

Carbon-nitrogen molecules in GaAs and GaP

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A carbon-nitrogen molecule in GaAs and GaP is investigated by using first-principles density functional pseudopotential calculations. The formation energy calculations show that the molecule favors substituting for an anion site (As or P) over being an interstitial under all equilibrium growth conditions. Under *p*-type conditions, the molecule exhibits the characteristic triple bonding and acts as a donor. When the Fermi level is higher (*n* type), the molecule acts as an acceptor by accepting electrons into its antibonding states and exhibits double or single bonding. The bond length and vibrational frequencies for each configuration are calculated and compared to those in recent experiments. Trends in the changes in bond length and vibrational frequencies with respect to the number of electrons in the antibonding states are discussed.

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I. INTRODUCTION

Small amounts of nitrogen can strongly affect the electronic properties, such as the band gap and electron effective mass, of GaP and GaAs. This opens up an opportunity to continuously modify the band gap (as well as other properties) of these III-V semiconductors for advanced electronic and optoelectronic devices. This prospect has stimulated substantial research on dilute GaAsN and GaPN alloys both experimentally¹⁻⁷ and theoretically.⁸⁻¹⁴ It is therefore very important that defects and impurities in these alloys are studied in detail. Carbon is a common impurity in various growth techniques^{15,16} and sometimes, it is intentionally used as a *p*-type dopant;¹⁷⁻²⁰ complex formations between C and N could therefore be an important issue. Recently, Ulrici and Clerjaud²¹ observed a sharp local vibration mode at 2087 cm⁻¹ (at *T*=7 K) in GaP and a similar mode in GaAs. They identified it as a CN complex with a triple bond (between C and N) aligned along the [100] direction.

An experimental work²¹ rigorously identified the chemical composition and the dipole direction of the complex; however, the actual location of the CN molecule in the lattice is still unclear. Both CN substituting on anion sites (CN_{As} in GaAs or CN_P in GaP) and interstitial CN (CN_i) are potentially consistent with experiment and were proposed as possible models in Ref. 21. In other semiconductor compounds (such as ZnO, GaN, and ZnSe), small diatomic molecules such as N₂, O₂, or CN have been studied both by first-principles calculations and by different experiments and found to prefer substitution on an anion site.^{15,22-25} However, the energy difference between the substitutional and interstitial sites varies from material to material; explicit calculations are therefore required to determine which site is more favorable for a given material.

In this paper, we use first-principles calculations to calculate the formation energies of CN_{As(or P)}} and CN_i. We find that, similar to other semiconductor compounds that have been studied before, CN energetically prefers substituting on anion sites of GaAs and GaP over interstitial sites in all thermal equilibrium growth conditions. We also calculate the vibrational frequency of the complex and find reasonable

agreement with the measured value. The CN molecule behaves very similarly in GaAs and GaP, and therefore, we will focus our discussion on CN in GaAs. Numerical results will be reported for both GaAs and GaP.

II. COMPUTATIONAL METHOD

Our calculations are performed by using density functional theory with the local density approximation (LDA).²⁶ We use ultrasoft pseudopotentials,²⁷ as implemented in the VASP code.²⁸ The Ga 3*d* electrons are treated as valence electrons. The cutoff energy for the plane-wave basis set is 262 eV. We use a supercell with 64 atoms for the defect studies, and a 2 × 2 × 2 shifted Monkhorst-Pack special *k*-point grid (Γ point not included) is employed for the Brillouin zone integration. The calculated GaAs lattice constant (5.60 Å, which is within 1% of the experimental value) is used. The electronic deep levels introduced by CN are examined by taking averages over the special *k* points. All the atoms are relaxed by minimization of the Hellmann-Feynman forces until all the forces are less than 0.05 eV/Å.

The formation energies of CN_i and CN_{As} are defined, following Refs. 22 and 29, as

$$E_f(\text{CN}_i^q) = E_{\text{tot}}(\text{CN}_i^q) - E_{\text{tot}}(\text{bulk}) - \mu_C - \mu_N + qE_F,$$

$$E_f(\text{CN}_{\text{As}}^q) = E_{\text{tot}}(\text{CN}_{\text{As}}^q) - E_{\text{tot}}(\text{bulk}) - \mu_C - \mu_N + \mu_{\text{As}} + qE_F, \quad (1)$$

where $E_{\text{tot}}(D^q)$ is the total energy of the supercell with defect *D* in charge state *q*. $E_{\text{tot}}(\text{bulk})$ is the total energy of the supercell without a defect. μ_C , μ_N , and μ_{As} are the chemical potentials of a C atom, an N atom, and an As atom, respectively. For convenience, μ_C and μ_{As} are referenced to the energy of a C atom in diamond and an As atom in solid As, respectively. μ_N is referenced to the energy of an N atom in a free N₂ molecule. Growth conditions for GaAs are close to equilibrium, requiring that $\mu_{\text{Ga}} + \mu_{\text{As}} = \mu_{\text{GaAs}} = -0.69$ eV (calculated GaAs heat of formation), where μ_{Ga} is a chemical potential of a Ga atom, which is referenced to the energy of a Ga atom in bulk Ga. E_F is the electron Fermi level with

respect to the valence-band maximum (VBM).

