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Theoretical Study of Neutral and Anionic Group III Nitride Clusters: M_nN_n (M = Al, Ga, and In; n = 4−6)

Aurora Costales,* Anil K. Kandalam, and Ravindra Pandey

Department of Physics, Michigan Technological University, Houghton, Michigan 49931

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We report the results of a theoretical study of M_nN_n (M = Al, Ga, and In; n = 4, 5, 6) neutral and anionic clusters, focusing on the changes in structural and electronic properties upon the addition of an electron to the corresponding neutral clusters. Overall, the extra electron did not induce significant structural changes in Al_nN_n clusters, whereas it affected significantly the lowest energy configurations of Ga_nN_n and In_nN_n clusters. This may be attributed to the dominance of N−N bonds in Ga_nN_n and In_nN_n clusters in contrast to the dominance of Al−N bonds in Al_nN_n clusters. The atomic charge analysis showed that the extra electron is localized on the metal atoms, irrespective of the lowest energy structural configurations of these clusters.

I. Introduction

The group III nitride crystals have been studied extensively in the past decade. In recent years, clusters of these nitrides have been the focus of both experimental and theoretical studies with an aim to understand the device preparation processes. Theoretical studies based on density functional theory (DFT) calculations on Al_mN_n,[1−5] Ga_mN_n, and In_mN_n clusters[4,6,7] have been recently published. The vibrational spectra of small group III nitride clusters were reported recently by both theoretical and experimental studies.[4,6] Recent infrared spectroscopy experiments on AlN gas revealed the existence of a wide variety of neutral and charged clusters.[4,8,9] For the past two years, our research group has carried out systematic theoretical studies[10−14] of neutral group III nitride M_nN_n (M = Al, Ga and In; n = 1−6) clusters, in the framework of DFT. In these studies,[10,12,13] using DMol program suite,[15] the BPW91 form for the exchange and correlation functionals along with a double-numeric (DNP) basis set with polarization functions was employed.

A theoretical study on charged clusters (positive and negative) can be helpful in interpreting the experimental results such as mass spectroscopy together with the prediction of the electronic structure of the clusters. Moreover, no theoretical study was devoted to understanding the changes in the structural and electronic properties of these clusters, upon accommodating an electron. Hence, our research group, on the basis of our previous experience, has initiated a theoretical study of the anionic III nitride clusters. Our aim in this study is to analyze the differences in the structural and electronic properties between the neutral and anion III nitride clusters. In our recently reported DFT study of small anionic nitride clusters[16] ($M_nN_n^-$; n = 1, 2, 3), we employed the Gaussian 98 code,[17] as the DNP basis sets used for neutral cluster calculations[10,12,13] are less flexible and are not suitable enough to describe the negatively charged clusters.

The results obtained for the small neutral nitride clusters were in agreement with our previous studies[10,12] using the DMol program suite. However, when an electron was added to these clusters, significant structural changes were observed. Fueled by these interesting results, and also as a continuation to the above-mentioned work, we now report the structural and electronic properties of anionic III nitride (M_nN_n; n = 4, 5, 6) clusters. To assess the differences in the structural and electronic properties of the neutral and anion clusters at the same level of theory, the geometrical structures and electronic properties of neutral cluster configurations are also obtained using Gaussian 98 code.[17]

The rest of the paper is organized as follows. The computational method used for this work will be presented in section 2. In section 3, we present and discuss the results for both neutral and anionic clusters. We will start with the structural and energetic characterization of the different isomers. Later, we will discuss the vibrational analysis, the atomic, bonding, and electronic properties of the lowest energy isomer of these clusters. Conclusions will be given in section 4.

II. Computational Method

All electron calculations were performed on neutral and negatively charged M_nN_n (M = Al, Ga, and In; n = 4−6) clusters, in the framework of DFT, using *Gaussian 98* code.[17] The generalized gradient approximation (GGA) to density functional theory was employed in all the calculations. The gradient-corrected exchange functional due to Becke[18] and gradient corrected Perdew−Wang[19] correlation functional (BPW91) are employed here. In these electronic structure calculations, the 6-31G** basis set was used for N, Al, and Ga atoms, whereas a double-ζ valence polarization (DZVP) basis set was used for In atom.[20] The reliability of these basis sets was confirmed in our previous studies of nitride clusters.[11] For the anionic systems, diffuse basis functions are expected to play an important role in determining the structural configurations. The effect of the diffuse functions in the basis sets has therefore been analyzed in our previous study on small anionic clusters of group III nitrides.[16] Accordingly, a small but insignificant variation in the structural properties is expected in anionic clusters upon the inclusion of the diffuse functions in the basis set. We have therefore not included the diffuse functions in the 6-31G** basis sets employed in the present study.

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* Corresponding author. E-mail: mcostale@mtu.edu. Permanent address: Departamento de Química Física y Analítica, Facultad de Química, Universidad de Oviedo, 33006-Oviedo, Spain.

