

# Theoretical Study of Structural and Vibrational Properties of (AlP)<sub>n</sub>, (AlAs)<sub>n</sub>, (GaP)<sub>n</sub>, (GaAs)<sub>n</sub>, (InP)<sub>n</sub>, and (InAs)<sub>n</sub> Clusters with $n = 1, 2, 3$

Aurora Costales,\* Anil K. Kandalam, Ruth Franco,<sup>†</sup> and Ravindra Pandey

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

Received: October 19, 2001; In Final Form: December 13, 2001

The structure, geometry, and vibrational frequencies of several isomers of small group III–V (MX)<sub>n</sub> clusters ( $n = 1, 2, 3$ ; M = Al, Ga, In; X = P, As) have been investigated using density functional theory. The results reveal the same behavior as in the nitride clusters for monomers and dimers. The Al trimers exhibit a  $D_{3h}$  structure like the nitride, but the gallium and indium trimers exhibit a three-dimensional structure of  $C_s$  symmetry. The existence of strong X–X bonds dominates both the structure and the vibrations of the Ga and In trimers.

## I. Introduction

In recent years, study of the structural and electronic properties of small clusters has become a subject of academic, scientific, and technological interest. The group III–V semiconducting materials, which have been extensively studied in their bulk state, have recently been the focus of several experimental and theoretical studies for novel applications of their clusters.

Among the group III–V clusters, gallium arsenide has received a significant amount of interest from both experimental<sup>1,2</sup> and theoretical<sup>3–15</sup> scientists. The ultraviolet photoelectron spectra<sup>2</sup> of negatively charged GaAs clusters consisting of 2–50 atoms suggested a large gap between highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) in the corresponding neutral GaAs clusters. Electronic structure and stability of small GaAs clusters were investigated in detail by several theoretical studies based on Hartree–Fock (HF),<sup>11,15</sup> density functional theory (DFT),<sup>7,8</sup> configuration interaction theory (CI),<sup>4,13</sup> and the ab initio molecular dynamics Car–Parrinello method.<sup>9</sup> The results of these theoretical studies suggest the existence of several isomeric configurations for the larger GaAs clusters. It was also revealed that Ga and As in larger GaAs clusters prefer an alternating Ga–As bond arrangement in the minimum energy configurations. This is in contrast to what was reported for the larger GaN clusters preferring the N–N bond arrangement over the alternate Ga–N bond arrangement.<sup>16</sup> Some of the experimental and theoretical studies on the group III–V clusters were also focused on AlP,<sup>8,12</sup> GaP,<sup>9,13,17</sup> InP,<sup>18–20</sup> and AlAs.<sup>9,14</sup> We are not aware of any theoretical or experimental studies on InAs clusters.

In this paper, we report the results of a systematic theoretical study on the group III–V clusters family. The main focus of this work is to analyze the structural and vibrational properties of the group III–phosphide and –arsenide clusters and to put forward the analogies and differences in the behavior of these clusters with respect to the corresponding group III–nitride clusters.<sup>16,21</sup> The calculated results on GaAs clusters will serve

as a benchmark for the theoretical method employed here. Furthermore, none of the previous theoretical studies has reported either the vibrational spectra of the group III–V dimer and trimer clusters or the structural properties of GaP, Ga<sub>3</sub>P<sub>3</sub>, In<sub>n</sub>P<sub>n</sub>, and In<sub>n</sub>As<sub>n</sub> with  $n = 1, 2, 3$  clusters. Therefore, the work presented here provides new results for structural properties of GaP, Ga<sub>3</sub>P<sub>3</sub>, and In<sub>n</sub>X<sub>n</sub> (X = P, As and  $n = 1–3$ ) clusters, along with their vibrational spectra. It is expected that a detailed analysis of the vibrational spectra of these clusters will lead us to understand the nature of chemical bonding and stability of the group III–V clusters. Hence, this work will allow us to assess the variations in the nature of structural and vibrational properties of M<sub>n</sub>X<sub>n</sub> ( $n = 1–3$ ) clusters for different combinations of metallic M (M = Al, Ga, and In) and nonmetallic X (X = N, P, and As) atoms on the same footing employing density functional theory.