The local vibrational mode frequencies of the molecules are calculated by using the so-called frozen phonon approach,³⁰ in which we followed a practical methodology described in Ref. 31. Because C and N atoms have similar masses, we equally displaced C and N to calculate the potential energy of stretching and compressing bonds. The mass of the oscillator is taken as the reduced mass:

$$\mu = \frac{m_C m_N}{m_N + m_C}, \quad (2)$$

where m_C and m_N are the masses of C and N atoms. We find that the (harmonic) stretching vibrational frequencies of the oscillator agree very well with a full dynamic matrix calculation with the matrix constructed by displacing each and every atom in the supercell one at a time in all three principal axes directions. A test calculation (on $\text{CN}_{\text{As}}^{2+}$) shows that the agreement between the full dynamic and reduced-mass results is better than 5 cm^{-1} . An important benefit of the reduced-mass calculation (besides a significant reduction in computational effort) is that it allows us to calculate the anharmonic part of the vibration, which we found to be on the order of 20 cm^{-1} . The potential energy is evaluated at seven values of displacements, with a maximum amplitude of up to 10% of the C-N equilibrium bond distance. To test the accuracy of the approach, we calculated the stretch frequency of a C-N mode in the HCN molecule and obtained the value of 2057 cm^{-1} , which is slightly smaller than the experimental value of 2089 cm^{-1} .³² The calculated equilibrium C-N bond distance is fortuitously equal to the experimental value of 1.156 \AA . The small underestimation in vibrational frequency, which is by 32 cm^{-1} , is expected to be systematic. Therefore, we have added the value of $\omega_{ER}=32 \text{ cm}^{-1}$ to all of our calculated frequencies as a systematic correction.

III. RESULTS AND DISCUSSION

We investigated two forms of CN molecules in GaAs: at the substitutional As site and at the interstitial site. If initially the CN molecule is symmetrically placed at the As site (in the form of a split-interstitial configuration) with its principal axis aligned along the $[100]$ direction, due to the symmetry, the orientation of the molecule will remain unchanged even when relaxation is allowed. The resulting symmetric configuration, $\text{CN}_{\text{As}}(\text{sym})$, is shown in Fig. 1(a). However, this orientation is not the lowest energy one for all charge states. Breaking the symmetry causes the molecule (in some charge states) to spontaneously rotate, without any barrier, into an asymmetric configuration [Fig. 1(b), $\text{CN}_{\text{As}}(\text{asym})$ in the $2+$ charge state].

For an interstitial CN, there are two possible sites for the zinc-blende crystal: the tetrahedral interstitial sites surrounded by either Ga [$T_d(\text{Ga})$] or As atoms [$T_d(\text{As})$]. The calculations show that CN_i energetically prefers the $T_d(\text{Ga})$ site over the $T_d(\text{As})$ site. The $T_d(\text{Ga})$ site is surrounded by four Ga atoms in a tetrahedral configuration similar to the local structure surrounding a substitutional As lattice site. Again, if the molecule is initially placed in a high-symmetry orientation, $\text{CN}_i(\text{sym})$, the orientation remains fixed by sym-

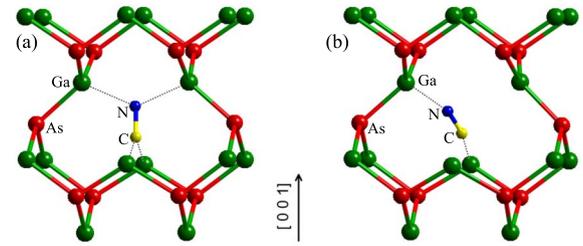


FIG. 1. (Color online) Local atomic geometry of a CN molecule substituting on an As site in GaAs: (a) symmetric configuration, $\text{CN}_{\text{As}}(\text{sym})$, and (b) asymmetric configuration, $\text{CN}_{\text{As}}(\text{asym})$. Both are shown for the $2+$ charge state.

metry, but breaking the symmetry can lead to rotation of the molecule into a lower-energy asymmetric configuration, $\text{CN}_i(\text{asym})$.

