Theoretical Study of Structural and Vibrational Properties of Al₃N₃, Ga₃N₃, and In₃N₃

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We report the results of a theoretical study of the nitride trimers (i.e., M₃N₃ with M = Al, Ga, and In) focusing on their structure, stability, and vibrational properties. The calculated results reveal a distinct structural difference between the most stable isomers of Al and those of Ga and In, which can be explained in terms of the evolution of the relative strengths of metal−nitrogen and metal−metal bonds in going from Al to Ga to In. It is also shown that the strength of the nitrogen−nitrogen bond still dominates the preferred fragmentation path for these clusters and that fragmentation occurs at a lower energy than ionization. Assignments to the frequencies of the various normal modes are made in terms of those of the MN monomers (Al₃N₃) or in terms of those of weakly bonded (M₃)⁺ and (N₃)⁻ subunits (Ga₃N₃ and In₃N₃).

I. Introduction

Group III nitrides have recently emerged as a choice for the next generation materials for applications in the microelectronic and optical industry.[1] Although the bulk nitrides have been the focus of several experimental and theoretical studies in recent times, a detailed knowledge of the physical and chemical properties of the nitride clusters is still lacking. This knowledge could be specially valuable for the understanding of the sputtering process by which the surface layers of the electronic devices are constructed.[2]

Previous experimental or theoretical studies of AlN and GaN clusters are scarce, and there are none devoted to InN, to the best of our knowledge. In a recent study, gas-phase nitride clusters were observed, during chemical vapor deposition (CVD) of AlN thin films from AlCl₃ and NH₃.[3] However, emphasis was more laid on the structural properties of the adducts than the (AlN)ₙ clusters themselves. In the case of GaN, experimental studies were conducted on the organometallic precursors for CVD of GaN heterostructures.[4] Here again, the structural properties of (GaN)ₙ clusters were not considered. On the other hand, theoretical studies include a multireference configuration interaction (MRCI) study performed on the AlN monomer[5] and calculations of AlN₃, Al₃N, and Al₂N₂ using the second-order Moller−Plesset (MP2) perturbation theory.[6] A recent time-dependent Hartree−Fock study on polarizabilities on GaN clusters (i.e., Ga₃N₃H₁₂ and Ga₄N₄H₁₈) reported their nonlinear optical properties considering the clusters in tetrahedral geometry.[7] In this study, it is suggested that GaN cluster-based materials can be considered for efficient photonic systems.

Our research group has recently initiated a theoretical study of small clusters of the group III nitrides in the framework of density functional theory (DFT). We began the study considering only monomer, triatomic, and dimer configurations of neutral and singly ionized clusters,[8,9] identifying a strong preference for N−N multiple bonds in the most stable isomers. In the absence of N−N bonds, the metal−nitrogen bond dominates,

although its strength decreases in going from Al to Ga and In. When there is a N−N bond, the strength of the metal−nitrogen bond is greatly reduced, being more like a van der Waals bond. At the same time, the weak metal−metal bond increases its strength from Al to Ga and In, becoming stronger than the metal−nitrogen bond for In₂N₂. This weakness of the metal−nitrogen bond in small nitride clusters is in contrast to what is expected in the corresponding bulk crystals at ambient conditions. Although the Al−N bond retains some of the bulk characteristics in Al₂N₂, Ga−N (In−N) bonds are the weakest in Ga₂N₂ (In₂N₂) indicating nonshared and almost nonpolar interactions.

In the present paper, we focus on stoichiometric M₃N₃ clusters (M = Al, Ga, and In) and report their equilibrium properties including configurational parameters, binding and fragmentation energies, and vibrational frequencies. This study is expected to provide further insight on the properties of small clusters of group III nitrides, on one hand, and also to shed some light into the emergence of their bulklike behavior with the increase in the size of the cluster. It is to be noted here that calculations on Al₃N₃ and Ga₃N₃ were performed previously[10,11] in a limited way in which several probable isomeric configurations were not considered, yielding a totally different conclusion than the one reported here. Furthermore, none of the previous theoretical studies considered In₃N₃. Therefore, the work presented here provides new results and insight into the structure and chemical bonding of M₃N₃ clusters, enabling us to assess both size and cation dependence of the structural properties at the same level of theory.

