

Quantum Chemical Modeling of Photoadsorption Properties of the Nitrogen-Vacancy Point Defect in Diamond

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Abstract: Quantum chemical calculations of geometric and electronic structure and vertical transition energies for several low-lying excited states of the neutral and negatively charged nitrogen-vacancy point defect in diamond (NV^0 and NV^-) have been performed employing various theoretical methods and basis sets and using finite model NC_nH_m clusters. Unpaired electrons in the ground doublet state of NV^0 and triplet state of NV^- are found to be localized mainly on three carbon atoms around the vacancy and the electronic density on the nitrogen and rest of C atoms is only weakly disturbed. The lowest excited states involve different electronic distributions on molecular orbitals localized close to the vacancy and their wave functions exhibit a strong multireference character with significant contributions from diffuse functions. CASSCF calculations underestimate excitation energies for the anionic defect and overestimate those for the neutral system. The inclusion of dynamic electronic correlation at the CASPT2 level leads to a reasonable agreement (within 0.25 eV) of the calculated transition energy to the lowest excited state with experiment for both systems. Several excited states for NV^- are found in the energy range of 2–3 eV, but only for the 1^3E and 5^3E states the excitation probabilities from the ground state are significant, with the first absorption band calculated at ~ 1.9 eV and the second lying 0.8–1 eV higher in energy than the first one. For NV^0 , we predict the following order of electronic states: 1^2E (0.0), 1^2A_2 (~ 2.4 eV), 2^2E (2.7–2.8 eV), 1^2A_1 , 3^2E (~ 3.2 eV and higher).

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Introduction

Diamond and diamond-like materials are finding increasing applications in various areas of modern technology because of their unique properties such as high thermal conductivity, exceptional hardness, high damage threshold of the host crystal, and chemical and thermal stability. Diamonds contain a variety of color centers owing to the presence of impurity atoms and vacancy complexes. Up to date, based on the absorption and luminescence spectra of diamond, more than 500 optical centers are

known, which are mostly related to the presence of defects.^{1–3} Approximately half of them are believed to be impurity related. Properties of these centers are of great interest and have been studied for more than 30 years because of the proposed

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applications of diamond as a laser source and high-efficiency photodetector for the UV radiation.^{4–7} Nitrogen is the dominant impurity in the bulk of natural and synthetic diamond.^{8–10} It is usually present in the form of substitution atoms (sometimes called type C nitrogen), which may be isolated or be present in aggregates. All synthetic diamonds, either HPHT (High Temperature-High Pressure) or CVD (chemical vapor deposition), contain type C nitrogen, except those from which nitrogen has been carefully excluded. C nitrogen gives rise to a characteristic IR spectrum with a broad peak around 1130 cm^{-1} ,¹¹ a sharp local mode peak at 1344 cm^{-1} , and it can also serve as an electron donor with ionization energy of $1.7\text{--}2\text{ eV}$.¹² The presence of C nitrogen gives rise to the P1 EPR signal.¹³ A single nitrogen atom impurity can be ionized, and then the N^+ ion generates an IR peak at 1332 cm^{-1} .¹⁴

In natural diamond, vacancies are present only after irradiation. The ground state of the neutral vacancy (V^0) is singlet; four electrons used to be attached to the removed atom form weak, stretched C—C bonds. EPR signals have been observed associated with V^- (S1)¹⁵ and with an excited state of V^0 .¹⁶ The optical band GR1 with zero phonone line (ZPL) at 1.673 eV has been attributed to V^0 , whereas ND1 with ZPL at 3.150 eV has been assigned to the negatively charged vacancy V^- .⁸ The migration energy for the vacancy is $\sim 2.3 \pm 0.2\text{ eV}$, and at the temperature of $\sim 600^\circ\text{C}$ neutral vacancies begin to migrate¹⁷ and to readily form complexes with impurities creating more stable optically active defects.

Several centers incorporating nitrogen are known to be thermally stable and to exhibit high quantum efficiency up to temperatures above 500 K . These centers are denoted as NV ($\text{N}\&\text{V}$), H3 ($2\text{N}\&\text{V}$), H2 ($2\text{N}\&\text{V}^-$), and N3 ($3\text{N}\&\text{V}$). They are respectively formed by combining the vacancy and one, two, or three N atoms and have C_{3v} and C_{2v} point symmetry. The exceptional properties of these diamond color centers, together with their high thermal conductivity, outstanding hardness, and high damage threshold of the host crystal caused substantial interest of researchers.^{1,3}

Nitrogen-vacancy (N-V) defects exhibit a particularly strong electronic transition, allowing detection of individual centers optically.⁶ This could be regarded as a good example of an individual quantum object with potential applications to the quantum information processing. These defects possess a remarkable photo and chemical stability, and therefore they have been proposed as light sources for high-resolution scanning-probe microscopy and quantum cryptography^{5–7,18} where a stable single-photon source with high quantum yield is required. Recently, nanosized diamond powders containing NV-defects were proposed as cellular biomarkers.¹⁹ The NV defect center in diamond has been extensively investigated both experimentally^{1,3,5–14,18,20–37} and theoretically.^{38–42} According to available experimental data,^{3,26} the neutral NV defect can capture an electron with formation of a negatively charged center. The ground state of this NV^- center is $^3\text{A}_2$, and the first triplet excited state is ^3E . Maxima of the photoadsorption (PA) and photoluminescence (PL) bands have been observed near 2.15 and 1.75 eV .²⁵ So as the Stokes shift is moderate in this case, geometric parameters of the $^3\text{A}_2$ and ^3E states do not differ significantly and vibrational wave functions with $n = 0$ for these electronic states overlap. This makes possible observation of a direct transition between the ground vibrational

states. The corresponding ZPL at 1.945 eV exhibits a strong inhomogeneous broadening attributed to a large strain variation in the ^3E state.²⁵

An electron from NV^- can be removed with formation of the NV^0 defect. In this case, the ZPL energy is higher, $\sim 2.16\text{ eV}$.^{28,29} The irradiation of NV^- centers with different sources ($2.21\text{--}2.43$, $2.53\text{--}2.76$, and $3.26\text{--}3.76\text{ eV}$ photons) causes significant variations in the PL band,³² which can be due to excitations of higher electronic states of NV^- , involvement of NV^0 centers into the process, or both. Hence, detailed information about properties of several excited states of the NV defects is required; and high-level quantum chemical calculations would be useful for this purpose.

Upon optical excitation, the saturation signal of the NV^- center is more than an order of magnitude lower than one would expect from a two-level system. Weak saturation of fluorescence intensity can be explained by the presence of a metastable singlet state (^1A). However, ensemble experiments give only small indication of this state to be present. More direct evidence for the metastable state (the shelving effect) was obtained in single center experiments.³ The shelving effect explains the decrease of the NV^- luminescence beyond a detectable level at temperatures below 80 K . On the basis of the temperature dependence of the single center fluorescence intensity, the energy difference between the ^3E and ^1A states was determined as $\sim 300\text{ cm}^{-1}$. Such a feature of the electronic structure creates some problems for using this defect, especially at low temperatures. This bottleneck can be overcome by employing a repumping laser, but the deshelving procedure leads to strong broadening of spectral lines.³ Because of the small energy gap between the ^3E and ^1A states, their relative position can be exchanged by modifying the defect vicinity or the defect itself. Another approach is to use a similar defect but with another structure and symmetry. Quantum chemical calculations would be also useful for testing different possibilities.