A. Substitutional CN molecules (CN_{As})

The substitutional molecule CN_{As} introduces a deep donor level (at approximately 0.25 eV) in the GaAs band gap, as shown in Fig. 2. The charge density (Fig. 3) of these levels resembles the $pp\pi^*$ molecular orbital of the CN molecule.²² The molecular orbital theory tells us that the CN molecule has the following molecular orbitals, which are in order of increasing energy: $ss\sigma$, $ss\sigma^*$, $pp\pi$ (doublet), $pp\sigma$, $pp\pi^*$ (doublet), and $pp\sigma^*$. In the neutral charge state, the CN molecule on an As site has 12 valence electrons: 9 from the CN itself and 3 more contributed from the surrounding Ga atoms. These 12 electrons occupy the CN molecular orbitals up to the lower $pp\pi^*$ level and leave the higher $pp\pi^*$ level empty. Because the lower $pp\pi^*$ level is located deep inside the GaAs band gap, CN_{As} can donate up to two electrons and become $\text{CN}_{\text{As}}^{2+}$ when the Fermi level of the system falls below the 0.25 eV donor level. The bonding between the C and N atoms in $\text{CN}_{\text{As}}^{2+}$ is a triple bond ($\text{C}\equiv\text{N}$), with a bond distance of $1.17\text{--}1.20 \text{ \AA}$ (depending on the orientation), which is in good agreement with the known triple-bond length between C and N in HCN of 1.156 \AA .³³

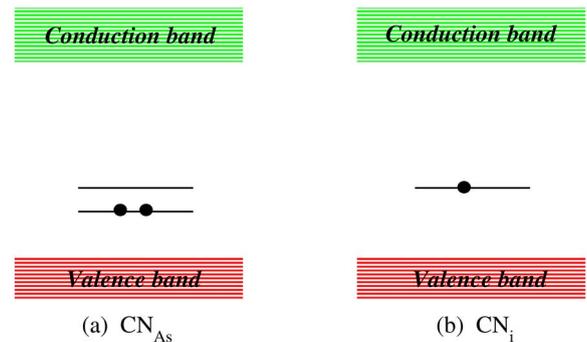


FIG. 2. (Color online) Schematic illustrations of the $pp\pi^*$ single-particle energy levels of the CN molecule in the GaAs band gap. (a) Substituting on an As site (CN_{As}) and (b) CN on an interstitial site (CN_i). The solid dots show the electron occupation for the neutral charge state.

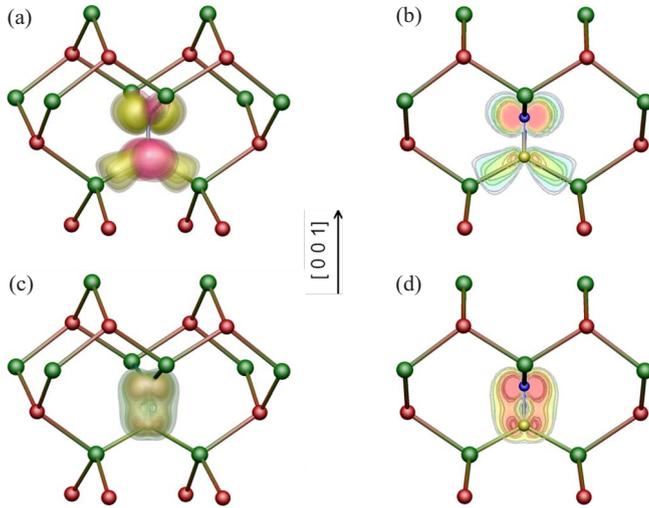


FIG. 3. (Color online) (a) Charge density of the $pp\pi^*$ states of CN_{As} that are located in the GaAs band gap. (b) Contour plot of one of the states in (a) in a (001) plane cutting through the CN molecule. (c) Charge density of one of the $pp\pi$ states of CN_{As} that resides below the valence-band maximum. (d) The corresponding contour plot of (c).

In the 2+ charge state, the $pp\pi^*$ level is unoccupied; hence, the CN_{As}^{2+} has little interaction with the surrounding neighbor. The molecule can therefore rotate quite freely, and it indeed moves away from the symmetric configuration to a new orientation that has a lower energy. Our calculated energy profile for the molecule rotating from the [001] to the (near) [110] direction, which is based on the nudged elastic band (NEB) method,³⁴ is shown in Fig. 4. We can see that starting from the symmetric [001] orientation, the molecule can rotate without any barrier to a new orientation in which the molecule's principal axis is nearly parallel with the [110] direction, lowering its energy by 0.27 eV in the process. By investigating the charge density (not shown), we found that the asymmetric configuration allows better interactions

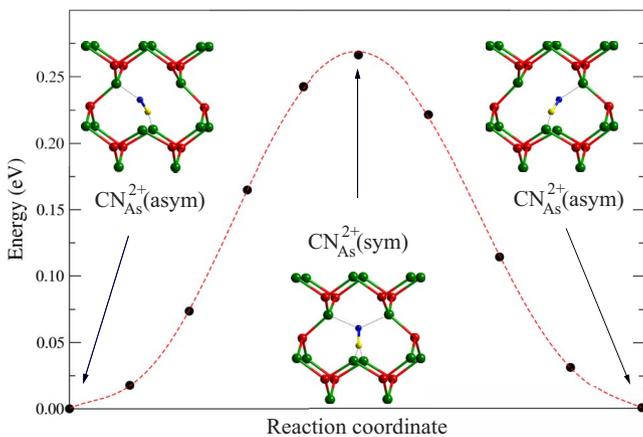


FIG. 4. (Color online) Calculated energy of CN_{As}^{2+} as the CN molecule rotates from the asymmetric to symmetric and back to an equivalent asymmetric configuration. The symmetric configuration is the saddle point along this path.