The rest of the paper is organized as follows. In section II, we give a brief description of the computational method used in this work. Results and discussion will be presented in section III for linear and nonlinear isomers of the nitride trimers. We will also discuss stability and vibrational features of the lowest-energy nitride trimers. Finally, we will summarize our conclusions in section IV.

II. Computational Method

Electronic structure calculations based on DFT were performed on various structural isomers of M₃N₃ having linear and

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nonlinear configurations. The gradient-corrected (GGA) density functionals for exchange (Becke[15]) and correlation (Perdew–Wang[16]) along with double numeric basis sets supplemented with d polarization functions (i.e., the DNP set) were used here. The frozen core approximation was used for all atoms in which $1s^2$, $1s^2 2s^2$, $1s^2 2s^2 2p^6$, and $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$ inner cores for N, Al, Ga, and In, respectively, were frozen during the self-consistent field (SCF) calculations. The accuracy and reliability of the modeling elements were examined in our previous study.[8] In the SCF calculations, the energy and density convergence criteria were fixed at 10^{-6} hartree and 10^{-6} e/bohr³, respectively. The geometry optimizations on symmetry-constrained multi-dimensional potential-energy surfaces were achieved with a gradient norm smaller than 10^{-3} hartree/bohr and an energy convergence of 10^{-5} hartree. It is to be noted here that calculations were not performed for the low-lying spin states individually. Instead, spin unrestricted calculations, in which the Aufbau principle determines the orbital occupancies, were performed. Except where explicitly noted, all of our calculations used the DMol program.[17]

For the lowest-energy configurations, an analysis of the stability was performed by computing the vibrational frequencies. A two-point finite difference formula with step size of 0.1 bohr was used to obtain the Hessian from analytic gradients. The first ionization potential of the most stable isomers of M₃N₃ clusters was also calculated in both vertical and adiabatic approximations. These are defined as the difference between the energies of the ionized and the neutral clusters, taking the ionized trimer in either the same geometry as in the neutral trimer (vertical) or its own optimum geometry (adiabatic). Finally, fragmentation energies were calculated as the difference between the energies of the cluster fragments and that of the cluster.

III. Results and Discussion

Several linear, planar, and nonplanar configurations of Al₃N₃, Ga₃N₃, and In₃N₃ were considered for the symmetry-constrained geometry optimization. The choice of each of these isomers was based on our study of triatomic and dimer clusters[8] of aluminum, gallium, and indium nitride, along with a theoretical study of Al₃P₃[12] and Ga₃As₃.[13,14] A sketch of the optimum geometries for each of the isomers is presented in Figure 1. We will begin the discussion with linear (one-dimensional) isomers, followed by nonlinear (two- or three-dimensional) isomers. Focusing on the lowest-energy isomers (Figure 2) only, we will then assess the stability and vibrations of Al₃N₃, Ga₃N₃, and In₃N₃ trimers.

A. Linear Isomers. Three linear isomers of M₃N₃ clusters, as shown in Figure 1a–c, were chosen here representing various combinations of metal–metal (M–M), metal–nitrogen (M–N), and nitrogen–nitrogen (N–N) bonds. All of these linear isomers were found to be in a triplet state in the equilibrium configuration.

Among the linear isomers of Al₃N₃, Al–N–Al–N–N–Al (**1b**) was found to be energetically more favorable, whereas the other two linear isomers are more than 1.35 eV higher in energy. This can be explained by looking at the number of Al–Al, Al–N, and N–N bonds present in each of the structures. The presence of the N–N bond in Al–N–Al–N–N–Al is responsible for its stability, being the stronger one. Although there are two such N–N bonds in Al–Al–N–N–N–Al, the strength of the second one should be smaller than that of the almost triple bond of Al–N–Al–N–N–Al. The two weak Al–N bonds to the N–N bonded unit are present in both trimers, but