Theoretical calculations of the properties of NV^- available in the literature were performed at the DFT level with local spin density approximation (LSDA) using a model cluster including about 70 atoms with a small Gaussian basis set.⁴¹ Another group employed self-consistent spin-polarized calculations within a generalized gradient approximation (GGA) using the full-potential linearized augmented plane wave (LAPW) method with periodic boundary conditions⁴² and the analysis of electronic states was carried out on the basis of Kohn-Sham eigenvalues. In ref. 41 a more accurate evaluation of optical transition energies was made by using the Slater transition method, in which the transition energy is calculated as a difference between first derivatives of the energy for the special state containing half electron at the donating and accepting orbitals with respect to occupation numbers of these orbitals. Similar approaches are widely used for modeling of other point defects in diamond.^{43–54}

The theoretical results for the NV^- center are in reasonable agreement with the experimental data, however, other publications offered different interpretation of the electronic structure of this defect.^{36,38} They cast a doubt on the thermal stability of the negatively charged defect and construe the observed properties exclusively based on the neutral state and the appearance of the Jahn-Teller effect. This triggered a discussion concerning vari-

ous explanations of the available experimental results and possible electronic structure of the defect responsible for the 1.945 eV ZPL band.^{27,39,40} In our opinion, the model from refs. 36 and 38 is not solidly substantiated. However, the approach used in ref. 41 is also not very reliable. First, a small basis set was used without polarization and diffuse functions, which usually leads to significant overestimation of excitation energies. Second, the DFT approach sometimes fails for open-shell point defects,^{55,56} underestimating transition energies. Therefore, for some systems reasonable agreement between the calculated and experimental results may be due to accidental error cancellation; in other similar cases the accuracy of theoretical results may be much lower. Hence, it is worthwhile to perform additional theoretical calculations of the NV⁰ and NV⁻ defects applying more sophisticated methods based on the multireference approach.

The studies (especially theoretical) of the defects containing two and three N atoms (N3, H3, H2) are scarce, despite the fact that these centers also have remarkable properties. It was proposed that N3 with ZPL of ~2.8 eV has electronic structure qualitatively similar to that of NV⁻: the ground state of the A-type, E and A excited states with a small energy difference where the A state is slightly lower.¹ Theoretical modeling⁴⁷ at the LSDA level did not reveal such states, and instead an excitation to a shallow a₁ trap localized outside the vacancy (a charge transfer transition) was suggested. Clearly, calculations with larger basis sets and utilizing more sophisticated theoretical methods would be informative. For the H3 defect with ZPL of ~2.33 or 2.46 eV^{1,31} additional higher states were found, possibly with involvement of the negatively charged state with ZPL of ~1.26 eV for the first transition.³¹ Quantum chemical calculations would be useful for elucidating the electronic structure and interpretation of the available data for these centers.

A vacancy in diamond can be combined with other impurities. Admixture atoms larger than C or N (Si and P) are unable to occupy the same position as the substituted C atom and are usually located approximately in the center of a di-vacancy giving rise to electronic structure with lower ZPL values of ~1.7 eV.^{41,48} Thus, combination of substitution atoms and a vacancy results in several weakened C—C bonds or unpaired electrons and creates a complex electronic system with electron transitions in IR, UV, and visible ranges. Variations of the type and the number of impurity atoms or functional groups give an opportunity to create optically active centers with different desirable properties. For selective production of quantum dots with required characteristics it is necessary to elucidate how the admixtures influence the defect properties and quantum chemical modeling can be a useful tool for this task. Therefore, the studies of optical properties of local defects in diamond represent a broad field for applications of quantum chemical calculations. As a first step in this direction, the goal of this article is modeling of photoadsorption properties of the nitrogen-vacancy defect.

However, one can expect that defects in diamond possess complicated, multideterminant wave functions, especially for excited electronic states. Hence, the modeling should be based on multireference methods, such as, for instance, CASSCF (MCSCF),^{57,58} MRDCI,⁵⁹ MRCI,^{58,60,61} and CASPT2.^{62,63} So as it is feasible, from the point of view of computational demands, to include only few electrons and molecular orbitals into an

active space of CASSCF calculations, the account for electron correlation in this approach is very limited, as dynamic correlation is not included. With proper selection of active space it can provide qualitatively correct description of the wave function and reasonable values of geometry parameters, but for energetic properties its accuracy is not sufficient. More sophisticated MRDCI and MRCI methods give accurate results for small molecules, but for moderate-size systems it is not feasible to take into account electron correlation for all valence electrons, and therefore these approaches are also limited. At present, the most suitable approach for multireference systems with several tens of valence electrons is CASPT2,^{62,63} where the account of electron correlation for all valence electrons is performed on the basis of a CASSCF wave function utilizing the second order perturbation theory. The CASPT2 method is mainly used in this work for calculations of excitation energies for NV-defects in diamonds.

The Choice of Model Clusters and Calculation Details

Quantum chemical calculations of a diamond fragment and the NV-defect were carried out using three types of model clusters with termination of broken boundary bonds by H atoms, C₂₁H₂₈, C₃₅H₃₆, and C₅₁H₅₂ (see Fig. 1). In the first system, the central atom is surrounded by two carbon shells forming a C₁₇ system, but in this case it is impossible to terminate all boundary bonds by H atoms, as some centers become very close to each other. This difficulty can be overcome by adding four C atoms with the same bond distances and bond angles as those in diamond but with torsion angles shifted by 60°: see the C₂₁H₂₈ cluster, where boundary C atoms have two CH bonds each. Another, but more expensive way to solve this problem is to use a larger C₃₅H₃₆ cluster, where C atoms from the second shell have one CH bond each. In the C₅₁H₅₂ cluster, all C atoms from the second shell have C—C bonds only; to avoid crowding of boundary H we used the same approach as for the C₂₁H₂₈ system. Additionally, we also used a small C₅H₁₂ model cluster for testing purposes.

Geometry optimization of the C₅₁H₅₂ cluster was performed at the HF and B3LYP levels with the standard 6-31G* basis set for central 17 atoms and 6-31G for all remaining atoms. Outer C atoms were kept frozen in the crystalline positions, and coordinates of the C atoms from the first and second shells and all H atoms were fully optimized. The same approach was used for C₃₅H₃₆ and additionally we carried out full optimization with the 6-31G* basis set. Geometries of smaller clusters were fully optimized at the HF, B3LYP, and MP2 levels of theory. The GAUSSIAN 03 program package⁶⁴ was utilized for these calculations. The calculated C—C bond lengths are in good agreement with the experimental value for diamond for all models in use, but the most accurate results with deviations from experiment of only ~0.01 Å were obtained at the HF and MP2 levels; at B3LYP the C—C distances are slightly overestimated (see Table 1). The influence of the cluster size on the calculated geometric parameters appeared to be weak.

Modeling of the NV-defect was based on the three clusters discussed earlier. The vacancy was placed in the center of the