TABLE I. Calculated bond lengths d_{C-N} , stretching frequencies ω , and formation energies E_f (for the Fermi level at the VBM) of CN molecules in GaAs in the symmetric (asymmetric in parentheses) configurations. For each charge state, the lower-energy configuration is shown in boldface.

Charge state (q)	d_{C-N} (Å)	ω (cm^{-1})	E_f (eV)	
			Ga rich	As rich
CN on the As site (CN_{As})				
2+	1.20	1779	2.42	3.11
	(1.17)	(2052)	(2.15)	(2.84)
1+	1.25	1481	2.42	3.11
	(1.22)	(1734)	(2.46)	(3.15)
0	1.30	1328	2.58	3.27
	(1.25)	(1345)	(3.08)	(3.77)
1-	1.35	1173	3.13	3.82
	(1.31)	(1182)	(3.34)	(4.03)
2-	1.38	1095	4.03	4.72
	(1.40)	(1097)	(3.82)	(4.51)
CN on the interstitial site (CN_i)				
1+	1.20	1897	4.41	4.41
	(1.19)	(1934)	(3.85)	(3.85)
0	(1.25)	(1519)	(4.37)	(4.37)

between the bonding pp states of CN and two of the surrounding Ga atoms, resulting in a lower formation energy.

Starting from CN_{As}^{2+} , when the Fermi level is raised, the defect levels characteristic of $pp\pi^*$ molecular orbitals become occupied with electrons, and the charge state of CN_{As} increases from 2+ to 1+, 0, 1-, and 2-. Because these defect states correspond to antibonding orbitals of the free molecule, occupying them leads to an increase in the CN bond length (of approximately 0.05 Å per electron added), as shown in Table I. In addition, the charge density plots [Fig. 3(a) and 3(b)] reveal that the $pp\pi^*$ states hybridize with the dangling-bond states of the surrounding Ga atoms in the directions in which the density lobes are pointing. For instance, the lower two lobes in Fig. 3(b) clearly show the bond formation between the C atom and two Ga atoms, whereas the upper two lobes still maintain the molecular $pp\pi^*$ features. Because of the possibility of bond formation with the neighboring Ga atoms, CN_{As}^{1+} , CN_{As}^0 , and CN_{As}^{1-} all favor the symmetric configuration.³⁵

CN_{As}^{2-} , on the other hand, favors an asymmetric configuration (with a different orientation from that of CN_{As}^{2+}). Because the $pp\pi^*$ states are fully occupied, the molecule tries to optimize the Coulombic interaction between these $pp\pi^*$ states and its four Ga neighbors. Since the charge distribution for the CN molecule is not symmetric (the N atom is more electronegative than the C atom), the asymmetric configuration allows the N side of the molecule to bind with three Ga atoms instead of two, making the configuration more stable.

The formation energies of CN_{As} are shown in Table I (Table II for CN in GaP) and plots as a function of Fermi level are shown in Fig. 5 for two growth conditions: Ga rich ($\mu_{Ga}=0$) and As rich ($\mu_{As}=0$). As can be seen from Eq. (1),

TABLE II. Calculated bond lengths $d_{\text{C-N}}$, stretching frequencies ω , and formation energies E_f (for the Fermi level at the VBM) of CN molecules in GaP in the symmetric (asymmetric in parentheses) configurations. For each charge state, the lower-energy configuration is shown in boldface.

Charge state (q)	$d_{\text{C-N}}$ (Å)	ω (cm^{-1})	E_f (eV)	
			Ga rich	P rich
CN on the P site (CN_p)				
2+	1.20	1734	2.25	3.13
	(1.18)	(2028)	(2.12)	(3.00)
1+	1.25	1517	2.40	3.28
0	1.31	1352	2.75	3.63
1-	1.36	1197	3.58	4.46
	(1.33)	(1283)	(3.74)	(4.62)
2-	1.39	1113	4.77	5.65
	(1.41)	(1105)	(4.50)	(5.38)
CN on the interstitial site (CN_i)				
1+	1.21	1875	4.43	4.43
	(1.19)	(1933)	(3.96)	(3.96)
0	(1.26)	(1511)	(4.82)	(4.82)

