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 experimentally and theoretically. It is therefore very important that defects and impurities in these alloys are studied in detail. Carbon is a common impurity in various growth methods, and it could therefore be an important issue. Recently, Ulrici and Clerjaud 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 work 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\(_{\text{As}}\) in GaAs or CN\(_{\text{P}}\) in GaP) and interstitial CN (CN\(_{\text{i}}\)) 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 N\(_2\), O\(_2\), or CN have been studied both by first-principles calculations and by different experiments and found to prefer substitution on an anion site. 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\(_{\text{As(\text{or} P)}}\) and CN\(_{\text{i}}\). 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, as implemented in the VASP code.28 The Ga 3d 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\(\times\)2\(\times\)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\(_{\text{i}}\) and CN\(_{\text{As}}\) are defined, following Refs. 22 and 29, as

\[
E_f(CN_{\text{i}}) = E_{\text{tot}}(CN_{\text{i}}) - E_{\text{tot}}(\text{bulk}) - \mu_C - \mu_N + qE_F,
\]

\[
E_f(CN_{\text{As}}) = E_{\text{tot}}(CN_{\text{As}}) - E_{\text{tot}}(\text{bulk}) - \mu_C - \mu_N + \mu_{\text{As}} + qE_F,
\]

where \(E_{\text{tot}}(D^n)\) 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. \(\mu_C\), \(\mu_N\), and \(\mu_{\text{As}}\) are the chemical potentials of a C atom, an N atom, and an As atom, respectively. \(\mu_N\) is referenced to the energy of an N atom in a free N\(_2\) 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 \(\mu_{\text{Ga}}\) 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, 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:

$$\mu = \frac{m_CM_N}{m_S + m_C}$$  \hspace{1cm} (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 $\text{CN}_{\text{As}}^{\text{sym}}$) 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$^{-1}$. The calculated equilibrium C-N bond distance is fortuitously equal to the experimental value of 1.156 Å. The small underestimation in vibrational frequency, which is by 32 cm$^{-1}$, is expected to be systematic. Therefore, we have added the value of $\omega_{\text{pp}} = 32$ 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 [$T_d$(Ga)] or As atoms [$T_d$(As)]. The calculations show that $\text{CN}_i$ energetically prefers the $T_d$(Ga) site over the $T_d$(As) site. The $T_d$(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 symmetry, 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 ($\text{CN}_{\text{As}}$)

The substitutional molecule $\text{CN}_{\text{As}}$ 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. 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, $\text{CN}_{\text{As}}$ 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 (C≡N), with a bond distance of 1.17–1.20 Å (depending on the orientation), which is in good agreement with the known triple-bond length between C and N in HCN of 1.156 Å.

![Fig. 1.](image1) 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.

![Fig. 2.](image2) (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 ($\text{CN}_{\text{As}}$) and (b) CN on an interstitial site ($\text{CN}_i$). The solid dots show the electron occupation for the neutral charge state.
In the 2+ charge state, the pp$\pi^*$ level is unoccupied; hence, the CN$_{As}$ 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, 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 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$_{As}$ 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),

![Contour plots](image)

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).

![Energy profile](image)

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>
<thead>
<tr>
<th>Charge state (q)</th>
<th>$d_{CN}$ (Å)</th>
<th>$\omega$ (cm$^{-1}$)</th>
<th>$E_f$ (eV)</th>
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<tbody>
<tr>
<td></td>
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<tr>
<td>CN on the As site (CN$_{As}$)</td>
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<td></td>
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<tr>
<td>2+</td>
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<td>1779</td>
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<td></td>
<td>(1.17)</td>
<td>(2052)</td>
<td>(2.15)</td>
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<td>1+</td>
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<td>1481</td>
<td>2.42</td>
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<td></td>
<td>(1.22)</td>
<td>(1734)</td>
<td>(2.46)</td>
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<td>1328</td>
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<td>(1.25)</td>
<td>(1345)</td>
<td>(3.08)</td>
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<td>1−</td>
<td>1.35</td>
<td>1173</td>
<td>3.13</td>
</tr>
<tr>
<td></td>
<td>(1.31)</td>
<td>(1182)</td>
<td>(3.34)</td>
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<tr>
<td>2−</td>
<td>1.38</td>
<td>1095</td>
<td>4.03</td>
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<tr>
<td></td>
<td>(1.40)</td>
<td>(1097)</td>
<td>(3.82)</td>
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</table>