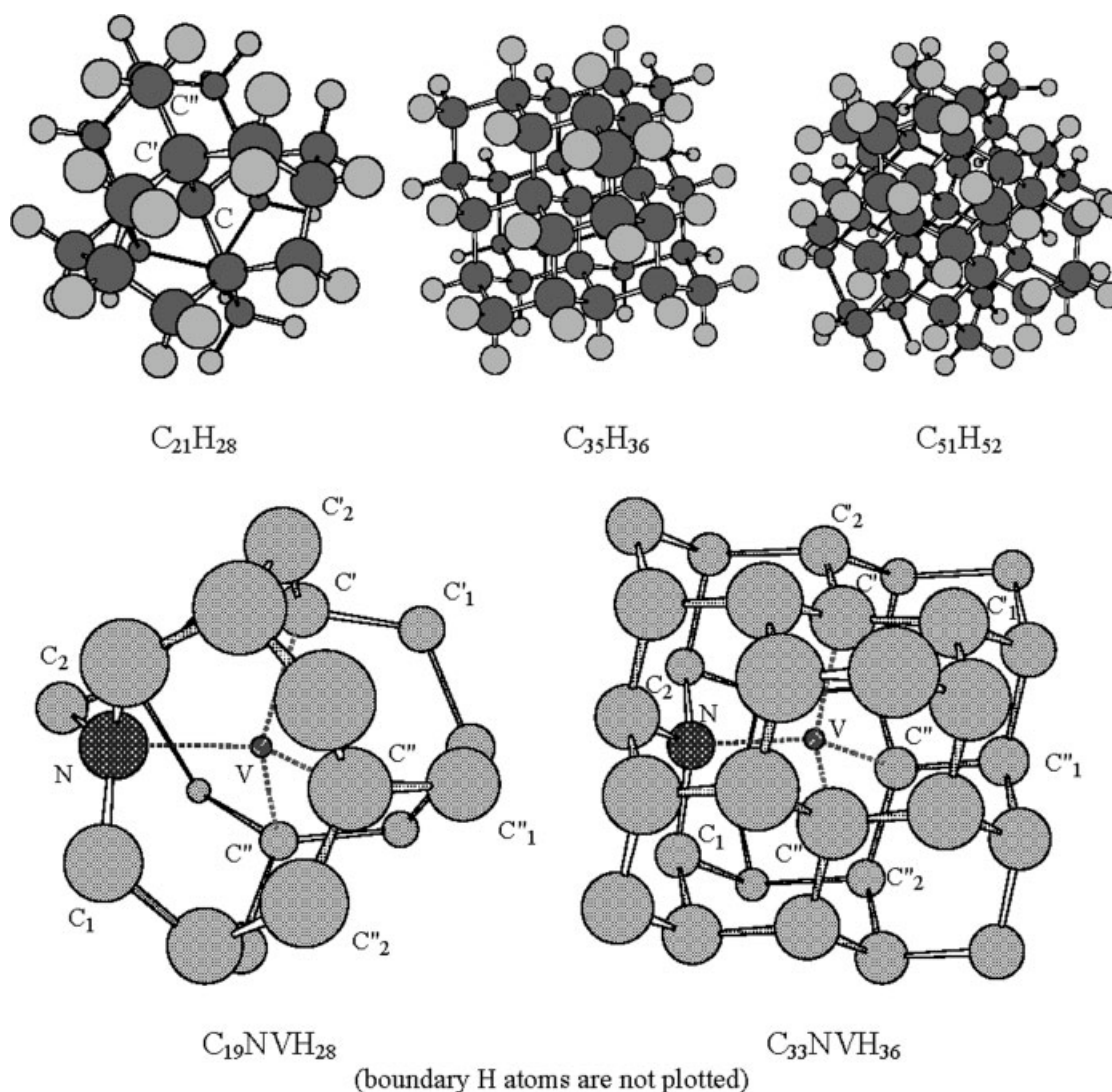


Figure 1. Model clusters used for simulations of a diamond fragment and the nitrogen-vacancy (NV) defect in diamond.

cluster and one C atom from the inner shell was replaced by N (see Fig. 1). The outer atoms were kept frozen in the positions of the defect-less system, and atomic coordinates for the first and second shells (four and 12 C atoms, respectively) were optimized within C_s symmetry constraints to allow for possible Jahn-Teller distortion. So as the NV defect can have a negative charge, the basis set used for the calculations of the initial clusters was augmented by diffuse s- and p-functions as in the 6-31+G* basis set for atoms from the first shell and s-functions for atoms from the second shell. Three electronic states were calculated: negatively charged triplet (nt), neutral doublet (d), and neutral quartet (q). Calculations were performed at the HF and B3LYP level and no principal differences between electronic structures obtained by these two methods were found.

The electron density of HF boundary molecular orbitals (MOs) for the smallest (C_3NVH_{12}) and middle-size ($C_{33}NVH_{36}$)

model clusters are plotted in Figures 2 and 3, respectively. In both systems, the compositions and shapes of appropriate MOs are similar, but the picture for the small cluster is more simple and clear. The lowest MO from this group (HOMO-1) corresponds to the nitrogen lone pair; it is doubly occupied in all considered states. The next MO (HOMO) is mainly constructed from broken bonds of vacancy-related C atoms; it has weak C—C bonding and C—N antibonding characters. This MO is doubly occupied in the negative triplet and neutral doublet states, but singly occupied in the quartet state. The next two MOs (SOMO-A' and SOMO-A'') are components of the doubly degenerate E orbital with a nonbonding C—C character. These MOs are singly occupied in the nt and q states and share one electron in the d state. The unoccupied (empty) MOs are very diffuse; LUMO is similar to a Rydberg-type s atomic orbital (AO) and LUMO +1 is reminiscent of a p-AO. However, one

Table 1. Optimized Geometric Parameters of Model Clusters Without Defects.

	R ₁ (HF)	R ₁ (B3LYP)	R ₁ (MP2)	R ₂ (HF)	R ₂ (B3LYP)	R ₂ (MP2)
C ₅ H ₁₂ ^a	1.535	1.540	1.530	—	—	—
C ₂₁ H ₂₈ ^a	1.569	1.576	1.563	1.564	1.570	1.560
C ₃₅ H ₃₆	1.557	1.565, 1.564 ^a	—	1.547	1.540, 1.551 ^a	—
C ₅₁ H ₅₂	1.548	1.548	—	1.561	1.563	—

R₁ and R₂ are C—C distances in the central fragment containing 17 carbon atoms and in the second layer surrounding the central fragment, respectively. The experimental C—C bond length in diamond is 1.546 Å.

^aFull geometry optimization was carried out with the 6-31G* basis set. Otherwise, the 6-31G* basis set was used for seventeen central C atoms and 6-31G for all others atoms. The positions of the central atoms were optimized and the coordinates of outer (boundary) carbons were frozen in crystalline positions.

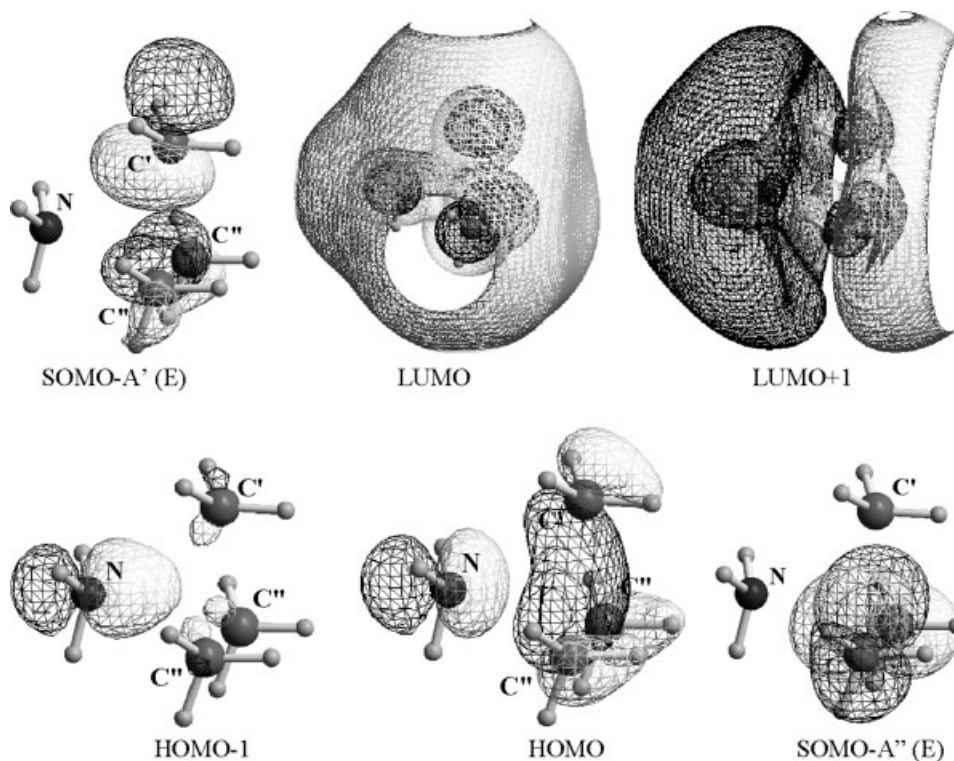
has to keep in mind that when these orbitals are involved in multideterminant CASSCF wave functions, their shapes can significantly change.

In the quartet state, three unpaired electrons are located mainly at inner C atoms with broken bonds and occupy orbitals of e- and a-types ($a^1e^1e^1$), as the actual symmetry of the system is C_{3v}. As compared to the defect-less system, atoms of the inner shell are shifted from the center by 0.20–0.25 Å in the small cluster and by 0.10–0.12 Å in the biggest one; the shift is more significant for C atoms than for the nitrogen. Nevertheless, distances between chemically bonded atoms are similar with deviations of only 0.01–0.03 Å (Table 2). Atoms from the second layer exhibit only a small shift from the center, ~0.01 Å. In

all the models, interatomic bonds between threefold coordinated atoms and their nearest neighbors (N—C' and C—C'') are 0.05–0.07 Å shorter than the C—C distance in the defect-less cluster.

In the doublet state the occupancy of different components of degenerate e-orbitals is not equivalent, which leads to Jahn-Teller distortion. However, in the system under investigation it concerns mainly electronic distribution, especially spin density (Table 3), so as the geometric distortion is very weak; distances from the center are split by 0.01–0.02 Å, whereas the splitting of bond lengths is practically zero (Table 2). The main trends in geometry changes are approximately the same as for the quartet state.