the slope of the plot indicates the charge state of the CN molecule. In our plots, only the lowest energy charge state (at a given Fermi energy) is shown. For example, $\text{CN}_{\text{As}}(\text{asym})$ is stable in the 2+ charge state when the E_F of the system is located between 0.0 and 0.25 eV; therefore, the line has a slope of 2. For $0.25 \text{ eV} < E_F < 0.70 \text{ eV}$, the symmetric configuration becomes more stable and the neutral and 1- (for a narrow range near $E_F = 0.70 \text{ eV}$) charge states are the lowest in energy. At higher E_F , the asymmetric configuration with the 2- charge state, i.e., $\text{CN}_{\text{As}}^{2-}(\text{asym})$, becomes the most stable.³⁶ Therefore, the stable configurations in order of increasing E_F are as follows: $\text{CN}_{\text{As}}^{2+}(\text{asym})$, $\text{CN}_{\text{As}}^0(\text{sym})$, $\text{CN}_{\text{As}}^{1-}(\text{sym})$, and $\text{CN}_{\text{As}}^{2-}(\text{asym})$. $\text{CN}_{\text{As}}^{1+}$ is never stable. Because CN is substituting on the As site to form CN_{As} , its formation energy is lower in the Ga-rich condition than that in the As-rich condition. The plots also show that the formation energy of CN_{As} is always lower than that of CN_i for both the Ga- and As-rich conditions throughout the entire Fermi-energy range, with an energy difference of at least 1 eV. This implies that CN_{As} is far easier to form than CN_i .

The trends in bonding discussed above are reflected in our calculated values of vibrational frequencies, which show that the frequency is highest for $\text{CN}_{\text{As}}^{2+}$ (2052 cm^{-1} for an asymmetric configuration and 1779 cm^{-1} for a hypothetical sym-

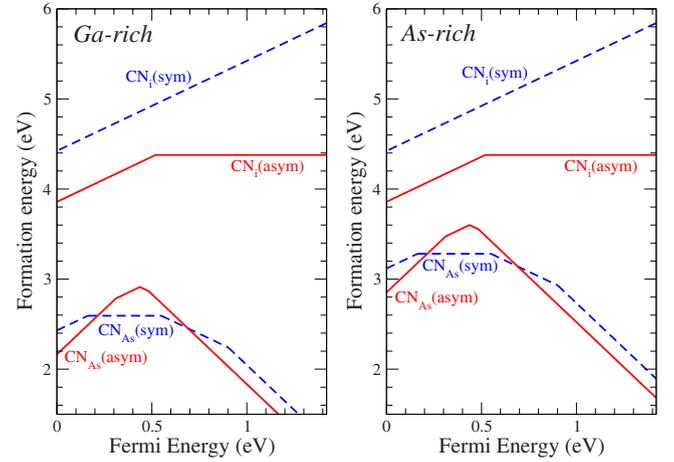


FIG. 5. (Color online) Formation energies of CN molecules in GaAs as a function of the Fermi energy. The solid lines and dashed lines represent the asymmetric and symmetric configurations, respectively.

metric configuration). This is because in the 2+ charge state, the bonding states of the molecule are all occupied and the antibonding states ($pp\pi^*$) are all empty. As electrons are added into the antibonding states of CN_{As} , the C-N bond is weakened and the frequency is reduced to 1481, 1328, 1173, and 1097 cm^{-1} for $\text{CN}_{\text{As}}^{1+}$, CN_{As}^0 , $\text{CN}_{\text{As}}^{1-}$, and $\text{CN}_{\text{As}}^{2-}$, respectively.

B. Interstitial CN molecules (CN_i)

The CN molecule has a total of nine electrons filling its molecular orbitals in the following order: $ss\sigma$, $ss\sigma^*$, $pp\pi$ (doublet), and with the last electron occupying $pp\sigma$. This leaves the $pp\sigma$ bonding state half-occupied and able to accept one more electron. Due to the strong bonding nature in the CN molecule, this $pp\sigma$ state has a low energy. When the molecule is placed in GaAs, the $pp\sigma$ state lies below the VBM and always becomes fully occupied. At the same time, the insertion of CN at an interstitial site also creates strain in nearby Ga-As bonds, leading to Ga-As bond extension (or breaking). The broken Ga-As bonds are shown in dotted lines in Fig. 6. CN_i is stable in two charge states: 1+ and neutral. We initially used symmetric configurations in our calculations [Fig. 6(a)], but this configuration can spontaneously relax into asymmetric configurations with lower energies [Fig. 6(b) and 6(c)] if symmetry breaking is allowed. The energy change as the CN_i rotates from the symmetric configuration into the asymmetric one (for 1+ charge state) calculated by using the NEB method is shown in Fig. 7. Figure 7 shows that the asymmetric configuration is favored