Figure 1. Structures, symmetries, and total energies (in hartree) for several isomers of M₃N₃ (M = Al, Ga, and In). Nitrogen and metal atoms are represented by small and large filled circles, respectively.
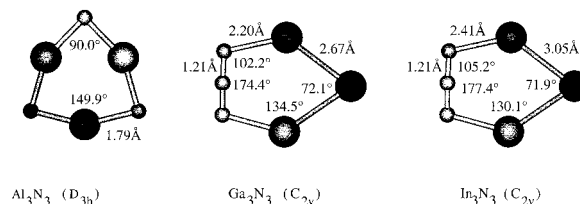
		M = Al	M = Ga	M = In
a		−891.54392	−5939.53992	−17393.34510
b		−891.59453	−5939.53874	−17393.29880
c		−891.54063	−5939.46549	−17393.18963
d	C_{2v}	−891.57797	−5939.57845	−17393.38362
e	D_{3h}	−891.62690	−5939.50584	−17393.21391
f	C_s	−891.60356	−5939.59120	−17393.38269
g	C_{2v}	−891.54904	−5939.56287	−17393.37097
h	C_{2v}	−891.60380	−5939.54052	−17393.30122
i	C_{2v}	−891.50311	−5939.39047	−17393.15292
j	C_{2v}	−891.54585	−5939.55066	−17393.35663
k	C_{2v}	−891.56413	−5939.54469	−17393.33169
l	C_{2v}	−891.54991	−5939.53315	−17393.19493

Figure 2. Lowest energy stable isomers of Al₃N₃, Ga₃N₃, and In₃N₃. Nitrogen and metal atoms are represented by small and large filled circles, respectively.

the latter has two strong Al–N bonds compared to a weak Al–Al bond and the second weaker N–N bond (similar to an azide ion, N₃⁻). The higher energy N–Al–N–Al–N–Al isomer does not have any N–N bonds, which were shown to be stronger than Al–N bonds in AlN dimers.[8,9]

In Ga₃N₃ and In₃N₃ linear isomers, the trend is quite different. Because Ga–N and In–N bonds are weaker than Al–N bonds and Ga–Ga and In–In bonds are stronger than Al–Al bonds, formation of the M–M–N–N–N–M isomer is favored instead of the M–N–M–N–N–M one. That is, two weaker metal–nitrogen bonds can now be broken to create a second (weaker) N–N bond and a metal–metal bond. This preference is barely enough in Ga₃N₃, but more than enough in In₃N₃, to make structure **1a** to be the lowest-energy linear isomer. Furthermore, the metal–metal separation is smaller in M₃N₃ than that in the corresponding metal monomer (M₂), indicating a stronger metal–metal bond in the trimer. For example, the Ga–Ga bond length in the isomer **1a** is 2.57 Å, whereas the corresponding separation in Ga₂ is 2.80 Å. We can conclude that, as we move from Al to Ga to In, weakening of the metal–nitrogen bond leads to an azide-like configuration, with somewhat stronger

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metal−metal bonds, to stabilize the linear configuration of the nitride trimers.

B. Nonlinear Isomers. Several nonlinear isomers, including planar (**1d** to **1j**) and nonplanar (**1k** and **1l**), were also considered for the geometry optimization.

In Al_3N_3, the hexagonal configuration of D_{3h} symmetry (**1e**) is predicted to be the lowest-energy structure. Here, the Al−N separation is 1.79 Å, about the same as in the monomer. In going from a linear (**1c**) to hexagonal (**1e**) configuration, there is a gain in energy of about 2.34 eV because of the formation of an extra metal−nitrogen bond. Because the binding energy of the AlN monomer[8] is 2.74 eV, bending of the metal−nitrogen bonds to form a cyclic ring costs about 0.4 eV. It is also important to note that the formation of metal−nitrogen bonds, accompanied with large charge transfers and large valence shell distortions, is preferred over the formation of nitrogen−nitrogen bonds. This is due to the fact that isomers with N_2 (or N_3) subunits use either weak metal−N_2 (or −N_3) or metal−metal bonds to form a cyclic ring or 3-D structure. Hence, the possibility of forming a stronger metal-nitrogen bond leads to a stable **1e** isomer in Al_3N_3. Another factor stabilizing the **1e** isomer is the short metal−metal distance within the ring, 2.54 Å, similar to that of 2.50 Å in Al_2, indicating some degree of metal−metal bonding in the hexagonal configuration.

