doped nanodiamonds in Table I. By analyzing these values for the SiV frozen systems (right columns in Table I), an average splitting of $\sim0.27$ eV is already noted for the computed $^{2} E_{u}(e_{u}^{3}e_{g}^{1}) \rightarrow^{2} E_{u}(e_{u}^{3}e_{g}^{1})$ excitations. As mentioned before, although the SiV frozen conformation has an overall $C_{1v}$ symmetry, both the asymmetry in the surface and the different spatial overlap of the filled MOs of $e_{u}$ symmetry with the VB can be responsible for the energy splitting in the two $^{2} E_{u}(e_{u}^{3}e_{g}^{1}) \rightarrow^{2} E_{u}(e_{u}^{3}e_{g}^{1})$ transitions even in these frozen conformations [see the different overlaps with the VB in Fig. 3(b)]. The asymmetric overlap between $e_{u}$ MOs with the VB is, therefore, the key reason for both the excitonic behavior (analyzed in the previous paragraph) and the asymmetry of...
the absorption peak in the visible range for the SiV-doped systems. A similar interpretation has been previously provided for silicon-doped nanodiamonds of similar dimensions [33].

The effect of lattice reorganization on the $^2E_u(e_u^4e_g^2) \rightarrow ^2E_u(e_u^3e_g^3)$ excitations as a function of the system size can be also analyzed in Table I (from right to left). The geometry reorganization is responsible for an additional blueshift in vertical excitation energies from $\sim 0.07$ (first excitation) to $\sim 0.25$ eV (second excitation) with respect to the unrelaxed conformations. The degree of splitting of the two $^2E_u(e_u^4e_g^2) \rightarrow ^2E_u(e_u^3e_g^3)$ excitations for the SiV relaxed systems are comparable to the ones computed for the SiV frozen, suggesting that the interactions of these levels with the VB band and surface are already significant to induce asymmetry in these excitations even in the SiV frozen-doped systems.

Since the relative position of the SiV defect with respect to the nanodiamond surface can further perturb the overall symmetry of the system, we inspected how the location of the SiV center within the nanodiamond can affect the SiV ZPL transitions. As the SiV center moves away from the C$_{3v}$ (pseudolocal $D_{3d}$ in SiV frozen systems) symmetry center, its global symmetry is no longer C$_{3v}$. As a result, the set of MOs of $e_u$ and $e_g$ symmetries as shown in Fig. 3(b) are even more energetically different due to the different interactions of the $x$ and $y$ subsets of the $e_u$ and $e_g$ MOs [see their asymmetric distributions in Fig. 3(b)] as the SiV moves closer to the surface (e.g., positions 2–4 in Fig. 6). The consequence of the symmetry breaking due to the defect position on $^2E_u(e_u^4e_g^2) \rightarrow ^2E_u(e_u^3e_g^3)$ excitations is summarized in Table II. A splitting of $\sim 400$ meV of SiV midgap transitions is observed when the SiV moves away from the C$_{3v}$ center of the nanodiamond for the SiV frozen. The magnitude of the splitting is not very sensitive to the defect position with respect to the surface, although the overall values show an overall 0.1-eV blueshift for the SiV positions closest to the surface (larger if the systems are allowed to relax as can be determined by looking at the values on the left in the table). This splitting of midgap transitions has been previously shown to be sensitive to the defect position relative to the surface, but its absolute value for SiV defects appears to be larger than for the NV center [22]. Both the SiV$^-$ peak position and the broadening of the emission linewidth have experimentally been proved to be

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<th>Position</th>
<th>SiV relaxed</th>
<th>SiV frozen</th>
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<tr>
<td>1</td>
<td>1.59</td>
<td>1.51</td>
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<tr>
<td>2</td>
<td>1.99</td>
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<td>1.67</td>
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<tr>
<td>4</td>
<td>2.07</td>
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**FIG. 6.** Schematic layout of the four SiV positions in the C$_{180}$SiH$_{254}$ system used to investigate anisotropic effects on SiV midgap optical transitions.