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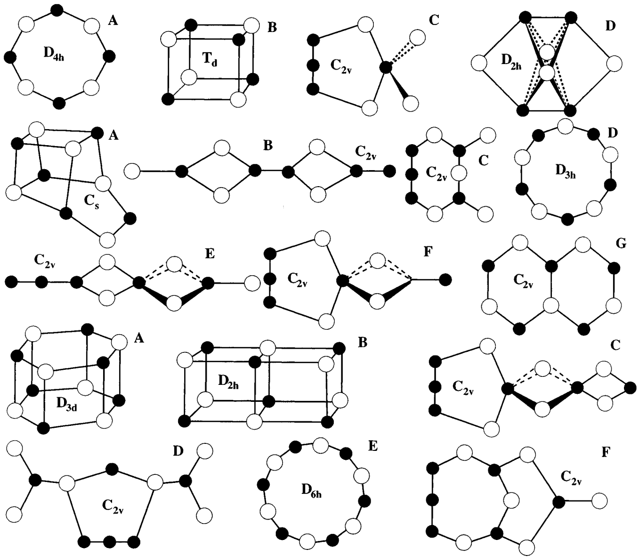

Figure 1. Schematic representation of the different isomers considered in this study. Nitrogen atoms are represented by small filled circles, and the metallic ones are represented by larger empty circles. M_4N_4, isomers A, B, C, and D; M_5N_5, isomers A, B, C, D, E, F, and G; M_6N_6, isomers A, B, C, D, E, and F.

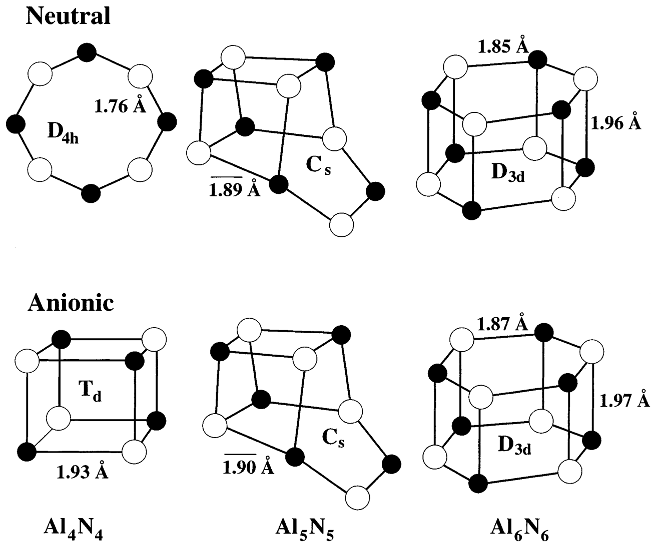

Figure 2. Lowest energy structures of neutral and anionic Al_nN_n clusters. Nitrogen atoms are represented by small filled circles, and the Al atoms are big empty circles.

The geometrical parameters for both the neutral and anionic clusters were fully optimized, with a convergence criteria of 10^{-4} hartree/Å and 10^{-9} hartree for gradient and energy, respectively. The stability of the lowest energy configurations (both neutral and anionic) were analyzed by computing the vibrational frequencies under the harmonic approximation. Atomic charges for the lowest energy isomers were studied under the atoms in molecules theory (AIM).[21] Atomic properties were integrated with Promega algorithm, using the AIMPAC95 package.[22] The precision of integrations is taken care of with an error in the total charge less than 10^{-3} *e*.

III. Results and Discussion

The structural configurations considered in the present study, for the geometry optimization are based on the results of our previous work[13] on neutral M_nN_n (M = Al, Ga, and In; n = 4−6) clusters. Only the three lowest energy structural configurations for each of the clusters, obtained from a previous study,[13] are employed in the present work, and these isomers are collected in Figure 1. The list of the optimized structural parameters for all configurations considered in this study can be obtained from the authors (mcostale@mtu.edu).

A. Structural Properties. In the neutral Al_nN_n clusters, except for Al_5N_5, the lowest energy structures are found to be the same as those in our previous DMol calculations.[13] The lowest energy structures of both neutral and anionic Al_nN_n clusters, are given in Figure 2.

In Al_4N_4, an octagonal planar ring structure with D_{4h} symmetry, an Al−N distance of 1.76 Å, and an Al−Al distance of 2.72 Å, is the lowest energy structure. A cubic configuration is found to be the next lowest energy structure, 0.42 eV higher in energy. Hence, a competition between the 2-dimensional and 3-dimensional structures in stabilizing the cluster starts to emerge here. However, when we move to Al_5N_5 clusters, the three-dimensional structure takes over, with an Al−N capped-cubic structure, having C_s symmetry, being the lowest energy structural configuration. The planar ring structure with D_{5h} symmetry closely follows, being 0.06 eV higher in energy. The average Al−N distance in this capped-cube structure is 1.87 Å with Al−N distances ranging from 1.75 to 1.93 Å. In Al_6N_6, a hexagonal prism belonging to the D_{3d} point group symmetry, with two nonequivalent metal−nitrogen bonds (1.85 Å intraplane and 1.95 Å interplane), is the lowest energy configuration.

The addition of an electron to the Al_nN_n clusters did not affect the configurational symmetry of the lowest energy structures, with the exception of the Al_4N_4 cluster. For the anionic Al_4N_4 cluster, the cubic configuration is the lowest energy structure. The planar ring structure, the lowest energy isomer in neutral Al_4N_4, is found to be 0.53 eV higher in energy. This reversal in the lowest energy structures can be analyzed with the help of the molecular orbital picture of these structural configurations. The lowest unoccupied molecular orbital (LUMO) in the neutral ring structure is mainly concentrated on the N atoms, with a small antibonding contribution for the Al−N interaction, whereas the LUMO of neutral cubic structure is a nonbonding orbital, mainly located on the Al atoms. Hence, the addition of an electron favors the latter case, i.e., a preference for the nonbonding over the antibonding orbital. Moreover, the atomic charge analysis supports this argument (see section 3.3), showing that the extra electron is located over the aluminum atoms.