CN on the interstitial site (CN)$_{i}$

<table>
<thead>
<tr>
<th>Charge state (q)</th>
<th>$d_{CN}$ (Å)</th>
<th>$\omega$ (cm$^{-1}$)</th>
<th>$E_f$ (eV)</th>
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<td>4.41</td>
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<td></td>
<td>(1.19)</td>
<td>(1934)</td>
<td>(3.85)</td>
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<tr>
<td>0</td>
<td>(1.25)</td>
<td>(1519)</td>
<td>(4.37)</td>
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TABLE I. Calculated bond lengths $d_{CN}$, stretching frequencies $\omega$, 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.
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TABLE II. Calculated bond lengths $d_{CN}$, stretching frequencies $\omega$, 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.

<table>
<thead>
<tr>
<th>Charge state $(q)$</th>
<th>$d_{CN}$ ($\text{Å}$)</th>
<th>$\omega$ ($\text{cm}^{-1}$)</th>
<th>$E_f$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CN on the $P$ site (CN$_p$)</td>
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<td>2+</td>
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<td>1734</td>
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<td>(1283)</td>
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<td>(1105)</td>
<td>(4.50)</td>
<td>(5.38)</td>
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<td>CN on the interstitial site (CN$_i$)</td>
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<tr>
<td>1+</td>
<td>1.21</td>
<td>1875</td>
<td>4.43</td>
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<tr>
<td>(1.19)</td>
<td>(1933)</td>
<td>(3.96)</td>
<td>(3.96)</td>
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<tr>
<td>0</td>
<td>1.26</td>
<td>1511</td>
<td>4.82</td>
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</table>

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, CN$_{As}$(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 eV < $E_F$ < 0.70 eV, the symmetric configuration becomes more stable and the neutral and 1− (for a narrow range near $E_F$=0.70 eV) charge states are the lowest in energy. At higher $E_F$, the asymmetric configuration with the 2− charge state, i.e., CN$_{As}^{2−}$(asym), becomes the most stable. Therefore, the stable configurations in order of increasing $E_F$ are as follows: CN$_{As}^{2+}$(asym), CN$_{As}^{0}$(sym), CN$_{As}^{2−}$(sym), and CN$_{As}^{2−}$(asym). CN$_{As}^{+}$ 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 CN$_{As}^{2+}$ (2052 cm$^{-1}$ for an asymmetric configuration and 1779 cm$^{-1}$ for a hypothetical symmetric configuration). This is because in the 2+ charge state, the bonding states of the molecule are all occupied and the antibonding states (pp*$\sigma^*$) 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 CN$_{As}^{1+}$, CN$_{As}^{0}$, CN$_{As}^{1−}$, and CN$_{As}^{2−}$, 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.
The occupation of the VBM of GaAs and GaP are shown in Tables I and II. The frequency is 

\[ \omega = 1519 \text{ cm}^{-1}. \]

over the symmetric one by \( \sim 0.6 \text{ eV} \). 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 \( pp^\pi \) 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 \text{ eV} above the VBM (see Fig. 2). This 

leads to the +/0 transition level of CN, at 0.5 \text{ eV} above the 

VBM. The occupation of the \( pp^\pi \) level leads to the increase in 

the CN bond to 1.25 \text{ 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 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 \text{ cm}^{-1} (1897 \text{ cm}^{-1} for a hypothetical 

symmetric configuration) is comparable to that of 

\( CN_{2s}^\pi \text{ (asym)} \), which has a similar electron occupation on the 
molecule. For the neutral charge state \( CN_n \), with an electron occupying the \( pp^\pi \) state, the C-N bond length increases to 