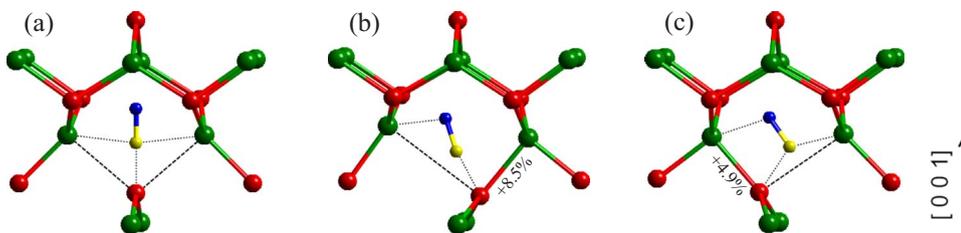


FIG. 6. (Color online) Local atomic geometry of interstitial CN molecules in GaAs: (a) $\text{CN}_i^+(\text{sym})$, (b) $\text{CN}_i^+(\text{asym})$, and (c) $\text{CN}_i^0(\text{asym})$.

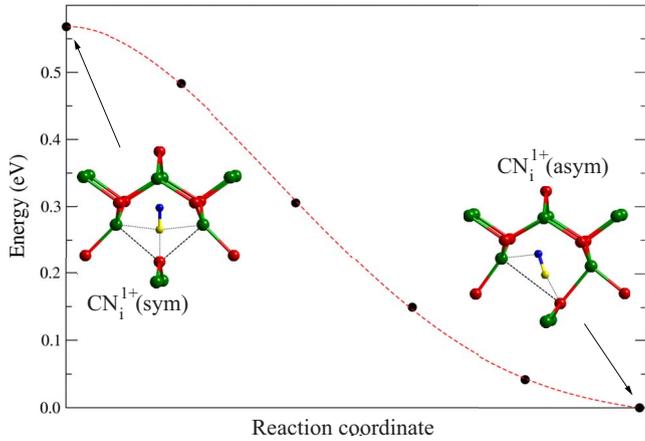


FIG. 7. (Color online) Calculated energy of CN_i^{1+} as the CN molecule rotates from a symmetric to an asymmetric configuration. The rotation occurs without any barrier and lowers the energy by almost 0.6 eV.

over the symmetric one by ~ 0.6 eV. We can clearly see in the asymmetric configuration [Fig. 6(c)] that only one of the Ga-As bonds is now broken (another bond is extended from a typical Ga-As bond). One of the two electrons released from the broken bond goes to the $pp\sigma$ state of the CN molecule, whereas another one is removed, resulting in the 1+ charge state. As an additional electron is added (increasing the charge state of the defect from 1+ to neutral), the additional electron goes to the $pp\pi^*$ level, which is located at approximately 0.5 eV above the VBM (see Fig. 2). This leads to the $+/0$ transition level of CN_i at 0.5 eV above the VBM. The occupation of the $pp\pi^*$ level leads to the increase in the CN bond to 1.25 Å and is reflected in an enhanced binding between the molecule and its neighbors [Fig. 6(c)] compared to the 1+ charge state [Fig. 6(b)]. Because the electron density of the $pp\pi^*$ state has four lobes pointing outward, which is similar to Fig. 3(b), when this state is occupied, the molecule can gain energy by turning the lobes to form bonds with the neighboring atoms.

Vibrational frequencies for the stretching modes of CN_i in GaAs and GaP are shown in Tables I and II. The frequency is higher for the CN_i in the 1+ charge state, which has all the bonding states occupied and the antibonding states empty. The frequency of 1934 cm^{-1} (1897 cm^{-1} for a hypothetical symmetric configuration) is comparable to that of $\text{CN}_{\text{As}}^{2+}$ (asym), which has a similar electron occupation on the molecule. For the neutral charge state CN_i , with an electron occupying the $pp\pi^*$ state, the C-N bond length increases to 1.25 Å and the vibrational frequency decreases to 1519 cm^{-1} .

C. General trends of the bond length and the vibrational frequency

Our results show that the C-N bond distance becomes larger (and the vibrational frequency becomes lower) as more electrons are added into the $pp\pi^*$ states. Our investigations of the various configurations of CN molecules in GaAs and GaP allow us to quantitatively study the relation-