In the Al_5N_5 and Al_6N_6 anionic clusters, however, the extra electron did not modify the symmetry of the lowest energy isomers and also did not induce any significant changes in the Al−N distances from their respective neutral lowest energy configurations. For the Al_5N_5 capped-cube, the maximum change in a given Al−N distance is 0.04 Å with a 0.01 Å deviation in the average Al−N distance. In Al_6N_6, the addition of an electron made no significant difference in the Al−N bond length.

Hence, both neutral and anionic Al_nN_n clusters have a similar structural feature, namely, the Al−N bond dominated lowest energy configurations. However, an interesting contrast between the neutral and anionic clusters is seen in the competition between two-dimensional and three-dimensional structures. The neutral AlN clusters require 10 atoms (Al_5N_5) to have a stable three-dimensional structure, whereas the anionic AlN clusters require only 8 atoms (Al_4N_4) to have a stable 3-dimensional structure.

The lowest energy structures of both neutral and anionic Ga_nN_n clusters are given in Figure 3. It can be seen that the

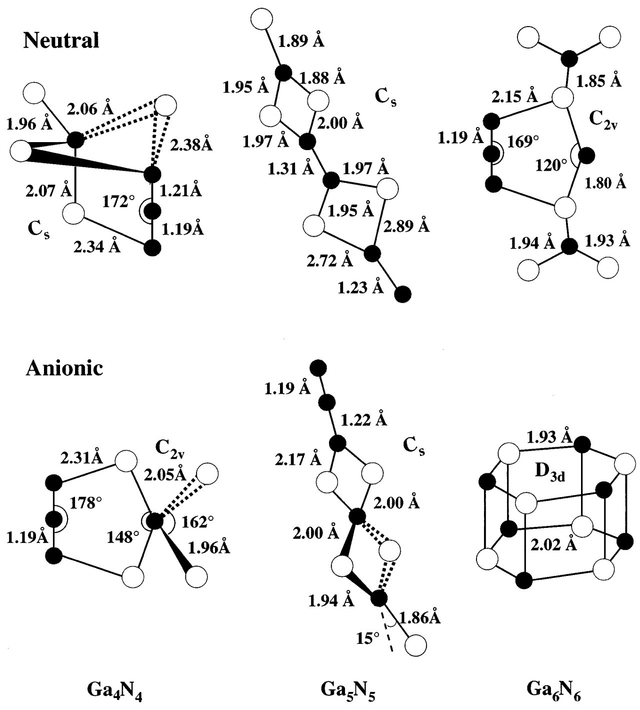

Figure 3. Lowest energy structures of neutral and anionic Ga_nN_n clusters. Nitrogen atoms are represented by small filled circles, and the Ga atoms are big empty circles.

lowest energy isomers of all the neutral and anionic Ga_nN_n clusters contain strong N−N bonds, with an exception for $Ga_6N_6^-$.

To assess the nature of the N_2 and N_3 subunits in these clusters, we have optimized the N_2 and N_3^- molecular geometries and have also computed the vibrational frequencies at the same level of theory employed for the nitride clusters. For the N_2 molecule, the N−N bond distance is 1.12 Å and the vibrational frequency is 2358 cm^{-1}, in excellent agreement with the experimental values.[23] For the N_3^- anion, we have obtained 1.20 Å for the interatomic distance, in very good agreement with the experimental value 1.19 Å.[24] The bending frequency value is 641 cm^{-1} and the experimental one[25] is 640 cm^{-1}; the symmetric stretching is 1304 cm^{-1} and the asymmetric stretching is 2112 cm^{-1}, whereas the experimental values are 1350 cm^{-1} (ref 26) and 1986 cm^{-1} (ref 24), respectively.

In the Ga_4N_4 cluster, the initial configuration of the neutral cluster was similar to that of the corresponding anion, with C_{2v} symmetry. However, the presence of an imaginary value in the vibrational frequency calculations showed it to be unstable. Hence, by breaking the symmetry and reoptimizing the cluster configuration, we found the stable minimum. The neutral Ga_4N_4 (see Figure 3) is a three-dimensional structure, with C_s symmetry, and contains a N_3 subunit. The average N−N distance (1.20 Å) in this N_3 subunit is the same as that seen in the N_3^- ion. The octagonal planar ring (the lowest energy structure in the neutral Al_4N_4), is about 2.45 eV higher in energy. The addition of an electron to Ga_4N_4 did not affect the presence of the N_3 subunit in its lowest energy configuration. However, the neutral and anion structures are not exactly the same. The $Ga_4N_4^-$ cluster has C_{2v} symmetry, with the coordination index for one of the terminal N atoms in this N_3 subunit lowered from 2 metallic atoms in neutral to 1 metal atom in anion (see Figure 3). The lowering of the coordination index, however, induces a very small increase in the N−N bond strength in the N_3 subunit, decreasing the N−N bond length from 1.21 to 1.19 Å.