In the negative triplet state the wave function has C_{3v} symmetry and the additional electron occupies the a MO giving rise

**Figure 2.** Electron density plot of boundary orbitals for the smallest C₃NV cluster obtained from HF calculations.

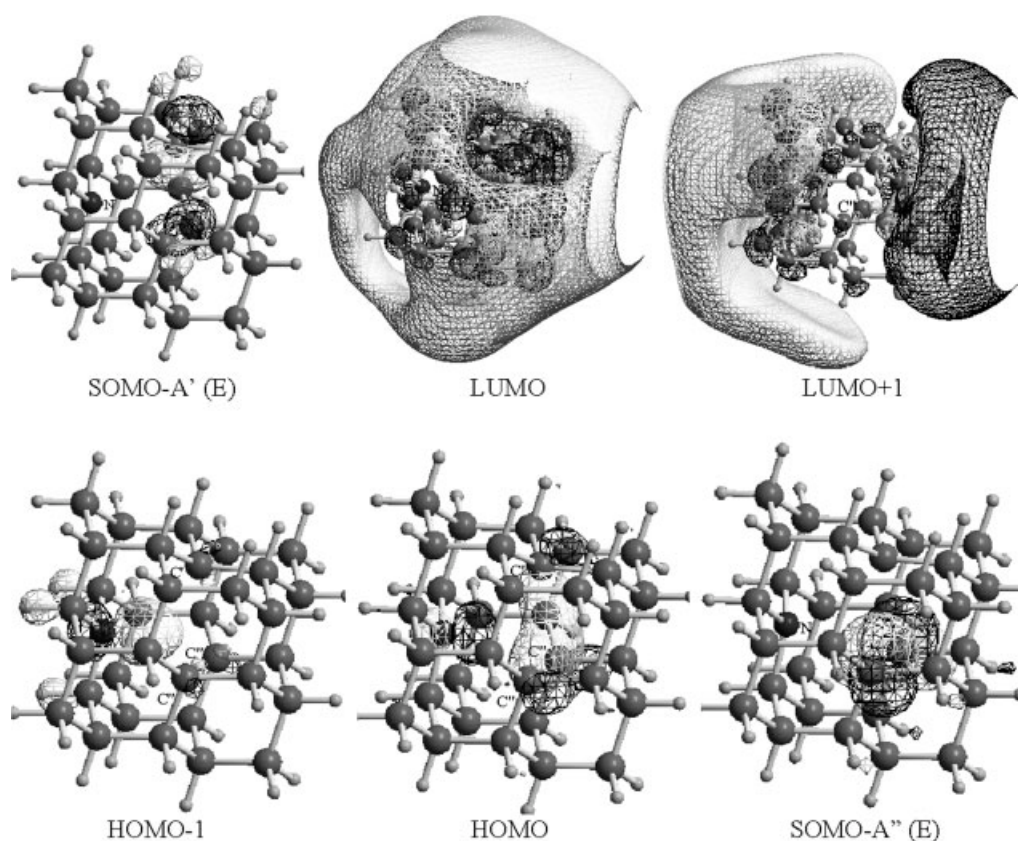


Figure 3. Electron density plot of boundary orbitals for the middle-size $C_{33}NV$ cluster obtained from HF calculations.

to the $a^2e^1e^1$ electronic configuration. The main change in geometry compared to the neutral states is a larger shift of N and smaller shifts of C atoms, apparently due to the effect of the

additional electronic density, which is redistributed at the broken bonds of the defect (Table 2). At the HF level, the negative triplet state is less stable than the neutral doublet and quartet, how-

Table 2. Optimized Interatomic Distances $R(AB)$, in Å, and Relative Energies E_r (in eV) for Model Clusters Containing the NV-Defect in Different Electronic States.

System, method, spin state	E_r	R (VN)	R ($VC^{f,g}$)	R ($NC_{1,2}$)	R ($C^{f,g}C^{f,g}_{1,2}$)	R ($VC'_{1,2}$)	R ($VC''_{1,2}$)
A1, HF, nt	1.97	1.85	1.78	1.47	1.50, 1.51	2.52	2.53–2.55
A1, HF, d	0.00	1.78	1.80, 1.82	1.48	1.51	2.52	2.54–2.56
A1, HF, q	0.17	1.77	1.83	1.48	1.51	2.52	2.55–2.56
A1, B3LYP, nt	0.00	1.88	1.79	1.47	1.50	2.54	2.54
A1, B3LYP, d	0.07	1.82	1.79, 1.82	1.48	1.50–1.51	2.54	2.55
A1 B3LYP, q	0.36	1.78	1.85	1.49	1.50	2.54	2.55
A2, HF, nt	2.14	1.70	1.67	1.48	1.50, 1.51	2.50	2.51, 2.52
A2, HF, d	0.00	1.66	1.71, 1.72	1.49	1.50–1.51	2.50–2.51	2.52–2.53
A2, HF, q	0.26	1.65	1.74	1.50	1.50, 1.51	2.50	2.53
A3, HF, nt	2.19	1.68	1.61	1.49	1.52, 1.54	2.53	2.53, 2.54
A3, HF, d	0.00	1.64	1.66, 1.68	1.51	1.52–1.53	2.53	2.53–2.54
A3, HF, q	0.31	1.63	1.67	1.51	1.52, 1.53	2.53	2.54

nt, d, and q denote negative triplet, neutral doublet, and quartet spin states, respectively. A1, A2, and A3 designate $C_{19}NVH_{28}$, $C_{33}NVH_{36}$, and $C_{49}NVH_{52}$ model clusters. The 6-31+G* basis set was used for central atoms 1–4 (the first layer around the vacancy), 6-31G* with a diffuse s-AO at atoms 5–16 (the second layer around atoms 1–4), and 6-31G for all other atoms.

Table 3. Interatomic Distances $R(AB)$, in Å, for the Ground States of the NV^{-1} and NV^0 Defects Optimized at the CASSCF level.

$R(AB)$	VN	VC'	VC''	NC ₁	NC ₂	C'C' ₁	C'C' ₂	C''C' ₁	C''C'' ₂
$1^3A'', (8,11)^a$	1.887	1.770	1.764	1.47	1.47	1.51	1.52	1.53	1.52
$1^3A'', (4,11)^a$	1.886	1.765	1.769	1.47	1.47	1.51	1.52	1.51	1.52
$1^2A', (8,11)^a$	1.844	1.825	1.781	1.48	1.48	1.52	1.52	1.53	1.52
$1^2A'', (8,11)^a$	1.843	1.774	1.806	1.48	1.48	1.52	1.53	1.52	1.52
Averaged ^b	1.844	1.800	1.793	1.48	1.48	1.52	1.52	1.52	1.52
$1^2A', (4,11)^a$	1.829	1.822	1.777	1.48	1.48	1.52	1.52	1.53	1.52
$1^2A'', (4,11)^a$	1.829	1.771	1.804	1.48	1.48	1.52	1.53	1.52	1.52
Averaged ^b	1.829	1.796	1.790	1.48	1.48	1.52	1.52	1.52	1.52

The A1 model cluster was used in the calculations. The basis sets were 6-31+G* for N, C', C'' atoms, 6-31G* + s(0.0438) for C atoms 5–16 in the second layer, and 6-31G basis set for all other atoms.

^aActive space used in CASSCF calculations.

^bAveraged between two $1^2A'$ and $1^2A''$ components of the 1^2E state, which should be degenerate within C_{3v} symmetry.

ever, the inclusion of electron correlation stabilizes the negatively charged state.

For negative triplet and neutral doublet, geometric parameters were additionally optimized at the CASSCF level with two active spaces, including 8 or 4 active electrons distributed on 11 MOs (Table 3). For the NV^{-1} defect the resulting geometry is slightly distorted from C_{3v} symmetry, probably due to a limited active space; the inclusion of extra vacant orbitals into the active space, from (8,11) to (4,11), results in the geometry closer to the C_{3v} -symmetric structure. Nevertheless, the CASSCF optimized geometric parameters are similar with the two active spaces and very close to those obtained at B3LYP (compare Tables 2 and 3). For neutral doublet (NV^0) the distortion of geometry from C_{3v} symmetry is more substantial; it concerns mainly the distances between the vacancy center and vacancy-related C atoms, for which the differences reach 0.02–0.04 Å. Depending on the optimized state, $1^2A'$ or $1^2A''$, the deviations have opposite signs and almost equal absolute values, and the averaged geometry is very close to C_{3v} symmetry (Table 3). So as one can expect equal populations of both $1^2A'$ and $1^2A''$ components in the degenerate 1^2E state, the geometry of NV^0 in this state will probably have C_{3v} symmetry.