This paper is organized as follows. In section II, details of the computational techniques employed in this study are given. Results are presented and discussed in section III, where we discuss the structural properties of the group III–phosphide and –arsenide clusters. Vibrational properties of the lowest energy phosphide and arsenide clusters are also discussed in this section. We give a summary and conclusions of the present study in section IV.

## II. Methodology

Electronic structure calculations were performed on various structural isomers of M<sub>n</sub>X<sub>n</sub> ( $n = 1–3$ ; M = Al, Ga, In; X = P, As) clusters in the framework of density functional theory (DFT) using the program Dmol.<sup>22</sup> Gradient-corrected (GGA) Becke exchange functional<sup>23</sup> and Perdew and Wang<sup>24</sup> correlation functional were employed in these calculations. A double numerical basis set, supplemented with *d* polarization functions (DNP), was employed for all the atoms of the clusters under study. The accuracy of these basis sets has been confirmed by our previous studies<sup>16,21</sup> on the group III–nitride clusters. The unrestricted spin levels together with Fermi occupations were used to determine the optimal orbital occupations in a given cluster that yield the lowest energy. In the SCF calculations, the density tolerance was set to  $10^{-6}$  e/bohr<sup>3</sup>. The geometric parameters were fully optimized with a convergence criterion

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

<sup>†</sup> Permanent address: Departamento de Química Física y Analítica, Facultad de Química, Universidad de Oviedo, 33006-Oviedo, Spain.

**TABLE 1: Spectral Symbol, Bond Length, Vibrational Frequency, and Dipole Moment of the MX Monomers (M = Al, Ga, In; X = N, P, As)<sup>a</sup>**

	<sup>2S+1</sup> Λ	R <sub>e</sub> (Å)	ω <sub>e</sub> (cm <sup>-1</sup> )	μ <sub>e</sub> (D)
AlN				
GGA/DNP <sup>21</sup>	<sup>3</sup> Π	1.82	710	3.06
AlP				
GGA/DNP (this work)	<sup>3</sup> Σ	2.46	348	1.21
HF/6-31G* <sup>8</sup>	<sup>3</sup> Σ	2.43	381	
AlAs				
GGA/DNP (this work)	<sup>3</sup> Σ	2.57	282	0.89
GaN				
GGA/DNP <sup>21</sup>	<sup>3</sup> Σ	2.06	447	2.04
GaP				
GGA/DNP (this work)	<sup>3</sup> Σ	2.51	276	1.66
GaAs				
exp 1	<sup>3</sup> Σ	2.53	215	
GGA/DNP (this work)	<sup>3</sup> Σ	2.61	206	1.37
HF/TZ+P <sup>6</sup>	<sup>3</sup> Σ	2.61		
InN				
GGA/DNP <sup>21</sup>	<sup>3</sup> Σ	2.28	378	2.43
InP				
GGA/DNP (this work)	<sup>3</sup> Σ	2.72	236	2.20
InAs				
GGA/DNP (this work)	<sup>3</sup> Σ	2.80	171	1.80

<sup>a</sup> The values for the nitride monomers are taken from our previous study.

for gradient component set to 10<sup>-3</sup> hartree/bohr and energy tolerance set to 10<sup>-5</sup> hartree.

For the lowest energy configurations, the analysis of the stability was carried out by computing the vibrational frequencies under the harmonic approximation, employing analytic gradients in a two-points finite difference formula with a step size of 0.1 bohr.

### III. Results and Discussion

We will begin our discussion with the results for MX (M = Al, Ga, In; X = P, As) monomers. The results for dimer and trimer clusters will be discussed in the subsequent subsections. We will conclude this section with the vibration analysis of the lowest energy structures. Particular attention is paid in the following discussion to compare the results for the phosphide and arsenide clusters with our previous work on the corresponding nitride clusters.<sup>16,21</sup>

**A. Structural Properties. 1. MX Monomers.** The calculated spectroscopic constants, i.e., bond length (*R<sub>e</sub>*), vibrational frequency (*ω*), and binding energy (*D<sub>e</sub>*), of the phosphide and arsenide monomers are collected in Table 1. The results for group III nitride monomers taken from our previous study<sup>21</sup> are also included in the Table 1 for comparison.