The lowest energy configurations of neutral and anionic Ga_5N_5 clusters are collected in Figure 3. The neutral Ga_5N_5 cluster has two N_2 subunits in its lowest energy structure. One of the two N_2 subunits is at one end of this structure and is termed as the terminal N_2, whereas the other N_2 subunit, bonded to four gallium atoms is termed as the central N_2. This structure can be seen as a combination of Ga_5N_3 and the terminal N_2 subunit. However, these two N_2 subunits with large N−N bond distances (1.31 Å in central N_2 and 1.23 Å in terminal N_2) are not exactly like an N_2 molecule (N−N: 1.12 Å) because of the high coordination of metallic atoms for these subunits. The difference between the N−N bond lengths of these two N_2 subunits can be attributed to the different metal atom coordinations. The presence of four Ga−N bonds for the central N_2 subunit, in comparison to only two Ga−N bonds for the terminal N_2, resulted in the elongation, hence and weakening, of the N−N bond in the former. Moreover, the terminal N_2 subunit, with its weak bonds with metal atoms (Ga−N: 2.89 Å, 2.72 Å), can be treated as a weakly bonded N_2 molecule. The molecular orbital picture of this neutral isomer revealed the LUMO to be an antibonding orbital, concentrated over the central N_2 subunit. Hence, the addition of an electron to this isomer results in destabilization and is not expected to be a preferred structure for $Ga_5N_5^-$ cluster. In fact, the lowest energy isomer of $Ga_5N_5^-$ is not the same as that of the neutral cluster. For the $Ga_5N_5^-$ cluster, the lowest energy isomer has a N_3 subunit, bonded to two mutually perpendicular rhombic units. Originally, this structure had C_{2v} symmetry, with the terminal Ga atom aligned with all the N atoms. However, the vibrational frequency calculation for this structure resulted in an imaginary frequency. By moving the terminal Ga atom in the direction of the normal coordinates of this frequency, a real minimum with C_s symmetry was obtained. The average N−N distance for the N_3 subunit is approximately 1.20 Å, same as that in the azide N_3^-. The two nitrogen atoms in the Ga_5N_2 subunit are having a 4-fold and 3-fold coordination with the Ga atoms. This indicates the requirement of at least 3-fold coordination for N atoms to break the N−N bonds in agreement with our previous conclusions.[13]

In the Ga_6N_6 neutral cluster, the lowest energy isomer is a planar configuration with N_3 subunit. Although this structure has an azide subunit, the other part of the cluster is dominated by metal−nitrogen bonds. This isomer can be seen as a Ga_6N_3 unit bonded to N_3. In this cluster it can be seen that the N atoms that are free from the N−N bonds have a 3-fold metal coordination. Again, for GaN neutral clusters, a minimum of 3-fold coordination is required for the N atoms to break the strong N−N bonds. The Ga−N bond dominated hexagonal prism (the lowest energy structure in Al_6N_6) is the next lowest energy structure, 0.51 eV higher in energy. This hexagonal prism is energetically degenerate ($\Delta E = 0.004$ eV) with another planar structure containing a N_3 and Ga_6N_3 subunits (structure F, in Figure 1). The average metal−nitrogen bond length decreases from 2.17 Å in Ga_4N_4 to 1.93 Å in Ga_6N_6, indicating the strengthening of the Ga−N bond with the increase of the cluster size. The fact that the hexagonal prism is the second lowest energy configuration, and its competition with a planar structure with a N_3 subunit, also indicate the increasing importance of three-dimensional structures and the fact that the GaN cluster is starting to prefer a Ga−N bond dominated 3-dimensional structure. In fact, upon adding an electron to the Ga_6N_6 clusters, the hexagonal prism configuration is found to be the lowest energy structure, followed by a planar N_3 dominated structure ($\Delta E = 0.20$ eV, isomer F in Figure 1).

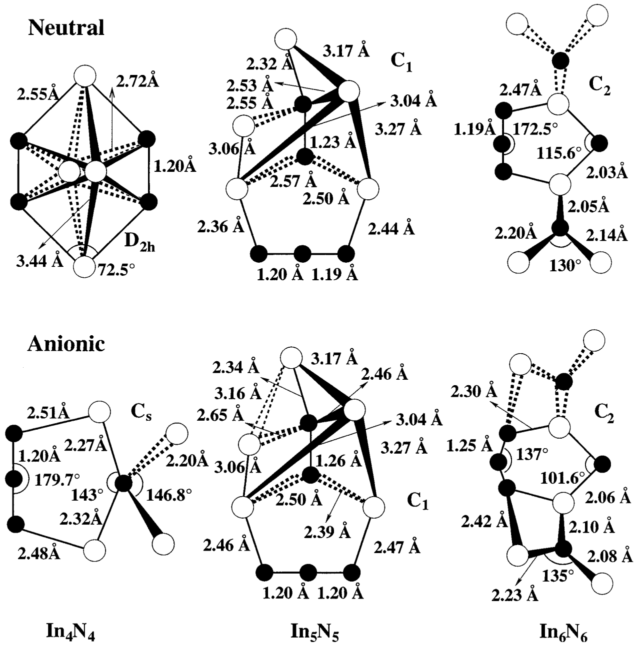

Figure 4. Lowest energy structures of neutral and anion In_nN_n clusters. Nitrogen atoms are represented by small filled circles, and the In atoms are big empty circles.

The In_nN_n clusters are found to prefer 3-dimensional structures, dominated by either N_2 or N_3 subunits. The lowest energy isomers of neutral and anionic In_nN_n clusters are given in Figure 4. For In_4N_4 clusters, the lowest energy configuration has two N_2 subunits with each of them bonded to four metal atoms. Due to the high metal coordination for these N_2 subunits, the N−N bond distances (1.20 Å) are elongated when compared to the N−N bond length (1.12 Å) in the N_2 molecule. However, the LUMO for this stable structure has an antibonding character, making it unstable upon the addition of an extra electron. Hence, for the $In_4N_4^-$ cluster, a different structure, with C_s symmetry, is the lowest energy configuration. This structure is analogous to $Ga_4N_4^-$ in Figure 3 and contains a N_3 subunit bonded to the In_4N subunit.