The results obtained with clusters of different size are similar; the most significant difference concerns the shift of inner shell atoms from the center in the smallest cluster, but bond distances are much closer to each other. For the $NVC_{49}H_{52}$ and $NVC_{33}H_{36}$ systems all characteristics are very similar. We tried to use the small cluster with frozen atoms of the second shell, where the atomic coordinates were taken from $NVC_{49}H_{52}$, but the results did not change significantly. Additionally, we tested the effect of the basis set extension by adding diffuse p-functions to the second layer atoms. The results were almost identical to those obtained with the initial basis set.

There is no substantial difference between geometric parameters calculated within the HF and B3LYP methods, however, relative energies of the electronic states were significantly affected. At the B3LYP level negative triplet is the most stable, but the difference between the nt and d states is small (Table 2) and it remains small at MP2, 0.0 and 0.2 eV, respectively. At the nt

geometry (vertical ionization) the calculated energy differences between nt, d and q states are slightly higher, 0.4 and 0.8 eV. The basis set extension to 6-311+G* for the first shell and 6-31+G* for the second one gives the energy differences of 0.5, 0.9 eV at B3LYP and 0.3, 0.7 eV at MP2. With the large $NVC_{49}H_{52}$ cluster, the relative stabilities did not change significantly, 0.1 and 0.7 eV at B3LYP.

Mulliken spin distributions at the HF and B3LYP levels are qualitatively similar, but there are some quantitative differences. Unpaired electrons are located mainly at the three inner C atoms of the defect, producing spin polarization of electron density at the atoms linked to this group; the spin density at N and at N-bound C atoms remains weakly disturbed. So as the determination of Mulliken charges and densities is rather arbitrary, especially for basis sets containing diffuse functions, we also calculated isotropic Fermi contact couplings at the ^{14}N and ^{13}C nuclei as a measure of spin distribution. Considering this property, the qualitative picture remains the same: the largest constants are found for the threefold coordinated C atoms, much smaller values (~ 10 times as small) and with opposite signs—for their neighbors, and nearly zero—at nitrogen and N-bound C nuclei. These results indicate that the nitrogen-related electron distribution is rather rigid and is not involved in electronic rearrangement with variations of the electronic state of this defect.

Excited States of the NV^{-} Defect

In NV^{-} , three hybrid orbitals of the C atoms around the vacancy form a_1 and e orbitals and the ground state of this system ($^3A_2$) has the $a_1^2e^1e^1$ electronic configuration with two unpaired electrons occupying the degenerate e orbitals. Additionally, the N lone pair (LP) corresponds to a lower doubly occupied a_1 MO. The first triplet excited state may be formed by the $a_1 \rightarrow e$ electronic transition at the vacancy-related C atoms and could be of the ^3E type. Formation of higher excited states can be achieved with the involvement of the N lone pair (the $a_1^2 \rightarrow e^1$ transition) or e^1 and unoccupied MOs (LUMOs). To test this schematic picture and to estimate the influence of the basis set quality and

Table 4. Relative Energies (eV) and Oscillator Strengths (in bold) for Lowest Excited States of the NV[−] Defect Calculated at the Ground Triplet State Geometries.

System, method	1^3A_2	1^1E	1^1A_1	1^3E	2^1E	2^3E	2^3A_2
A0, CIS(D)	0.0	–	–	1.90, 0.155	–	3.20, 0.059	1.69, 0.023
A0, CAS(14,14)	0.0	0.28	0.75	0.96, 0.152	1.07	1.24, 0.070	–
A0, MRCI(14,12) ^a	0.0	0.37 <i>0.42</i>	1.11 <i>1.17</i>	1.35 <i>1.43</i>	1.36 <i>1.43</i>	1.56 <i>1.52</i>	–
A0, CAS(8,15)	0.0	0.38	0.96	1.14, 0.134	1.20	1.37, 0.072	–
A0, MRCI(8,12) ^a	0.0	0.43	1.16	1.41 <i>1.46</i>	1.47	1.61 <i>1.65</i>	–
A1, TD-B3LYP	0.0	–	–	1.52, 0.088	–	2.21, 0.014	2.13, 0.001
A1, CAS(8,11)	0.0	0.44	1.00	0.98, 0.188	1.13	1.22, 0.097	–
A1, MRCI(8,10) ^a	0.0	0.45 <i>0.50</i>	1.22 <i>1.23</i>	1.30 <i>1.36</i>	1.37 <i>1.37</i>	1.66 <i>1.61</i>	–
A1, CAS(8,11) ^b	0.0	–	–	1.15, 0.137	–	–	–
A1, MRCI(8,10) ^{a,b}	0.0	–	–	1.41 <i>1.46</i>	–	–	–
A2, TD-B3LYP	0.0	–	–	1.58, 0.124	–	1.88, 0.031	2.04, 0.012

A0 and A1 are the C₃NVH₁₂ and C₁₉NVH₂₈ model clusters, respectively. The basis sets used were the following, in A0: 6-311+G* for C and N atoms and 6-31G for H; in A1: 6-31+G* for four central atoms, 6-31G* + s(0.0438) for atoms 5–16 in the second layer and 6-31G for all other atoms.

^aDavidson-corrected MRCI energies are given in italic.

^bBased on state-averaged CASSCF calculations for two states.

model cluster size on the calculated excitation energies, we initially performed TD-DFT(B3LYP) calculations of vertical excitation energies for several lowest tripled states (Table 4). The qualitative picture according to the aforementioned scheme was reproduced only with the smallest 6-31G basis set for the C₁₉NV model cluster (A1). The first excited state (1^3E , ~1.8 eV) is then formed by the $a_1^2 \rightarrow e^1$ transition, the LP(N) $\rightarrow e^1$ excitation creates the 3^3E state (~4.3 eV), and all other available states in the 3.6–4.5 eV range are formed mainly by excitations from the singly occupied e^1 to empty MOs. However, the basis set extension by including polarization and diffuse functions changes this picture significantly. The addition of diffuse functions on the vacancy-related N and C atoms in the first layer around V leads to a moderate decrease of the 1^3E energy by ~0.15 eV, but the other states fall down drastically, by about 1 eV. The diffuse functions on C atoms from the second layer cause a further energy decrease, especially for the second and higher excited states. The effect of polarization d-functions is weaker and the difference between the calculated values with the 6-311+G* and 6-31+G* basis sets is rather small. With our best basis set (atoms 1–4: 6-311+G*; 5–16: 6-31+G*; 17–20: 6-31+G), the relative energy of the 1^3E state, ~1.4 eV, is significantly underestimated and the next higher excited states lie in the close range of 1.71–2.44 eV (Table 4). The 1^3E state is formed mainly by the $a_1^2 \rightarrow e^1$ transition, but the contributions of $e^1 \rightarrow$ LUMOs are also substantial; the other states are formed mainly by the $e^1 \rightarrow$ LUMOs excitations, while the LP(N) $\rightarrow e^1$ excitation is not involved. With the larger C₃₃NVH₃₆ cluster, the relative energy of the first excited state remains nearly unchanged, but the other states are lower in energy than those for the smaller cluster (Table 4). So as all these states are formed with contribution of diffuse (Rydberg-type) orbitals, their excitation energies should be largely underestimated at the TD-DFT level. In all cases the first excitation exhibits the largest oscillator strength and the other transitions are much weaker (Table 4). Certainly, we have to keep in mind

imperfection of this theoretical method, which usually significantly underestimates excitation energies for states with diffuse electronic distribution, and so the effect of diffuse functions might be overestimated in the TD-DFT calculations. Nevertheless, these calculations demonstrate that the influence of diffuse functions is essential, and they need to be included at least for the vacancy-related atoms to adequately reproduce the transition energy even for the lowest excited states. In all cases, the excited states are formed with contributions from several one-electron transitions with significant weights. This indicates that in this system the excited states have multideterminant wave functions. It should be also noted that the strong influence of diffuse functions on the calculated excitation energies in cluster models may point to the fact that the excited states extend beyond the cluster border and may have nearly-conduction band character, in which case such cluster is no longer appropriate to describe the corresponding state.