For all the phosphide and arsenide monomers, <sup>3</sup>Σ is predicted to be the ground state. For the GaAs monomer, our calculated *R<sub>e</sub>*, *ω*, and *D<sub>e</sub>* are in very good agreement with the corresponding experimental results, providing confidence in the computational approach employed in this work. We are not aware of any experimental study determining spectroscopic constants for AlP, AlAs, GaP, InP, and InAs monomers.

In the group III–V monomers, the calculated *R<sub>e</sub>* is found to be mainly dependent on the atomic size: it increases when descending from Al to Ga to In or when descending from N to P to As. The *D<sub>e</sub>* and *ω* values reflect the decrease in the strength of the chemical bond when going down in both the III and V groups in this series. Although the decrease in the frequencies may be due to an increase in the reduced mass, we have verified that the force constants follow the same decreasing trend. In phosphide and arsenide monomers, the dipole moment increases

**TABLE 2: Spin Multiplicity, Bond Lengths (Å), and Bond Angle (degrees) of the Lowest Energy Rhombus Isomer of M<sub>2</sub>X<sub>2</sub> (M = Al, Ga, In; X = N, P, As) Dimers<sup>a</sup>**

	<sup>2S+1</sup>	R <sub>M-X</sub>	R <sub>X-X</sub>	R <sub>M-M</sub>	A <sub>X-M-X</sub>
Al <sub>2</sub> N <sub>2</sub> , <i>D</i> <sub>2h</sub>					
GGA/DNP <sup>21</sup>	1	2.10	1.29	4.00	36
Al <sub>2</sub> P <sub>2</sub> , <i>D</i> <sub>2h</sub>					
GGA/DNP (this work)	1	2.53	2.08	4.62	48
HF/6-31G* <sup>8</sup>		2.53	2.04	4.64	48
Al <sub>2</sub> As <sub>2</sub> , <i>D</i> <sub>2h</sub>					
GGA/DNP (this work)	1	2.67	2.34	4.80	52
Ga <sub>2</sub> N <sub>2</sub> , <i>D</i> <sub>2h</sub>					
GGA/DNP <sup>21</sup>	1	2.20	1.27	4.21	34
Ga <sub>2</sub> P <sub>2</sub> , <i>D</i> <sub>2h</sub>					
GGA/DNP (this work)	1	2.59	2.08	4.74	47
MRSDCI <sup>13</sup>	1	2.57	2.10	4.69	48
Ga <sub>2</sub> As <sub>2</sub> , <i>D</i> <sub>2h</sub>					
GGA/DNP (this work)	1	2.71	2.34	4.88	51
HF/TZ+P <sup>6</sup>	1	2.71	2.29		
MRSDCI <sup>3</sup>	1	2.68	2.30		51
In <sub>2</sub> N <sub>2</sub> , <i>D</i> <sub>2h</sub>					
GGA/DNP <sup>21</sup>	1	2.44	1.25	4.71	30
In <sub>2</sub> P <sub>2</sub> , <i>D</i> <sub>2h</sub>					
GGA/DNP (this work)	1	2.80	2.08	5.20	44
In <sub>2</sub> As <sub>2</sub> , <i>D</i> <sub>2h</sub>					
GGA/DNP (this work)	1	2.90	2.34	5.31	48

<sup>a</sup> The values for the nitride dimers are taken from our previous study.<sup>21</sup>