The lowest energy isomers of both neutral and anionic In_5N_5 clusters have the same structure, of C_1 symmetry, that contains N_2 and N_3 subunits. The N_3 subunit is quite similar to the free azide molecule. However, the N_2 subunit shows a larger N−N distance (1.26 Å) than that in the N_2 free molecule, because the two nitrogen atoms have a high coordination index, one of them having an almost tetrahedral environment. It is also important to notice that the In−In interactions show a range of distances very close to those of the In_2 molecule (3.10 Å), and in some cases even smaller than this. The movements of the atoms out of the plane of the original C_{2v} structure[13] to reach this complex stable isomer tend to approximate the metallic atoms together. Thus, metal−metal bonds can be formed by stabilizing the cluster. In section 3.3, we will discuss the molecular graph for this isomer.

The lowest energy configuration of the neutral In_6N_6 cluster is similar to that of the Ga_6N_6 cluster (see Figures 4 and 3). In In_6N_6, however, the two off-ring NIn_2 groups with a 3-fold coordinated nitrogen are about 7° in and out of plane from the remaining In_2N_4 subunit of the cluster, resulting in C_2 symmetry for this structure. In this stable isomer, although the metal−N_3 bond distances are larger than in the InN monomer (In−N: 2.27 Å), the other M−N distances in the cluster are smaller, thereby indicating the strengthening of the metal−nitrogen bonds with the increase in the cluster size. This emphasizes the importance of high metal coordination for the nitrogen atoms to have strong metal−nitrogen bonds in the nitride clusters. The addition of an electron to the neutral cluster maintains a similar structure. However, the N_3 subunit of the anion is bent with an angle of 135°, and the N−N distances are increased by 5%. The end N atoms of the N_3 group and the terminal In atoms of the off-ring NIn_2 group approach a distance of 2.42 Å, forming two new In−N bonds in this negatively charged cluster. These two new bonds are compensating the loss of the multiple character of the N−N bonds in the bent N_3 subunit.

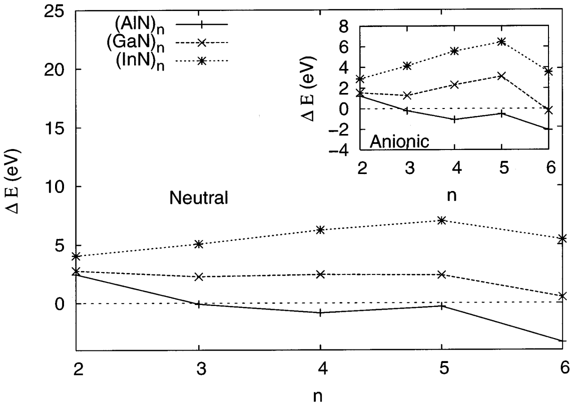

Figure 5. Evolution of the competition between structures dominated by N−N bonds and M−N bonds with cluster size *n*.

To analyze the competition between the M−N bond dominated structures and the N−N bond dominated ones in these clusters, the energy difference, $\Delta E = E_{\mathrm{M-N}} - E_{\mathrm{N-N}}$ between the lowest energy isomers in both cases is calculated for neutral and anionic clusters. With this definition, $\Delta E > 0$ means that N−N bonded structures are preferred, whereas $\Delta E < 0$ means that M−N bonds are dominating the cluster skeleton. The evolution of this energy difference with the cluster size n is plotted in Figure 5. The energy difference for small nitride clusters (M_nN_n; $n = 2, 3$) is taken from our previous work.[16]

In neutral and anionic Al_nN_n clusters, the ΔE value is always negative, except for the dimer, indicating a preference for Al−N dominated structures over the N−N dominated ones as their lowest energy configurations. Moreover, the absolute value of ΔE increases with n, indicating the growing importance of metal−nitrogen bonds in stabilizing the Al_nN_n clusters. However, a different picture is seen in Ga_nN_n and In_nN_n clusters. In these clusters, ΔE is always positive indicating the preference of N−N bonds over the metal−nitrogen bonds in their lowest energy configurations. However, in GaN clusters, this energy difference decreases smoothly: 2.45 eV in Ga_4N_4, 2.38 eV in Ga_5N_5, and 0.51 eV in Ga_6N_6. In neutral Ga_nN_n clusters, although the competition between N−N dominated structures and M−N dominated structures is increasing with the cluster size, there are still not enough metal−nitrogen bonds to break all the N−N bonds (N_3 subunit) in the lowest energy configurations. However, for the $Ga_6N_6^-$ cluster, the lowest energy configuration is dominated by M−N bonds. In neutral In_nN_n clusters, an opposite increasing ΔE trend with cluster size up to the pentamers is observed; however, the hexamers show a decrease in ΔE. This opposite trend and also the large ΔE in neutral and anionic In_nN_n indicate the structural differences not only with Al_nN_n clusters but also with Ga_nN_n clusters. It shows a weaker character of the M−N bond going down in the group from aluminum to gallium to indium. The indium compounds need a higher coordination index in the In−N bond to

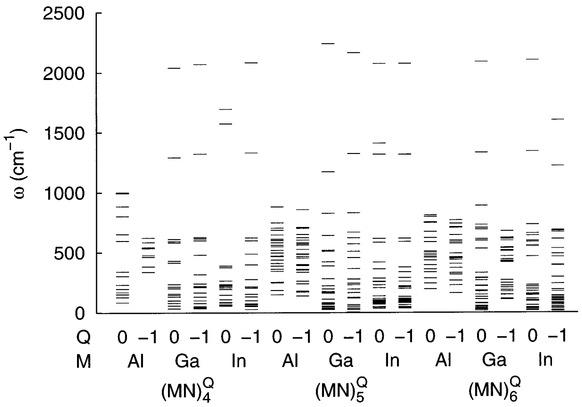

Figure 6. Vibrational frequency spectra of neutral and anionic M_nN_n clusters.

compensate the breaking the N−N ones. The change in the sign of the slope of ΔE versus n in Ga_6N_6 and In_6N_6, both neutral and negative, is significant, allowing us to predict that both compounds are close to the size in which the alternated M−N bond will dominate the structures as it happens in the bulk phase.