CASSCF calculations of excited states were performed using two model clusters, small C₃NH₁₂ and moderate C₁₉NVH₂₈. The small cluster was used for the active space selection and a qualitative analysis of the results and then the excitation energies were refined with the moderate model cluster. The calculations with different active spaces demonstrated that in the lowest excited states four electrons from the threefold-coordinated C atoms are localized close to the center of the cluster at the vacancy position. Contributions from the electrons involved in bonding of these atoms with the rest of the bulk (CC' bonds) and from the N-related electrons, both from the N lone pair and NC' bonds, are small; the occupation numbers of the corresponding MOs included into the active space remain to be close to 2.0. Significant deviations from 2.0 or 0.0 are found for the occupation numbers of the MOs, corresponding to highest occupied ($a_1^2e^1e^1$) and lowest unoccupied orbitals of the ground state determinant, which are composed from the AOs of threefold coordinated C atoms and diffuse functions. This means that the lowest excitations of the NV-defect are formed by electronic redistribution at the C atoms with broken

Table 5. Relative Energies (in eV, With Respect to the $1^3A''$ State) and Oscillator Strengths (in bold) for 10 Lowest States of the NV^- Defect Calculated with the $C_{19}NVH_{28}$ Model Cluster at the Ground Triplet State Geometry.

State	CAS(8,15) B1	CAS(4,14) B1	CAS(4,14) B1a	CAS(4,14) B2	CAS(4,14) B2a	State	CAS(4,14) B2a
$1^3A'$	1.03, 0.067	1.39, 0.051	1.00, 0.154	1.36, 0.028	1.09, 0.158	$1^1A''$	0.42
$2^3A''$	1.10, 0.036	1.40, 0.053	1.00, 0.150	1.36, 0.028	1.10, 0.156	$1^1A'$	0.42
$3^3A''$	1.14, 0.012	1.52, 0.001	1.23, 0.016	1.46, 0.000	1.31, 0.008	$2^1A'$	1.09, 0.349
$2^3A'$	1.15, 0.000	1.52, 0.005	1.23, 0.015	1.47, 0.000	1.31, 0.006	$2^1A''$	1.26, 0.012
$4^3A''$	1.19, 0.013	1.52, 0.001	1.35, 0.004	1.49, 0.018	1.43, 0.004	$3^1A'$	1.26, 0.008
$3^3A'$	1.20, 0.004	1.54, 0.000	1.33, 0.000	1.49, 0.017	1.40, 0.000	$3^1A''$	1.37, 0.073
$4^3A'$	1.38, 0.083	1.74, 0.101	1.45, 0.035	1.69, 0.085	1.52, 0.028	$4^1A''$	1.51, 0.115
$5^3A''$	1.49, 0.068	1.74, 0.103	1.45, 0.034	1.69, 0.088	1.52, 0.028	$4^1A'$	1.52, 0.113
$6^3A''$	1.67, 0.020	2.03, 0.020	1.53, 0.092	2.01, 0.025	1.60, 0.090	$5^1A''$	1.91, 0.149
$5^3A'$	1.78, 0.025	2.16, 0.021	1.53, 0.089	2.11, 0.021	1.60, 0.087	$5^1A'$	1.92, 0.168

State-averaged CASSCF calculations with equal weights for A' and A'' states were employed. The basis set notation is the following: B1, 6-311+G* for N, C', and C'' atoms, 6-31G* for C atoms 5–16 in the second layer, 6-31G for all other atoms; B1a – 6-311+G* for C' and C'', 6-31G + s(0.0438) for atoms 5–16, 6-31G for all other atoms; B2, 6-31+G* for N, C', C'', 6-31G* for atoms 5–16, 6-31G for all other atoms; B2a, 6-31+G* for N, C', C'', 6-31G* + s(0.0438) for atoms 5–16 C, 6-31G for all other atoms.

bonds around the vacancy. The calculated CASSCF excitation energies are underestimated as the experimental vertical transition $^3A_2$ – ^3E energy should be about 2.15 eV,²⁵ but expansion of the active space toward vacant orbitals leads to a better description of the excitation energies (Table 4). Apparently, in this system the inclusion of empty MOs is essential for more complete account of electron correlation.

The use of the MRCI method gives slightly better results, however, the transition energies remain too low. The second excited triplet state 2^3E is only 0.2–0.3 eV higher than 1^3E , but has much lower oscillator strength (Table 4). State-averaged calculations for two states, 1^3A_2 and 1^3E , instead of three states, 1^3A_2 , 1^3E , and 2^3E , generate slightly higher energies and there is no substantial difference between the results for the small C_3NVH_{12} and moderate $C_{19}NVH_{28}$ clusters. The lowest singlet state 1^1E is found to lie 0.4–0.5 eV higher in energy than the ground state triplet and the second singlet 1^1A_1 state is 0.1–0.2 eV lower than the first excited triplet 1^3E , the experimental energy gap between them being about 0.04 eV. Although these calculations produce a qualitative correct picture of the lowest excited states, the quantitative description is flawed as the excitation energies are significantly underestimated. In our opinion, the main reason for these discrepancies is the use of a rather limited active space in the MRCI calculations. Additionally, we tried to test the CIS(D) approach^{64,65} for this system. It produces reasonable energy difference between the 1^3A_2 and 1^3E states, but gives 1^3A_1 as the lowest excited triplet instead of 1^3E (Table 4). This matches neither experimental observation nor the results of multireference calculations, and so the single-determinant-based CIS(D) method is not appropriate here.

Now we consider higher excitations of the NV^{-1} center. Calculations were carried out using the moderate $C_{19}NVH_{28}$ model cluster with several basis sets and active spaces. So as only the C_s point group instead of C_{3v} was utilized, the active spaces necessarily included both symmetry-equivalent a' and a'' orbitals originated from e MOs. Nevertheless, at the CASSCF(8,15) level with active space including 8 electrons on 15 MOs, the energies

and oscillator strengths f of the A' and A'' states degenerate within C_{3v} symmetry are slightly different. For instance, the difference in energies of the $1^3A'$ and $2^3A''$ components of 1^3E is ~ 0.07 eV and $f(2^3A'')$ is equal to approximately a half of the $f(1^3A')$ value (see Table 5). When the active window is shifted up toward vacant orbitals and the two lowest MOs with occupation numbers of ~ 1.98 are excluded in the (4,14) active space, the splitting in the properties of the symmetry-equivalent states is much lower. Additionally, this leads to higher excitation energies. With the B1 and B2 basis sets including diffuse functions on the vacancy-related atoms, the components of 1^3E state, $1^3A'$, and $2^3A''$, show moderate f values; the calculated oscillator strengths are higher for the components of 4^3E , $4^3A'$, and $5^3A''$, whereas for the other states they are lower. The addition of diffuse functions for the atoms from the second layer around the vacancy (B1a and B2a basis sets) leads to a decrease of excitation energies for all considered states and the f values become highest for the 1^3E components, followed by those for the 5^3E state, while the other oscillator strengths are calculated to be low (Table 5). For singlet states calculated with the (4,14) active space and B2a basis set at the CASSCF level, the lowest 1^1E state is about 0.4 eV higher than the ground triplet state and the first excited singlet ($1^1A'$) is ~ 0.01 lower than first excited triplet 1^3E (Table 5). Summarizing, there is no principal differences in the results of CASSCF calculations for lowest excited states. At this level of theory, the qualitative picture seems to be described reasonably well, but the excitation energies are significantly underestimated.

Next, we considered the effect of dynamic electron correlation using CASPT2 calculations with the MOLCAS program package.⁶³ As before, the calculations were carried out with two different basis sets (B3 and B3a, see Table 6) and two active states for CASSCF calculations, wave functions from which were used as initial approximation for CASPT2. The more complete account of electron correlation leads to an increase of the calculated excitation energies. With the best available basis set B3a and (4,16) active space including as many empty MOs as

Table 6. CASPT2 Relative Energies (in eV, With Respect to the $1^3A''$ state) for 10 Lowest Excited States of the NV^- Defect Calculated with the $C_{19}NVH_{28}$ Model Cluster at the Ground Triplet State Geometry.