1.25 \text{ Å} and the vibrational frequency decreases to 

1519 \text{ 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 investiga-
tions of the various configurations of CN molecules in 

GaAs and GaP allow us to quantitatively study the relation-

ship between the electron occupation (of the CN molecule) 

and the bond length as well as the vibrational frequency. To 

do this, we define \( \Delta q \) 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 \( pp^\pi \) 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\textsuperscript{+} ion. For the CN molecule in GaAs, this 

occupation corresponds to the lowest charge state, i.e., \( CN_{2s}^\pi \) and 

\( CN_{1s}^{+} \). 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., \( CN_{2s}^{+} \)), 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 anti-

bonding states (i.e., \( CN_{4s}^{+} \)), making \( \Delta q = -5 \), the C-N bond is 

reduced to a single bond. Our calculations thus show that 

\( CN_{NN} \) can have its bond strength varied from a triple bond 
down to a single bond depending on the electron occupation 

\( CN_{NN} \), on the other hand, can only exhibit the bond strength 
of a triple bond (\( CN_{1s}^{+} \)) or a triple bond with one electron in the 

antibonding state \( CN_{0s}^{+} \) (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 \( \Delta q \) is 

shown in Fig. 8(b). The bond distance, especially of the sym-

metric configurations, clearly show a linear trend with \( \Delta q \). 
The deviations from the linear trend in the case of some of 

the asymmetric configurations can be attributed to the inter-

action with neighboring host atoms. A linear fit between 

the bond distance and \( \Delta q \) for all data points yields 

\[ d_{CN}(\text{ Å}) = a \Delta q + b \]

\[ \omega (\text{ cm}^{-1}) = c \Delta q + d \]
interstitial configurations are energetically unfavorable compared to those of CN$_{As}$.(asy) 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’s $^{21}$ 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 CN$_{As}^{2+}$(asy) 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 (CN$_{As(i/As)}$ 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 CN$_{As}^{2+}$ and single donor CN$_i^{1+}$). The calculations with full relaxation show that triply bonded CN$_{As}^{2+}$ 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 CN$_{As}^{2+}$ 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 CN$_{As}^{2+}$ 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$_i^{2+}$, whereas CN$_{As}^{2+}$ can accept one, two, three, or four electrons (depending on the Fermi level) and becomes CN$_{As}^{3+}$, CN$_{As}^{4+}$ (metastable), CN$_{As}^{5+}$, or CN$_{As}^{6+}$ 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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26 LDA provides a lattice constant of bulk GaP that is slightly in better agreement with that of experiment. On the other hand, generalized gradient approximation (GGA) provides a slightly better lattice constant for GaAs. Test calculations show that the choice of LDA/GGA only slightly affects the numerical value of energy and vibration frequency but does not change the main conclusions.
35 CNAs in the +1 and 0 charge states is stable in the symmetric configuration. Test calculations for +1 showed that a dimer initially tilted by as much as 15° away from the symmetric direction, i.e., the [001] direction, spontaneously rotated back after relaxations. The asymmetric configurations are only metastable. The (higher-energy) metastable asymmetric configuration for each charge state is found by initially aligning the CN molecule along the [110] direction and allowing relaxation of its neighbors before letting the molecule itself relax. The metastable asymmetric configurations are higher in energy than the symmetric ones by 0.1 and 0.5 eV for the +1 and neutral charge states, respectively. The dimer qualitatively behaves the same in asymmetric ones by 0.1 and 0.5 eV for the +1 and neutral charge states, respectively. The dimer qualitatively behaves the same in asymmetric configurations.
36 Although 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.