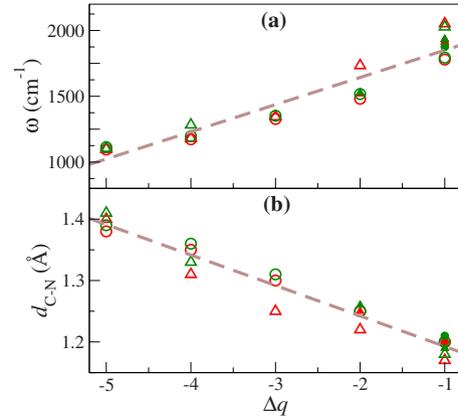


FIG. 8. (Color online) (a) Calculated vibrational frequencies and (b) C-N bond distances for various configurations of a CN molecule in GaAs and GaP as a function of charge Δq inserted into the molecule, which are measured relative to a neutral free CN molecule with nine electrons. The solid symbols are for interstitial CN and the open symbols are for substitutional CN. The colors code the host material (red for GaAs and green for GaP), whereas the symbols are used to distinguish the symmetric (circle) from the asymmetric (triangle) configurations. The CN molecule is characterized as triply, doubly, or singly bonded for $\Delta q = -1, -3,$ and -5 , respectively. The dashed lines are linear fits to all of the data points.

ship between the electron occupation (of the CN molecule) and the bond length as well as the vibrational frequency. To do this, we define Δq as the additional charge being added to the CN molecule relative to the neutral free CN molecule. A free CN molecule has nine electrons, which occupy the molecular states up to half of the $pp\sigma$ state. Since this state is located below the VBM of GaAs, it is always fully occupied. This means that at least one electron from the host has to be added to the molecule ($\Delta q = -1$) and the electron occupation of the molecule becomes the same as that of a free (triple-bonded) CN^- ion. For the CN molecule in GaAs, this occupation corresponds to the lowest charge state, i.e., $\text{CN}_{\text{As}}^{2+}$ and CN_i^{1+} . As the Fermi energy is raised, electrons are inserted into the antibonding states ($pp\pi^*$ states) of the CN molecule, thus weakening the C-N bond. When two electrons are inserted into the antibonding state (i.e., CN_{As}^0), making $\Delta q = -3$, the C-N bond is reduced to a double bond instead of a triple bond. When four electrons are inserted into the antibonding states (i.e., $\text{CN}_{\text{As}}^{2-}$), making $\Delta q = -5$, the C-N bond is reduced to a single bond. Our calculations thus show that CN_{As} can have its bond strength varied from a triple bond down to a single bond depending on the electron occupation. CN_i , on the other hand, can only exhibit the bond strength of a triple bond (CN_i^{1+}) or a triple bond with one electron in the antibonding state (CN_i^0) (which can be considered as halfway between a double bond and a triple bond).

A plot of the C-N bond distance as a function of Δq is shown in Fig. 8(b). The bond distance, especially of the symmetric configurations, clearly show a linear trend with Δq . The deviations from the linear trend in the case of some of the asymmetric configurations can be attributed to the interaction with neighboring host atoms. A linear fit between the bond distance and Δq for all data points yields

$$d_{\text{C-N}} = -0.0496\Delta q + 1.143, \quad (3)$$

where $d_{\text{C-N}}$ is the bond distance between C and N in Å. The bond length increases by approximately 0.05 Å for every electron inserted.

The vibrational frequency decreases as the bond is extended. The relationship between the frequency and Δq is shown in Fig. 8(a). Again, a linear trend is seen. A linear fit yields

$$\omega = 207\Delta q + 2057, \quad (4)$$

where ω is the vibration frequency in cm^{-1} , i.e., the frequency is redshifted by approximately 200 cm^{-1} for every electron that is inserted. Deviations from the fit (on the order of 100 cm^{-1}) occur because the actual frequency also depends on other factors such as the detailed local geometry. Still, the linear fit in Eq. (4) nicely highlights the general trend, even if it does not provide a completely accurate prediction of the frequency.

D. Discussion and comparison with experiment

Ulrici and Clerjaud²¹ performed a polarized infrared absorption spectroscopy on C-doped dilute-nitride GaAs and GaP. They observed a sharp local vibrational mode at 2087.1 cm^{-1} (at $T=7 \text{ K}$) in GaP and a similar mode (2088.5 cm^{-1}) in GaAs. They identified it as a CN complex with a triple bond (between C and N) aligned along three equivalent $\langle 100 \rangle$ directions. Their C and N assignments were based on their observation of additional weak peaks at 2031 and 2048 cm^{-1} , which exhibit an intensity ratio and frequency shift that match the natural abundance and predicted frequency shift for C^{13} and N^{15} isotopes. The orientation of the molecule was confirmed by polarized IR absorption under different types of uniaxial stress.