Triplet states	Active space and basis set				Singlet states	Active space and basis set			
	(8,15) B3	(8,14) B3a	(4,16) B3a	(4,16) B3a ^a		(8,15) B3	(8,14) B3a	(4,16) B3a	(4,16) B3a ^a
$2^3A''$	2.10	1.55	1.79	1.91	$1^1A''$	0.15	−0.06	0.34	0.63
$1^3A'$	2.10	1.57	1.79	1.91	$1^1A'$	0.28	0.15	0.35	0.62
$3^3A''$	2.25	1.82	2.09	2.21	$2^1A'$	1.51	1.31	1.59	1.63
$2^3A'$	2.25	1.85	2.07	2.21	$2^1A''$	2.14	1.65	1.97	1.96
$4^3A''$	2.30	1.99	2.23	2.33	$3^1A'$	2.18	1.66	1.97	1.96
$3^3A'$	2.31	1.93	2.20	2.30	$3^1A''$	2.20	1.83	2.15	2.19
$4^3A'$	2.48	2.05	2.30	2.36	$4^1A''$	2.42	1.98	2.30	2.33
$5^3A''$	2.53	2.05	2.31	2.36	$4^1A'$	2.41	1.99	2.29	2.31
$6^3A''$	2.67	2.20	2.38	2.75	$5^1A''$	2.62	2.12	2.47	2.70
$5^3A'$	2.66	2.18	2.39	2.74	$5^1A'$	2.60	2.22	2.48	2.65

State-specific calculations were carried out separately for A' and A'' states. The basis set notation is the following: B3, aug-cc-pVDZ for N, C', and C'' atoms, 6-31G* for C atoms 5–16, 6-31G for all other atoms; B3a, the same as B3, but with 6-31G* + s(0.0438) for atoms 5–16. The experimental vertical $^3A_2$ - ^3E excitation energy is ~ 2.15 eV.²⁵

^aAt the geometry taken from the $C_{49}NV^-$ cluster in the triplet ground state.

possible, the calculated lowest excitation energy is underestimated by ~ 0.35 eV as compared to the experimental value (Table 6). The energetic order of singlet states does not changed significantly after the refinement at the CASPT2 level in comparison to that obtained at CASSCF.

As was discussed earlier, geometric parameters optimized for the moderate $C_{19}NVH_{28}$ model cluster are slightly different as compared to those for the larger model systems, mainly due to the shift of the vacancy-related atoms away from the vacancy center (Table 2). The calculations with the geometric parameters optimized for the $C_{49}NV^{-1}$ model cluster lead to a moderate increase of about ~ 0.1 eV for the energies of the 1^3E – 4^3E states and for the 5^3E state the energy change is more significant (Table 6). This reduces the deviation of the calculated lowest excitation energy for the 1^3E state from experiment to ~ 0.25 eV. For singlet states notable changes can be seen only for 1^1E and 4^1E .

In summary, combining the CASSCF and CASPT2 results, we predict the following sequence of electronic states for the NV^- defect in diamond:

1^3A_2 , 1^1E , 1^1A_1 , 1^3E , 2^1E , 1^1A_2 , 2^3E , 3^1E , 3^3E , 4^3E , 4^1E , 5^3E

The significant probabilities for excitations from the ground state according to the computed oscillator strengths are expected for the 1^3E and 5^3E states; the second adsorption band should be 0.8–1 eV higher in energy as compared to the first one. For singlet states, the oscillator strength between 1^1E and 1^1A_1 is large (Table 5), and so one can expect fast $1^1A_1 \rightarrow 1^1E$ de-excitation. It follows from this result that there exist a possibility to overcome the shelving effect for this center by stimulating the $1^1E \rightarrow 1^3A_2$ conversion.

Excited States of the NV^0 Defect

Within the single-determinant approach, the components of the wave function of the doubly degenerate 1^2E ground state of the

model $C_{19}NVH_{28}$ cluster are constructed in the following way: $\dots 42a'^2 30a''^2 43a' 44a' 45a' 31a''^0$ ($1^2A'$) and $42a'^2 30a''^2 43a' 44a' 45a' 31a''^0$ ($1^2A''$) within C_s symmetry. Here, the $43a'$ MO (HOMO-1) corresponds to the nitrogen lone pair and $44a'$ (HOMO), $31a''$, and $45a'$ (SOMO) orbitals are composed from the broken bonds of the carbon atoms located around the vacancy. The $44a'$ MO is doubly occupied and placing one electron on the degenerate $31a''$ or $45a'$ MOs gives the $1^2A'$ or $1^2A''$ components of the degenerate ground state. Hence, one can expect that the lowest excited states will be formed by transferring one electron from the doubly occupied HOMO-1 or HOMO to the empty or singly occupied $45a'$ or $31a''$ SOMO.

B3LYP calculations for NV^0 give the ground state wave function with nonequivalent occupations of the degenerate e orbitals and TD-B3LYP calculations with the 6-311+G* basis set at vacancy related atoms and 6-31G* at all others produce 4 lowest excited states in the range from 2 to 3 eV. In contrast to NV^{-1} , not only electrons from the broken bonds of three-coordinated C atoms around vacancy and diffuse functions but also the N lone pair participate in their formation. However, CASSCF calculations give a rather different qualitative result. Test computations with the minimal active space including only $44a'$, $45a'$, and $31a''$ MOs generate the following wave functions for the ground state components: $44a'^{1.4} 45a'^{0.6} 31a''^{1.0}$ and $44a'^{1.4} 45a'^{1.0} 31a''^{0.6}$ with separate treatment of the A' and A'' states, or $44a'^{1.4} 45a'^{0.8} 31a''^{0.8}$ in the case of state-averaged calculations. The $2^2A'$ and $2^2A''$ excited states in this case have very high energies of 5–6 eV, and the wave functions for these states do not correspond to a simple electron transfer from $44a'$ to $45a'$ or $31a''$ because the composition of these MOs in excited states is significantly changed, with appearance of large contributions from diffuse functions. The active space extension by including the empty MOs, which ensured reasonable results for the negative defect, does not change the qualitative picture for the neutral cluster; then the changes in orbital occupation numbers do

Table 7. CASSCF and CASPT2 (in Bold) Relative Energies (in eV, With Respect to the $1^2A'$ State) for Lowest Excited States of the NV^0 Defect Calculated with the $C_{19}NVH_{28}$ Model Cluster at the Ground Doublet State Geometry.

Active space	$1^2A''$	$2^2A''$	$2^2A'$	$3^2A''$	$3^2A'$	$4^2A''$	$4^2A'$
(3,15), B3a	0.01, 0.00	4.14, 3.63	4.05, 3.47	4.90, 4.28	4.18, 3.98	5.03, 5.03	4.58, 4.26
(5,16), B3a	0.23, 0.04	3.89, 3.32	4.04, 3.28	4.29, 4.61	4.17, 4.02	4.55, 4.94	4.57, 4.28
(7,15), B3a	0.03, 0.07	3.89, 2.90	4.10, 3.62	4.67, 3.11	4.30, 3.95	4.70, 4.64	5.04, 4.24
(9,15), B3a	0.94, 0.00	4.79, 3.29	4.02, 3.32	5.11, 4.52	4.11, 3.98	5.45, 5.28	4.53, 4.83
(9,13), B4a	−0.64, 0.20	2.44, 3.49	2.89, 3.23	2.77, 3.83	3.08, 3.48	2.80, 3.86	3.14, 3.51
(9,6), B3	0.08, 0.06	3.83, 2.38	4.36, 2.64	4.38, 2.88	6.01, 3.47	6.15, 4.38	6.26, 4.39
(9,7), B3	0.08, −0.16	4.33, 2.36	4.65, 2.85	4.72, 2.60	5.34, 3.93	6.21, 4.36	5.86, 4.64
(9,8), B3	−0.09, −0.07	4.07, 2.29	4.43, 2.75	4.44, 2.60	5.10, 3.97	5.92, 4.33	5.67, 4.54

State-specific calculations were carried out separately for A' and A'' states. The basis set notation is the following: B3, aug-cc-pVDZ for N, C', and C'' atoms, 6-31G* for C atoms 5–16, 6-31G for all other atoms; B3a, B3 + s(0.0438) for atoms 5–16; B4a, B3 + sp(0.01) for vacancy-related atoms + s(0.01) for atoms 5–16.

not exceed 0.01, but for the $2^2A'$ and $2^2A''$ states the excitation energies are lowered to 3.9 eV, and the $46a'$ MO gets involved in the $2^2A'$ wave function. With extended active spaces including several empty MOs, the lowest excitations correspond to the electron transfer not from $44a'$, but from $45a'$ and $31a''$ to higher empty MOs.