The calculated results for Ga_3N_3 do not follow the trend expected from Al_3N_3. Here, isomers with an azide-like (N_3) subunit are found to have lower energies than the cyclic **1e** isomer. The **1f** isomer is the one with minimum total energy, closely followed by the ring **1d** isomer and the **1g** isomer. A preference for azide-like subunits is also shown in linear configurations, where the total energy of **1a** is lower than that of **1b** or **1c**. In fact, the nitrogen−nitrogen distances are quite close to those of the linear N_3^- ion (i.e., 1.20 Å), with the largest deviation being shown by the **1f** isomer because of the bending of the N_3 subunit.

The calculated results also show that the presence of four metal−nitrogen bonds in **1f** is preferred over two metal−nitrogen and two metal−metal bonds present in both **1d** and **1g** isomers of Ga_3N_3. However, a small energy difference of about 0.3 eV between **1f** and **1d** isomers suggests to us that the competition among these bonds in Ga_3N_3 isomers is in a subtle balance. In any case, and contrarily to what was found in Al_3N_3, the cyclic isomer **1e** is 1.97 eV higher in energy. We may therefore conclude that the metal−nitrogen bond is not strong enough to be preferred over nitrogen−nitrogen bonds in Ga_3N_3.

Our analysis of the vibrational frequencies of the low-energy isomers of Ga_3N_3 has revealed the appearance of several imaginary frequencies in **1f** and **1g** isomers, thereby predicting them to be unstable. This does not happen with the **1d** isomer, which can then be regarded as representing a true minimum of the potential-energy surface of Ga_3N_3.

Starting optimization in $C1$ symmetry along the imaginary frequency eigenvectors of **1f** and **1g** isomers, we obtained asymmetric true minima for both structures which are very close to the original ones. However, these minima are again very shallow: the **1f** and **1g** configurations can easily be dissociated into smaller asymmetric fragments. Given the fact that **1d** is the lowest energy isomer for In_3N_3, as shown later, we prefer to choose **1d** as the stable structure of Ga_3N_3 for the analysis of subsection C.

Bending of the lowest energy linear **1a** configuration results in a gain of energy of about 1.05 eV for the **1d** configuration. The gain in energy is mainly due to the formation of a metal−metal bond with a distance of 2.67 Å. Because the bond distance

in Ga_2 is 2.80 Å, a stronger metal−metal bond is therefore expected in the **1d** isomer of Ga_3N_3.

Comparing our results to those of previously reported[11] calculations, we find that they do not agree. The hexagonal cyclic **1e** isomer of Ga_3N_3 was predicted to be the global minimum isomer,[11] whereas our calculations predict a preference for the N_3-bonded isomers, with the hexagonal cyclic **1e** isomer almost 2 eV higher in energy. These different conclusions are a result of the wider range of structural isomers considered in the present work. In ref 11, the global minimum structure was taken to be the same as that for Al_3N_3 without considering enough alternative structures, overlooking the increasing importance of metal−metal bonds over metal−nitrogen bonds in the Al, Ga, and In series. This increase of importance in the metal−metal bond is not only supported by the present study and our previous work on small nitride clusters[8] but it is also a manifestation of the well-known rule by which the metallic character increases as we go down in a column of the periodic table.

Although numerical and methodological errors may exist, the energy difference of about 2 eV (4.6 eV for In_3N_3) between the **1d** and the **1e** structures is certainly not within these errors. To further support our conclusion, we have performed preliminary Gaussian 98[18] calculations on isomers **1d**, **1e**, and **1f** of Al_3N_3, Ga_3N_3, and In_3N_3 at the DMol optimized geometries, using different levels of theory. We used a 6-31G(d,p) basis set for N, Al, and Ga, and a DZVP for In for these calculations. It is to be noted here that Gaussian 98 calculations employed the same GGA functional form used in DMol calculations to test the basis-set dependence (i.e., numerical vs analytical) in our prediction of the most stable isomers. Second- and fourth-order Moller−Plesset (MP2 and MP4) calculations (at DMol optimized geometries) using Gaussian 98 were also performed to check the consistency of predictions made by different methodologies. The Gaussian 98 results, in predicting the order of stable isomers, are in agreement with those reported here using DMol, although the energy differences between isomers are not the same. Hence, MP2 and MP4 calculations find the **1e** isomer to be the lowest-energy configuration for Al_3N_3, whereas it is the **1f** isomer followed by **1d** and **1e** for Ga_3N_3 and the **1d** isomer closely followed by **1f** isomer for In_3N_3, as predicted by GGA (DMol) calculations.