**FIG. 7.** CAM-B3LYP/6-31 $^+$G(d, p) midgap vertical excitation energies ($e_u$ to $e_g$, $\beta$ manifold) for the anionic SiV$^-$ systems (in eV) as a function of the SiV center position moving from the center (position 1) towards the surface (position 4) for the C$_{180}$SiH$_{254}$ system. Results are compared between the SiV relaxed (SiV center position is optimized, see the text) with the ones obtained by just inserting the SiV center by replacing the corresponding atoms (SiV frozen) in the center of the pure nanodiamond.

**TABLE II.** TD-CAM-B3LYP/6-31 $^+$G(d, p) midgap vertical excitation energies ($e_u$ to $e_g$, $\beta$ manifold) for the anionic SiV$^-$ systems (in eV) as a function of the SiV center position moving from the center (position 1) towards the surface (position 4) for the C$_{180}$SiH$_{254}$ system. Results are compared between the SiV relaxed (SiV center position is optimized, see the text) with the ones obtained by just inserting the SiV center by replacing the corresponding atoms (SiV frozen) in the center of the pure nanodiamond.
sensitive to either uniaxial stress or the position of the center within the matrix in a similar way to the predicted values ($\sim 200 \text{ meV}$ in some observed broadenings) [83–85]. As the ZPL is sensitive to the surface reorganization and the size of the system, SiV centers can be effective probes of the global and local distortions, i.e., mechanical stress or pressure.

D. Vibrational analysis

Vibrational spectroscopy can be very sensitive to the presence of defects since localized defects can strongly change the selection rules for infrared and Raman active modes. Presented in Fig. 7 are the Raman spectra for the 1.2-nm pure (black) and reduced SiV$^-$ (blue) nanodiamonds. Given the system size and the high computational cost of Raman calculations, a less expensive 6-31G(d) basis set was utilized for frequency and Raman intensity calculations. This choice is based on the observation that fully optimized geometries using 6-31+G(d, p) and 6-31G(d) bases show negligible differences especially at the defect center. For the calculation of the vibrational response, it has been noted that, for large systems, this level of theory is sufficient [86–89], although Raman intensity can be improved with additional diffuse functions. The energy range discussed covers the region mostly affected by the presence of the SiV defects (the C-H stretching modes localized on the surface at $\geq 3000 \text{ cm}^{-1}$ are not represented). Two distinctive regions can be located by observing the Raman spectrum; this last spectral region seems to be the most sensitive to the isotopic substitution of the silicon atom as can be inferred by the examination of Fig. 9(a) where the isotopic pure Raman spectra for the most abundant isotopes of silicon are reported ($^{28}\text{Si}$, $^{29}\text{Si}$, and $^{30}\text{Si}$ from top to bottom of the left panel). A progressive redshift of $\sim 1.5 \text{ cm}^{-1}$ is observed for the peak around $\sim 156 \text{ cm}^{-1}$ for each increase in the silicon atomic mass. In addition, the breathing mode at $\sim 442 \text{ cm}^{-1}$ [marked in red in Fig. 9(a) and represented in Fig. 9(b)] strongly shows a decrease in intensity as an effect of the isotopic mass increment. Vibrational Raman responses associated with the anionic SiV$^-$ and the Si substitutional defect were also compared. The substitutional defect was obtained by replacing a carbon atom close to the center of the $\sim 1.2$-nm pure nanodiamond with a Si atom and optimizing the resulting structure. The SiV$^-$ shows very distinct vibrational responses with respect to both the pure and the substitutional one (see Fig. S2 of the Supplemental Material [79]).

Unfortunately, the spectral region presenting the typical diamond Raman peak, involving the C-C lattice stretching motions reported at $\sim 1330 \text{ cm}^{-1}$ for bulk diamonds [91–93], is completely washed out by the hydrogen passivation of the surface. This problem is solved by setting the atomic mass of hydrogen to
FIG. 9. (a) B3LYP/6-31G(d) isotopically pure calculated Raman spectra for the three most abundant [98] silicon isotopes $^{28}\text{Si}$ (92%), $^{29}\text{Si}$ (5%), and $^{30}\text{Si}$ (3%) from top to bottom of the left panel for the $\sim 1.2$-nm-diameter SiV$^{-}$C$_{119}$SiH$_{104}$ fully optimized nanodiamond. (b) Displacement vectors of the most representative normal mode sensitive to the isotopic substitution.