B. Vibrational Properties. To assess the stability of the optimized structures, the vibrational frequencies were calculated and analyzed for the lowest energy isomers of both neutral and anionic M_nN_n clusters. The vibrational frequencies of the neutral and anionic clusters are plotted in Figure 6. It clearly reflects the structural differences between the lowest energy configurations of Al_nN_n clusters from those of Ga_nN_n and In_nN_n clusters and also the nature of the N−N bonded subunits in gallium and indium nitride clusters. The vibrational frequencies of these clusters range from 3 to 2200 cm^{-1}. However, most of these frequencies are concentrated below 1000 cm^{-1}. These vibrational modes correspond to the movements of the M−N bonds. Therefore, the entire frequency spectrum can be broadly classified into two regions: region 1, with frequencies smaller than 1000 cm^{-1}, associated with the M−N bonds, and region 2, with frequencies larger than 1000 cm^{-1}, involving N−N stretching modes.

In region 1, the low lying frequencies correspond to the metal−nitrogen bending modes, whereas the frequencies close to 1000 cm^{-1} correspond to either symmetric or asymmetric stretching modes of M−N bonds. All the vibrational frequencies of Al_nN_n clusters, both neutral and anionic, are in region 1, as there are no N−N bonds present in any of their lowest energy structures. The highest frequency (1000 cm^{-1}) of Al_4N_4 is a breathing mode and is higher than the frequency of the AlN monomer (749 cm^{-1}). There is a decreasing trend in the value of the highest frequency mode of the AlN clusters (1000 cm^{-1} in Al_4N_4, 880 cm^{-1} in Al_5N_5, and 809 cm^{-1} in Al_6N_6) with the increase of the size of the cluster. This trend can be attributed to the weakening of the Al−N bond strength and a larger coupling of Al−N bonds with the other Al and N atoms, as the size of the cluster increases from 8 atoms to 12 atoms.

The N_2 subunits are present only in the lowest energy configurations of In_4N_4 and Ga_5N_5 clusters. Hence, their vibrational frequency values in region 2 are expected to be similar in nature and also close to that of the N_2 molecule. However, their highest frequency values are found to be entirely different. In In_4N_4, with two N_2 subunits, the N−N stretching modes (1694 and 1571 cm^{-1}) are found to be much lower than the corresponding N−N stretching (2358 cm^{-1}) in the N_2 molecule. This is due to the fact that these N_2 subunits in the In_4N_4 cluster are far from the real N_2 molecule (N−N = 1.12 Å), with larger N−N distances (1.20 Å). Moreover, these N−N bonds have a high coordination of metal atoms (four metallic atoms). In Ga_5N_5; however, the highest frequency mode (2238 cm^{-1}), corresponding to the stretching of the terminal N_2 (see Figure 3), is quite similar to the corresponding N_2 frequency. This is obvious because the terminal N_2 is very weakly bonded to the Ga atoms, and as mentioned in the previous section, it can be considered as a weak N_2 molecule. This frequency is followed by another stretching mode (1170.8 cm^{-1}), considerably lower than the N_2 molecule stretching frequency. This normal mode corresponds to the stretching of the central N_2 subunit (see Figure 3), which is considerably weak, when compared to the N_2 molecule, with a large N−N bond length and a high metal atom coordination around the nitrogen atoms.

The remaining GaN and InN clusters have their highest frequency in the range of 2030 cm^{-1}. These frequencies are due to the stretching of the N_3 subunits in their lowest energy configurations. These normal modes are in very good agreement with the stretching normal mode (2112 cm^{-1}) of N−N bonds in the N_3^- ion. Hence, the N_3 subunits in these clusters are similar to that of an N_3^- ion. Both neutral and anionic In_5N_5 clusters show the same lowest energy configuration, but their vibrational spectra seem slightly different. This difference is because the stretching normal mode of the N_2 subunit in the neutral cluster (1406 cm^{-1}) is shifted to a lower value when an electron is added (1316 cm^{-1}) as a consequence of a larger N−N distance in the anionic cluster. This displacement makes this frequency almost degenerate with the symmetric stretching mode of the N_3 subunit (1313 cm^{-1} in anionic, and 1315 cm^{-1} in neutral), thus appearing as two indistinguishable lines.

The vibrational frequencies of the $Ga_6N_6^-$ cluster are expected to be similar to those of the $Al_6N_6^-$, because of their structural similarity. The highest normal mode for $Ga_6N_6^-$ (677 cm^{-1}) is found to be lower than the corresponding mode in $Al_6N_6^-$ (768 cm^{-1}). This difference is a consequence of the periodic properties that make the metal−nitrogen bond strength decreases in going down the group from Al to Ga to In.

C. Atomic and Bonding Properties. To study the effect of the extra electron on the distribution of atomic charges and on the chemical bonds in the nitride clusters, we have calculated the topological atomic charges of neutral and anionic clusters using the AIM theory. For small nitride clusters, the extra electron in the anions was found to be concentrated mostly on the metallic atoms of the cluster.[16] This trend is expected to continue for the anions of the larger clusters studied here. The topological atomic charges of neutral and anionic M_nN_n clusters are collected in Table 1.