As we have stated above, the **1d** isomer is also predicted to be the most stable isomer for In_3N_3. It is closely followed by the **1f** and **1g** isomers, although the latter is not stable, having an imaginary frequency in its vibrational spectrum. Interestingly, the metal−metal distance in the **1d** isomer is 3.05 Å, approximately 4% smaller than that in In_2. It therefore indicates that the metal−metal bond is stronger in the **1d** isomer of In_3N_3 than that in In_2.

An interesting qualitative conclusion can also be extracted by comparing energies of **1c** and **1e**, on the one hand, and **1a** and **1d**, on the other. The energy differences are likely to indicate, neglecting the bending effects, the relative strengths of metal−nitrogen and metal−metal bonds in these clusters. In the first case, the energy difference is 2.35, 1.09, and 0.88 eV for Al, Ga, and In clusters, respectively, whereas the respective values for the second case are 0.92, 1.05, and 1.05 eV. It can then be concluded that metal−nitrogen and metal−metal bonds have opposite tendencies when descending along the group III and that the metal−metal bond is in fact stronger in the polyatomic clusters of InN and almost equally stronger in GaN clusters. This is in contrast to the binding energies in diatomics, 1.76, 1.57, and 1.61 eV for Al_2, Ga_2, and In_2, and diatomic

TABLE 1: Ionization Potentials (IP), and Fragmentation Energies for Al$_3$N$_3$, Ga$_3$N$_3$, and In$_3$N$_3$[a]

	Al$_3$N$_3$ (eV)	Ga$_3$N$_3$ (eV)	In$_3$N$_3$ (eV)
vertical IP	8.48	6.82	6.30
adiabatic IP	8.34	6.32	5.90
M$_3$N$_3$ → 3 M + 3 N	19.66	17.49	16.94
M$_3$N$_3$ → 3 MN	11.40	10.16	10.52
M$_3$N$_3$ → M$_2$N$_2$ + MN	4.61	3.48	3.88
M$_3$N$_3$ → MN$_2$ + M$_2$N	1.46	0.68	1.42

[a] The first fragmentation reaction corresponds to the binding energy.

TABLE 2: Symmetry Labels and Frequencies (ω) of the Normal Modes of Vibration of M$_3$N$_3$ Clusters[a]

Al$_3$N$_3$-D_{3h}		Ga$_3$N$_3$-C_{2v}		In$_3$N$_3$-C_{2v}
mode	ω (cm^{-1})	mode	ω (cm^{-1})	ω (cm^{-1})
e''	200	b_2	33	32
a_2''	280*	a_1	97	91
e'	290*	b_1	98	61
a_1'	480	a_2	108	88
a_1'	620	a_1	145	116
e'	650	b_1	151	110
a_2'	820	b_1	250	228
e'	840*	a_1	275*	233*
		b_2	574	562
		a_1	598	591
		a_1	1209	1236
		b_1	1900*	1930*

[a] Infrared active modes of high intensity are indicated by a superscript asterisk.

nitrides, 2.74, 2.45, and 2.08 eV for AlN, GaN, and InN, where the heteronuclear bonding is clearly preferred. Thus, the preference for metal−metal bonds appears because of the complex and subtle electron density rearrangements that take place in polyatomic nitride clusters.

To conclude this subsection, we have also considered a few three-dimensional isomers (**1k** and **1l**), similar to those of the stable configurations of the apparently closely related compounds AlP[12] and GaAs.[13,14] These isomers are found to have higher energy($\simeq$1 eV) than the stable isomers and, hence, will not be discussed in what follows. A further three-dimensional isomer, a chairlike structure obtained by C_{3v} distortion of isomer **1e**, very closely related to the crystalline structures of the bulk nitrides, is also considered. However, optimization of this structure leads to the planar structure, similar to isomer **1e**, in all of the three trimers.