FIG. 10. TD-CAM-B3LYP/6-31+G(d, p) calculated XAS for the $\sim 1.2$-nm-diameter pure C$_{121}$H$_{104}$ (top, 10 states), and the reduced SiV$^{-}$C$_{119}$SiH$_{104}$ (bottom, 103 states) nanodiamonds. Carbon core $1s \rightarrow e_g$ and $1s \rightarrow \sigma^*$ transitions are grouped in orange (dashed) and green (solid), respectively. A Gaussian broadening has been applied to the individual transitions labeled with black lines to form the spectra with a full width half maximum value of 0.12 eV, and a uniform shift of 12 eV has been applied to the spectra to align theoretical results with experimental values. Contour plots of the molecular orbitals responsible for the carbon K-edge transitions with the pseudo-C$_3$ axis parallel to the z axis (entering the figure) using an isodensity value of 0.025 are also represented.

X-ray absorption spectroscopy

X-ray absorption spectroscopy (XAS) is extensively used for sample analysis since it is a highly element specific spectroscopic technique. The K-edge feature in the XAS is due to the excitations involving $1s$ core electrons and the virtual valence molecular orbitals; for these reasons the structure of these peaks can provide useful information on the local order around the absorbing centers [99–102]. The resulting carbon K-edge x-ray absorption spectra for the $\sim 1.2$-nm-diameter pure C$_{121}$H$_{104}$ and the reduced SiV$^{-}$C$_{119}$SiH$_{104}$ nanodiamonds are reported in Fig. 10. The pure nanodiamond presents a clear absorption peak starting at 290 eV due to the well-studied $1s \rightarrow \sigma^*$ transitions. As the SiV is introduced, several pre-edge transitions start to appear around 284–285 eV. The main peak at $\sim 290$ eV for the Si-doped systems is still due to several $1s \rightarrow \sigma^*$ electronic transitions as can be inferred by inspecting the MOs responsible for them in both the pure and the doped systems (see their representations in Fig. 10). The pre-edge peaks around 285 eV are due to the presence of the SiV defects, arising from several carbon $1s \rightarrow e_g$ transitions (see Fig. 10). These analyses suggest that the pre-edge feature experimentally observed at $\sim 285$ eV can be a signature of the presence of defects (i.e., SiV centers).
Although these carbon transitions are typically ascribed to sp$^2$-carbon atoms lying on the surface [48], it should be noted that these are also available to the dangling bonds surrounding carbon vacancies. However, in defects, such as NV and SiV, the presence of heteroatoms influences the 1s → eg carbon transition. Thus, the location of the carbon K-edge pre-edge features can be used to probe the presence of different dopants in diamonds [38].

IV. CONCLUSION

In this paper, the midgap states introduced by localized defects have been shown to affect UV-vis, x-ray, and vibrational transitions in diamonds approaching the nanoscale. Using group theory and the DFT electronic structure, we showed how the midgap states introduced by the reduced SiV center have a non-negligible overlap with the diamond VB and CB. This explains the size-dependent nature of the computed SiV ZPL, and we predict an effective excitonic mass for these transitions comparable to charge-transfer excitations in NV-doped nanodiamonds. We also found the ZPL to be sensitive both to the lack of symmetry in all systems analyzed and to the defect position by measuring the band position during the defect migration towards the surface. Two diamond Raman vibrational spectrum regions are predicted to be significantly modified by the SiV center: The large amplitude breathing (120–450-cm$^{-1}$) and the stretching (800–1400-cm$^{-1}$) motions of the lattice. Core 1s → eg (midgap states) transitions introduced by SiV centers are predicted to be responsible for the occurrence of pre-edge peaks in the computed carbon K-edge x-ray absorption spectrum for nanodiamonds, showing how this spectral region (~285 eV) can be influenced by the presence of localized defects. This paper provides an important ab initio analysis of the electronic and vibrational structures of semiconductors in the presence of midgap states due to localized defects, providing a molecular description of the spectroscopic changes in doped systems.

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[79] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevB.98.205405 for the change in the SiV structure for full-diamond optimization, the isotropic effects of silicon on the Raman spectroscopy, and enlarged images of the normal modes displayed in Fig. 8.