An inspection of Tables I and II shows that the measured frequency of 2087 cm^{-1} is most consistent with our calculated frequencies for triply bonded CN molecules with $\Delta q = -1$. A more detailed identification runs into some complications, however. There are four configurations with triple bonds covered in our study: $\text{CN}_{\text{As}}^{2+}(\text{asym})$, $\text{CN}_{\text{As}}^{2+}(\text{sym})$, $\text{CN}_i^{1+}(\text{asym})$, and $\text{CN}_i^{1+}(\text{sym})$. (1) $\text{CN}_{\text{As}}^{2+}(\text{asym})$ provides the best matching frequency to the experiment (lower by 36 cm^{-1} , which is well within the computational error bar). However, the molecule does not align along $\langle 100 \rangle$ but, instead, prefers to align in a direction close to $\langle 110 \rangle$. (2) $\text{CN}_{\text{As}}^{2+}(\text{sym})$ has the correct orientation; however, its frequency is too low (by 309 cm^{-1}), and, even more importantly, it is not energetically stable and spontaneously rotates to $\text{CN}_{\text{As}}^{2+}(\text{asym})$, lowering the energy by 0.27 eV. Therefore, we can rule out $\text{CN}_{\text{As}}^{2+}(\text{sym})$. (3) $\text{CN}_i^{1+}(\text{asym})$ is a possible candidate. Its calculated vibrational frequency is not too far from the observed value (lower by 154 cm^{-1}). However, its orientation also deviated from $\langle 100 \rangle$ by 16° . In addition, the interstitial configurations are energetically unfavorable compared to those of $\text{CN}_{\text{As}}^{2+}(\text{asym})$. (4) $\text{CN}_i^{1+}(\text{sym})$ is an unlikely candidate because it is not energetically stable. It can spontaneously rotate to the asymmetric configuration and gain 0.6 eV. In addition, its vibrational frequency is even lower than

that of the asymmetric configuration, widening the disagreement with experiment to 191 cm^{-1} .

Our first-principles calculations of vibrational frequencies for CN molecules in various configurations in GaAs and GaP therefore generally support Ulrici and Clerjaud's²¹ assignment of the 2087 cm^{-1} mode to a triply bonded CN molecule. However, our calculations also show that the triply bonded CN molecule (in either the substitutional or interstitial configurations) does *not* symmetrically align in a tetrahedral site surrounded by four Ga atoms. As a result, neither CN_{As} nor CN_i have the C-N axis aligned in the $\langle 100 \rangle$ direction, as proposed by Ulrici and Clerjaud.²¹ However, given a rather low rotation barrier of only 0.27 eV (Fig. 4), it is possible that $\text{CN}_{\text{As}}^{2+}(\text{asym})$ is constantly rotating, resulting in an average orientation in the $\langle 100 \rangle$ direction observed in the experiment.

IV. CONCLUSIONS

We have presented first-principles results for CN molecules in GaAs and GaP. The study covered two possible lattice locations: (1) CN molecules substituting for anions ($\text{CN}_{\text{As}(\text{or P})}$) and (2) interstitial CN molecules at the T_d site surrounded by four Ga atoms (CN_i). All possible charge states and various orientations were considered. The calculated formation energies show that the molecule favors substituting for the anion site over the interstitial configuration for all equilibrium growth conditions with a margin of at least 1 eV. The calculations predict the CN molecule to produce a level with a strong $pp\pi^*$ molecular orbital characteristic at approximately 0.5–0.8 eV above the VBM. In p -type conditions, where the Fermi level is located below this $pp\pi^*$ level, the molecules are triply bonded and form donor defect centers (double donor $\text{CN}_{\text{As}}^{2+}$ and single donor CN_i^{1+}). The calculations with full relaxation show that triply bonded $\text{CN}_{\text{As}}^{2+}$ and CN_i^{1+} do not symmetrically orient in the Ga tetrahedron but, instead, are tilted in order to gain better interactions with neighboring Ga atoms. The calculated vibration frequencies of the triply bonded $\text{CN}_{\text{As}}^{2+}$ and CN_i^{1+} are in reasonable agreement with the measurement by Ulrici and Clerjaud supporting their identification that the bonding is triple-bond type. Although neither CN_{As} nor CN_i have the C-N bond oriented along the $\langle 100 \rangle$ directions, as proposed by Ulrici and Clerjaud,²¹ the low rotation barrier of $\text{CN}_{\text{As}}^{2+}$ makes it possible that the molecule might be constantly rotating, leading to an average orientation in the $\langle 100 \rangle$ direction. At higher Fermi levels, the CN_i^{1+} can accept an electron and becomes CN_i^0 , whereas $\text{CN}_{\text{As}}^{2+}$ can accept one, two, three, or four electrons (depending on the Fermi level) and becomes $\text{CN}_{\text{As}}^{1+}$, CN_{As}^0 (metastable), $\text{CN}_{\text{As}}^{1-}$, or $\text{CN}_{\text{As}}^{2-}$, respectively. We found that the C-N bond length and vibrational frequency linearly change (to a good approximation) with the number of electrons added into the antibonding states of the molecule.

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- ³⁶Although the calculated LDA band gap (at the Γ point) for GaAs is only 0.6 eV, our calculations are performed at special k points wherein the lowest conduction band occurs at 1.08 eV above the VBM. Any defect levels that lie below 1.08 eV are therefore accounted for and can be properly occupied.