The extension of the active space down by inclusion of the doubly occupied $43a'$ MO (5 active electrons), does not cover the nitrogen lone pair. Alternatively, according to the character of the computed CASSCF wave function, a lower MO corresponding to C—C bonds of the vacancy-related atoms with their neighborhood gets into the active space, and the MO of the nitrogen lone pair remains out of the active space. Additionally, this leads to nonequivalent participation of the degenerate MOs in the active space. To restore the symmetry equivalence of these orbitals, one needs to additionally include the $30a''$ orbital and then the active space becomes (7,15). For the same reason, the active space with nine active electrons violates the equivalence of degenerate MOs and the nitrogen lone pair is again pushed out of the active space. The relative energies of the lowest excited states calculated with all considered active spaces remain overestimated. A significant decrease of CASSCF excitation energies (by ~ 1 eV) can be achieved by adding highly diffuse functions (with exponent of 0.01) at atoms from the first and second layers (see Table 7, B4a basis set). Apparently, all the transitions involved correspond to electron transfer to diffuse Rydberg-type orbitals.

The inclusion of dynamic electron correlation at the CASPT2 level however gives a rather contradictory result. Transition energies calculated with the B3a basis set with moderate diffuse functions decrease by 0.5–0.6 eV to 3.3–3.5 eV (Table 7). This is not sufficient to attain the experimental value, which should be close to 2.4–2.5 eV for the vertical excitation, if the differences between ZPL and the maximum of PA band for NV^0 and NV^- are similar; note that ZPL for NV^0 has been assigned to 2.16 eV.^{28,29} In contrast, the CASPT2 excitation energies calculated with the B4a basis set show an increase by up to 1 eV as compared to the CASSCF values (Table 7). The most probable reason of this failure is incorrect prediction of the order of excited states by CASSCF resulting in the absence of the appro-

priate states among available lowest CASSCF roots. To test this supposition we carried out calculations with the B3 basis set and (9,6) active space, in which we artificially limited participation of diffuse functions. Then, the lowest CASSCF excitation energies are rather high, in the range of 4–6 eV, and the $43a'$ MO (the N lone pair) is involved in the excitations in addition to the doubly occupied $44a'$ MO, which corresponds to a combination of broken bonds of C atoms around the vacancy. In this case both of these orbitals represent a mixture of the N lone pair and C broken bonds. When dynamic correlation is taken into account at the CASPT2 level, the excitation energies to these valence states drastically decrease; for instance, the value for $2^2A''$ becomes ~ 2.4 eV (Table 7). The main contribution to the resulting CASPT2 wave function of the $2^2A''$ state comes from the $3^2A''$ state at the CASSCF level (~ 0.72), but the coefficients of the $2^2A''$, $4^2A''$, and $5^2A''$ states are also significant (0.36–0.42). When the active space is extended by including additional empty orbitals as in (9,7) and (9,8) spaces, total energies of both the ground 1^2E and $2^2A''$ states increase because in this case the contributions of higher diffuse states in the wave function rise, while the weights of the lower states reduce. As a result, the $1^2E \rightarrow 2^2A''$ excitation energy does not change significantly. The energy variations for the $2^2A'$ and $3^2A''$ states are more substantial; $2^2A'$ is lower than $3^2A''$ with the (9,6) active space, but the order is reversed with the (9,7) and (9,8) active spaces (Table 7). So as the energy difference between $2^2A'$ and $3^2A''$ is not large, it is quite likely that these states are components of 2^2E , but the size of the active spaces used is not sufficient to achieve proper degeneration.

Combining the results obtained at the CASPT2 level with the B3 and B4a basis sets we predict the following order of electronic states for the NV^0 defect: 1^2E (0.0), 1^2A_2 (~ 2.4 eV), 2^2E (2.7–2.8 eV), 1^2A_1 , 3^2E , and so on (~ 3.2 eV and higher). One can see that the agreement of the CASPT2 calculated lowest excitation energy with experiment^{28,29} is quite reasonable. The first group of excitations involves electron transitions from HOMO-1 and HOMO to SOMO with participation of broken bonds of threefold-coordinated C atoms and the nitrogen lone pair, i.e., these are valence excited states. The second group corresponds to electron transitions from SOMO to highly diffuse states, simi-

lar to Rydberg states for molecules. To some extent, the first excited 1^2A_2 state in the NV^0 system is similar to the 1^3A_2 ground state in NV^- , but with the hole delocalized at HOMO-1 and HOMO and involving symmetrical combination of carbon broken bonds and the nitrogen lone pair. According to the computed Mulliken populations the excitation to 1^2A_2 leads to a transfer of $\sim 0.5 e$ from N to the vacancy-related C atoms. The oscillator strength for the $1^2A_2 \rightarrow 1^2E$ de-excitation evaluated using the transition dipole moment calculated by projecting CASSCF contributions onto the CASPT2 wave function is ~ 0.02 .

Concluding Remarks

We have performed quantum chemical modeling of the nitrogen-vacancy point defect in diamond employing a variety of theoretical methods and using finite NC_nH_m clusters with hydrogen atoms saturating broken C—C bonds on the boundary. The HF, B3LYP, and CASSCF approaches produced similar results for the geometry and electronic structure of the ground states for model clusters simulating the NV^0 and NV^- defects. In terms of geometry changes introduced by the defect, the atoms located directly near the vacancy are shifted from the vacancy center by 0.10–0.12 Å, whereas the positions of the atoms in the next layer remain nearly unchanged indicating a local character of geometry relaxation due to the defect. It is found that unpaired electrons in the doublet and quartet states of the neutral defect and the triplet ground state of the negatively charged defect are localized mainly on the three carbon atoms around the vacancy positioned in the center of model clusters and the electronic density on the N impurity atom and C atoms bound to it is weakly disturbed as compared to defect-less clusters. These results indicate that the nitrogen-related electronic distribution is rather rigid and is weakly spin polarized. The effect of the cluster size on the defect properties appears to be small; reasonably accurate results can be achieved with clusters containing only one additional carbon layer around the defect.

Wave functions of the lowest excited states of NV^0 and NV^- show a strong multireference character and contain significant contributions from diffuse functions. According to all calculations at the TD-DFT, CASSCF, MRCI, and CASPT2 levels, the lowest excited states involve various distributions of electrons on molecular orbitals localized close to the cluster center, i.e., the vacancy position, and originated from the broken bonds of threefold coordinated C atoms surrounding the vacancy and the N lone pair for NV^0 system. The contributions from the MOs responsible for the bonding of the vacancy-related atoms with the rest of the bulk are insignificant.

CASSCF calculations give underestimated excitation energies for the negative defect and overestimated energies for the neutral system. The inclusion of dynamic electronic correlation effects at the CASPT2 level leads to a reasonable agreement (within 0.25 eV) of the calculated transition energy to the lowest excited state with the experimental value for the NV^- system. Several excited states have been found in the energy range from 2 to 3 eV, but, according to the calculated oscillator strengths, only for the 1^3E and 5^3E states the excitation probabilities from

the ground state are expected to be significant. Here, the second adsorption band is predicted to lie 0.8–1 eV higher in energy as compared to the first one. For singlet states, a large oscillator strength was computed between 1^1E and 1^1A_1 , and one can expect the $1^1A_1 \rightarrow 1^1E$ de-excitation process to be fast. Therefore, it may be possible to overcome the shelving effect for this defect center by stimulating the $1^1E \rightarrow 1^3A_2$ conversion.

For the neutral NV^0 defect center, CASPT2 calculations result in significant reduction of transition energies for excited states involving valence orbitals as compared to the CASSCF values; for electronic states with high contributions of diffuse orbitals the difference between CASPT2 and CASSCF is small. As a consequence, the energetic order of excited states at the CASPT2 and CASSCF levels is different and the CASPT2 calculated excitation energy for the first excited 1^2A_2 state is in reasonable agreement with the experimental value. Both for the NV^- and NV^0 systems, taking into account dynamic electron correlation at the CASPT2 level leads to the most substantial energy decrease for the $1A_2$ state. In the negatively charged defect this is the ground state and the excitation energy increases, whereas in the neutral cluster this state is excited and hence the excitation energy is reduced. Nevertheless, for both defects the CASPT2 method appears to be adequate to describe the transition energies with reasonable accuracy.

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