In Al_nN_n clusters, the charge transfer from metal to nitrogen atoms is always larger than that in the Ga_nN_n or In_nN_n clusters. This is to be expected, as aluminum is more electropositive than either gallium or indium atoms. Moreover, for all the Al_nN_n clusters, there is a minimum of 2 e charge transfer from Al to N, indicating the high ionic character of the Al−N bond. In $Al_nN_n^-$ clusters, the extra electron is found to be located mostly on the Al atom ($\Delta Q_{Al} = -0.24\ e$ and $\Delta Q_N = -0.01\ e$ in Al_4N_4, $\Delta Q_{Al} = -0.16\ e$ and $\Delta Q_N = -0.01\ e$ in Al_6N_6, where $\Delta Q_i = Q_i(\text{anion}) - Q_i(\text{neutral})$). Moreover, in neutral AlN clusters, the charge transfer from Al to N atoms increases with the size of the cluster ($Q_N = -2.13\ e$ in Al_4N_4 and $Q_N = -2.24\ e$ in Al_6N_6). This increasing trend is a direct consequence of the increase in the coordination index with the cluster size. In this way, taking Al_5N_5 as an example, there are two different types of aluminum atoms depending on their coordination index: the Al atoms with 3-fold coordination show a charge transfer around 2.18 e, whereas for the Al atoms with 2-fold coordination it is 1.98 e.

TABLE 1: Topological Atomic Charges of the Most Stable Neutral and Anionic Isomers for the M_nN_n (n = 4−6, M = Al, Ga, and In) Clusters[a]

	M = Al		M = Ga			M = In		
system	Q_N	Q_{Al}	Q_N	Q_{N_2}/Q_{N_3}	Q_{Ga}	Q_N/Q_{N_2}	Q_{N_3}	Q_{In}
M_4N_4	−2.13	2.13	−1.65	−0.71	0.59	−0.79		0.39
$M_4N_4^-$	−2.14	1.89	−1.65	−0.75	0.35	−1.48	−0.76	0.26, 0.38
M_5N_5	−1.98, −2.17	1.98, 2.18	−1.54	−0.18, −1.62	0.57, 0.79	−1.08	−0.69	0.24, 0.53
$M_5N_5^-$	−2.07, −2.18	1.78, 2.01	−1.54, −1.62	−0.77	0.45, 0.59	−1.18	−0.76	0.04, 0.40
M_6N_6	−2.24	2.24	−1.35, −1.59	−0.71	0.60, 1.42	−1.20, −1.46	−0.77	0.58, 1.28
$M_6N_6^-$	−2.25	2.09	−1.40		1.24	−1.17, −1.45	−1.10	0.47, 1.20

[a] Analogous or similar atoms are given as an average in low symmetry structures, and N atoms are summed up when they belong to N_2 or N_3 subunits.

Thus, this increase in the charge transfer is mainly proportional to the coordination index. In addition, the interatomic distance is another factor in the charge transfer, because the electron density decays exponentially with the internuclear distance.[14]

In Ga_nN_n and In_nN_n clusters, the presence of N_2 and N_3 subunits in their lowest energy isomers results in a slightly different picture than in the AlN clusters. As happened in the AlN clusters, the extra electron is located over the metallic atoms. A general dependency of the atomic charge located over the nitrogens without N−N bonds (i.e., coordinated only to the metallic atoms) with the coordination index has again been observed: −1.35/−1.54/−1.65 *e* for the nitrogen coordinated with 2/3/4 gallium atoms and −1.17/−1.20/−1.54 *e* when coordinated with In atoms. These values support that the charge transfer decreases in going from gallium to indium and are also clearly smaller than those for Al.

The total charge over the N_3 subunit remains almost constant for all clusters independently of the metallic atoms or the neutral or anionic character of the cluster, with the only exception of the $In_6N_6^-$, which is −0.3 *e* lower than the rest of azides. In this cluster, the extra electron is not completely located over the indium atoms; on the contrary, the N_3 subunit accepts 30% of the extra electron. This results in the bending of the N_3 subunit and its bonding to two new In, which increases the coordination index, facilitating the acceptance of the extra charge. An analogous behavior was found in the neutral gallium and indium nitride trimers, which also showed a bent N_3 subunit.[16] The atomic charge accepted by the N_2 subunits varies more or less in a continuous way as a function of two variables: the coordination index and the interatomic distance.[14] So, it is possible to have two N_2 subunits with a very different charge in the same compound, Ga_5N_5. One of the N_2 subunits has two bonds with the gallium atoms and a total charge of −0.18 *e*. This fact supports that this terminal N_2 is weakly bonded to the rest of the cluster and is quite similar to the free N_2 molecule. However, the central N_2 accumulates −1.62 *e* due to the bonding with the four gallium neighbors.

We have also obtained the topological molecular graph, constructed by linking atoms that are endpoints of the topological bond paths.[21] Lines in all structures collected in Figures 3−5 correspond to the AIM bond paths obtained for each of them. This analysis allows us to confirm that the rearrangement of the indium atoms in both neutral and anionic In_5N_5 clusters around the N_2 subunit is due to the formation of several In−In bonds. In Figure 4, there is a line connecting each two atoms for which a topological bond path linking them exists. Also, the two new In−N bonds between the N_3 subunit and In of the NIn_2 off-ring group in $In_6N_6^-$, predicted on the basis of distance criteria in subsection 3.1, have been confirmed in the AIM framework. A surprising fact was the occurrence of In−In bonds in In_4N_4, forming a rhombus in a plane plane to that containing the two N_2 subunits. The existence of these bonds allows us to interpret In_4N_4 as a metallic cluster formed by four indium atoms, bonded to two N_2 molecules.