C. Stability and Vibrations. In this subsection, we will focus on the most stable isomers, **1e** of Al$_3$N$_3$ and **1d** of Ga$_3$N$_3$ and In$_3$N$_3$, whose configurational parameters are given in Figure 2. The calculated values of energies concerning their relative stabilities are gathered in Table 1.

We will first study the stability of neutral clusters with respect to their fragmentation into atoms and molecules. Considering only the binding energy, that required to fragmentate the molecule into atoms, all clusters seem to be very stable. The same is true if we consider fragmentation into heteronuclear diatomic molecules. Fragmentation into monomer (MN) and dimer (M$_2$N$_2$) is also difficult (around 4 eV). However, considering the formation of the most stable molecules (i.e., M$_2$N and MN$_2$), the fragmentation energy is small. Thus, M$_3$N$_3$ trimers are found to be stable against dissociation into smaller clusters, though fragmentation into asymmetric units appears to be the preferred fragmentation path.

Table 1 also includes the values of first ionization potential of these clusters, indicating a small difference between vertical and adiabatic values. Thus, ionization-induced distortion appears to be small for these trimers. The values of the ionization potential are similar to those of metal atoms,[8] clearly indicating the origin of the ionized electron. However, the energies required to dissociate these clusters via fragmentation paths are far less than those of the respective ionization potentials. Hence, dissociation of these clusters is more likely to happen than ionization, in the context of photoionization experiments.

Vibrational frequencies of the most stable trimers are listed in Table 2, together with the symmetry labels of the corresponding normal modes. Of all the normal modes allowed for electric dipole transitions in the infrared, a star marks those of highest intensity, with an intensity threshold of 10% of the intensity of the most intense mode (which happens to be also the one with largest frequency in all three clusters).

In Al$_3$N$_3$, the first two modes correspond to the out-of-plane bending, whereas the next two correspond to in-plane bending of the ring structure. Bending is symmetric in the nondegenerate modes and asymmetric in the degenerate ones. They are followed by stretching modes, symmetric (a_1', e') and asymmetric (a_2', e'). There is one caveat with e' modes; mixing is allowed by symmetry, and thus, stretching modes have also some contributions from in-plane bending modes. The most intense mode is found to be associated with the highest frequency, which corresponds to the asymmetric stretching of the six metal-nitrogen bonds in Al$_3$N$_3$.

The stretching modes of the Al$_3$N$_3$ trimer can be compared to those of the monomer, 710 cm^{-1}, and of Al$_2$N, 498 cm^{-1} (symmetric stretching) and 1014 cm^{-1} (asymmetric stretching). The symmetric (620 cm^{-1}) and asymmetric (820 cm^{-1}) stretching modes of the trimer are therefore below and above, respectively, those of the monomer frequency. This splitting of the symmetric and asymmetric modes is due to the coupling of the vibrations of different bonds. However, the splitting is smaller in Al$_3$N$_3$ than that in Al$_2$N. This can be attributed to a stronger coupling of bonds in Al$_2$N, because of its linear character.

Because the lowest energy isomers of Ga$_3$N$_3$ and In$_3$N$_3$ are isostructural, their vibrational modes are very similar. In Al$_3$N$_3$, all bending modes have lower frequencies than stretching modes, whereas in Ga$_3$N$_3$ and In$_3$N$_3$, the frequency order is governed by the nature of the bonds involved. This is because of the relatively larger strength of the nitrogen−nitrogen bond, which makes the N$_3$ unit as the most important structural feature of Ga$_3$N$_3$ and In$_3$N$_3$. Thus, the first eight frequencies (<300 cm^{-1}) in both Ga$_3$N$_3$ and In$_3$N$_3$ correspond to distortions of metal−metal and metal-nitrogen bonds, with the N$_3$ unit moving as a rigid structure. The b_2 and a_2 modes correspond to symmetric and asymmetric out-of-plane ring bending, which bends both metal−metal and metal−nitrogen bonds. The b_1 modes are due to a mixing of the asymmetric stretching of the M$_3$ unit and an asymmetric ring bending. In Ga$_3$N$_3$, the a_1 frequencies correspond to bending of metal−nitrogen bonds coupled with bending of Ga$_3$ and symmetric stretching of metal−nitrogen bonds coupled with symmetric stretching of Ga$_3$. However, in In$_3$N$_3$, these couplings are different: the lowest a_1 mode corresponds to the bending of metal−nitrogen bonds coupled with symmetric stretching of In$_3$, and the next a_1 mode corresponds to symmetric stretching of metal−nitrogen bonds coupled with bending of In$_3$. This difference is reflected on the dissimilar ordering in the frequency spectra. The last two frequency modes of this group are associated with the symmetric (a_1) and asymmetric (b_1) stretching of the metal−nitrogen bonds, in which M$_3$ and N$_3$ move as single and independent units.