TABLE 2: HOMO−LUMO Gap (eV) for the Most Stable Isomer in $(MN)_n$ Clusters (n = 4−6, M = Al, Ga, and In) (Configurations in Figures 3−5)

	tetramer	pentamer	hexamer
$(AlN)_n$	1.80	0.54	1.43
$(AlN)_n^-$	1.90	1.55	1.63
$(GaN)_n$	2.39	0.45	2.42
$(GaN)_n^-$	1.35	1.61	2.48
$(InN)_n$	0.98	1.35	2.05
$(InN)_n^-$	1.04	0.85	1.40

We have already employed the AIM theory in the study of the chemical bond in the neutral monomers and dimers of the group III nitrides,[11] in the analysis of the evolution of their chemical bonding in going from the molecules to the solid state,[14] and in the analysis of the small ionized clusters of group III nitrides.[16] The general features reported in our previous works are also found in this study and they can be summarized in three different categories of bonds: the M−N and the M−M bonds are nonsharing interactions, the former being polar and the latter nonpolar, and the N−N bond is a nonpolar and sharing interaction.

D. Electronic Properties. The HOMO−LUMO gap values for the lowest energy isomers of the nitride clusters have been computed and are collected in Table 2. As expected, a different behavior was observed in the aluminum clusters in comparison with the gallium and indium nitride clusters. The former shows a decreasing trend in the HOMO−LUMO gap with the cluster size, whereas in the latter the HOMO−LUMO gap values are increasing from tetramer to hexamer. For the gallium and indium nitrides, we can appreciate systems whose HOMO−LUMO gap values are small (Ga_5N_5, In_4N_4, and $In_5N_5^-$). The common feature of these compounds is the presence in their structures of a N_2 subunit. This subunit has strongly delocalized electrons, making the gap smaller.

Overall, the HOMO−LUMO gap of the nitride clusters is found to be controlled by the structural configuration. In this way, the dispersion of these values will be reduced when the structural isomers maintain a common structural motif, together with a common bonding nature (alternated M−N bond) when the size is increased. These structural motives should be the building blocks that allow us to generate the bulklike structure.

The adiabatic and vertical electron affinities of M_nN_n clusters are computed and given in Table 3. The electron affinity was calculated in accordance with the following definition: $EA = E_{neutral} - E_{anion}$. Vertical values correspond to detachment of an electron from the anion, maintaining the same geometry. It can be seen from Table 3 that, for a given size of the cluster, the electron affinity decreases as we move down in the group from Al_nN_n to Ga_nN_n and to In_nN_n. This trend is expected and is a manifestation of the evolution of the periodic properties.

TABLE 3: Vertical and Adiabatic Electron Affinity (EA, eV), for M_nN_n ($n = 4-6$, M = Al, Ga, and In) Clusters

	tetramer	pentamer	hexamer
vertical EA $(AlN)_n$	2.92	2.81	2.24
adiabatic EA	2.44	2.76	2.18
vertical EA $(GaN)_n$	2.46	2.99	3.07
adiabatic EA	1.84	2.47	2.52
vertical EA $(InN)_n$	2.16	1.87	2.47
adiabatic EA	1.59	1.54	1.58

We are not aware of any experimental or theoretical study about the electron affinity in these compounds. We therefore compare the calculated values with the experimental results from photoelectron spectroscopy measurements carried out for the Ga_nP_n and In_nP_n.[27,28] The gallium (indium) phosphide experimental values for the adiabatic electron affinity are 2.33 (2.15), 2.81 (2.10), and 2.74 (2.18) eV for $n = 4$, 5, and 6, respectively. As happened in the small group III nitride clusters study,[16] our results show values smaller than their respective values in phosphides. This trend can be explained as follows: the already charged nitrogen atoms do not accept the charge of the extra electron in the anionic clusters. However, in the phosphide clusters the extra electron is expected to be shared equally by all atoms, resulting in the behavior that was found in the anionic clusters of InAs.[29]

IV. Conclusions

The addition of an electron to the neutral group III nitride clusters induces significant structural changes in gallium and indium nitrides. The aluminum nitride clusters show a strong preference for the metal−nitrogen alternate bonds and also exhibit an unambiguous trend toward 3-dimensional structures. However, in gallium and indium clusters, the N_2 and N_3 subunits are still the dominant feature in their structural configurations. These clusters present planar-like structures, except for $Ga_6N_6^-$, In_5N_5, and $In_5N_5^-$. The extra electron is located over the metallic atoms as was the case with the small anionic clusters. The only exception is the $In_6N_6^-$, in which the N_3 subunit accepts some charge and ceases to be linear. The atomic charge analysis indicates that these clusters have a partial ionic character, which *decreases* when going down in the group III.

The breaking of the N−N bonds, the occurrence of 3-dimensional structures, and an increase of the coordination index are steps needed for the group III nitride clusters to reach the bulklike behavior. The analysis of our results indicates that only two of these steps have been reached in the aluminum nitride clusters. The last step, the 4-fold coordination for each atom remains to be achieved. Gallium and indium clusters do not satisfy any of these conditions at the sizes considered in this work, although it seems that the onset of the alternate bonding regime is near. Moreover, we do not find a clear growing pattern in these clusters that allows us to build the unit cell of the solid state. These facts show us that these clusters are still far away from the bulklike behavior.

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