The last four higher frequency modes (>500 cm^{-1}) of both Ga_3N_3 and In_3N_3 are almost exclusively due to movements of the N_3 subunit. The b_2 and a_1 modes, which are nearly equal, correspond to the bending of N_3, orthogonal and parallel to the ring plane, respectively. The small splitting of these modes ($\simeq 25$ cm^{-1}) confirms that the coupling with the vibrations of the rest of the cluster atoms is almost negligible. This is further supported by the fact that, when going from Ga_3N_3 to In_3N_3, the four largest frequencies are almost unchanged. In fact, as it happened also with the bond-lengths, the frequency spectrum of this N_3 unit is very close to that of the N_3^- ion, with frequencies 642, 1314, and 2078 cm^{-1} for the bending (degenerate), symmetric, and asymmetric stretching modes, respectively. The corresponding frequencies of Ga_3N_3 (In_3N_3) (i.e., 598 (591), 1209 (1236), and 1900 (1930) cm^{-1}) are smaller than those of the N_3^- ion, indicating a weaker N–N bonding because of the formation of metal–nitrogen bonds in these trimers. Furthermore, comparing the stretching modes of N_3 subunits (about 1700 cm^{-1} on average) with the vibrational frequency of N_2 (about 2300 cm^{-1}), we find support for our statement that nitrogen–nitrogen bonds in N_3 units are weaker than those in N_2 units.

Finally, we note here that all modes are infrared-active except for the a_2 bending mode. However, the b_1 mode ($\simeq 1900$ cm^{-1}) associated with asymmetric stretching of the N_3 unit, and the a_1 mode dominated by symmetric stretching of metal-nitrogen bonds, are the most intense modes in Ga_3N_3 and In_3N_3. Thus, they are expected to be the most prominent features of the vibrational spectra of these nitride trimers.

IV. Conclusions

A strong tendency to form nitrogen–nitrogen bonds is revealed in this study for Ga_3N_3 and In_3N_3, though it is not shown by Al_3N_3. The difference between Al_3N_3, Ga_3N_3, and In_3N_3 can be attributed to (i) the strength of the metal–nitrogen bond, which decreases in going from Al to Ga to In, (ii) the increasing importance of the metal–metal bond in going from Al to Ga to In, and (iii) the structural stability of the N_3^- subunit. The ring structures with relatively low stress and a large coordination number facilitate the formation of metal–nitrogen-bonded configurations, which are quite strong in the case of Al_3N_3. For Ga_3N_3 and In_3N_3, it is expected that clusters with greater coordination numbers will allow for non-nitrogen–nitrogen-bonded structures to be the lowest energy isomers, as they are in the crystalline state. Further study along this direction is in progress.

Regarding the stability of nitride trimers, the lowest energy fragmentation paths lead to nitrogen–nitrogen bonded molecules, which is in agreement with our previous studies on nitride dimers. For trimers, however, the odd number of nitrogen atoms favor the formation of M_2N clusters with strong metal–nitrogen bonds, whereas the third metal atom is likely to be weakly bonded to N_2. The ionization potentials of M_3N_3 clusters are much higher than their fragmentation energies, and thus, the products in photoionization experiments are likely to be ionized fragments of these clusters. Finally, most of the structural and vibrational properties of MN trimers can be explained either in terms of those of the MN monomers (in the case of Al_3N_3) or in terms of those of weakly bonded M_3^+ and N_3^- subunits (in the case of Ga_3N_3 and In_3N_3).

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