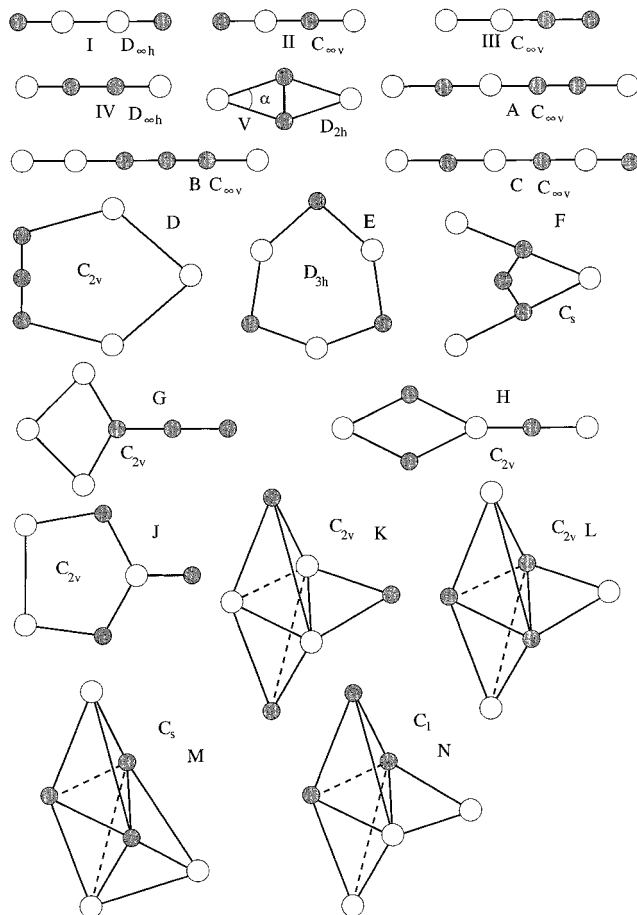
in going from Al to Ga to In, whereas it decreases in going from P to As (see Table 1). These variations can be explained by the difference in the electronegativity between the metallic atoms and nonmetallic atoms. This tendency can be seen as a balance between the charge transfer and the distance between cation and anion in the monomers. The latter effect dominates the increase of *μ<sub>e</sub>* along group III, with increasing distances, whereas the former one dictates the larger dipole moments of phosphides with respect to arsenides, owing to the high electronegativity of P. Since the electronegativity of N is even higher, nitrides have the larger dipole moment of each MX series. However, AlN shows the largest dipole moment of all monomers, in contrast with the tendency of MP and MAs. This is due to the extremely large charge transfer and electronic density deformation exhibited by AlN, as found in our previous study.<sup>25</sup>

**2. M<sub>2</sub>X<sub>2</sub> Dimers.** For the phosphide and arsenide dimers, the choice of the structural configurations considered is based on the results obtained in our previous work on the nitride dimers.<sup>21</sup> The structural configurations considered here for calculations are four different linear configurations, representing various M–M, M–X, and X–X bonds, and a rhombic structure (see Figure 1). As in the case of the nitride dimers, the rhombic configuration is the most stable structure for the phosphide and arsenide dimers whose structural parameters are given in Table 2. The relative energies of the next two lowest energy isomers with respect to the rhombic configuration are collected in the Table 3. Among the linear configurations, the X–M–M–X isomer is the least favorable. M–M–X–X is higher in energy than M–X–X–M for all the group III–V dimers. Hence, the M–M bond was found to be weaker than both X–X and M–X bonds. For Al<sub>2</sub>P<sub>2</sub>, Al<sub>2</sub>As<sub>2</sub>, and Ga<sub>2</sub>As<sub>2</sub>, the M–X–M–X configuration is the most stable linear isomer, whereas for the remaining dimers, M–X–X–M was found to be more favorable. Hence, the energy ordering of the X–X and M–X bonds is less clear when compared to what was predicted in nitride dimers.<sup>21</sup> (The binding energies and the bond distances of the linear isomers can be obtained from the authors.) The rhombus isomer is a singlet state for all the dimers under study. In this

**TABLE 3: Relative Energies of the Next Two Stable Isomers, with Respect to the Lowest Energy Isomer ( $D_{2h}$ ) in Dimer Clusters<sup>a</sup>**

	$\Delta E$ (eV)		$\Delta E$ (eV)
$\text{Al}_2\text{P}_2$		$\text{Al}_2\text{As}_2$	
$C_{\infty v}$ (II)	1.92	$C_{\infty h}$ (II)	1.58
$D_{\infty h}$ (IV)	2.12	$D_{\infty h}$ (IV)	2.17
$\text{Ga}_2\text{P}_2$		$\text{Ga}_2\text{As}_2$	
$D_{\infty h}$ (IV)	1.94	$C_{\infty v}$ (II)	1.83
$C_{\infty v}$ (III)	2.02	$D_{\infty h}$ (IV)	2.04
$\text{In}_2\text{P}_2$		$\text{In}_2\text{As}_2$	
$D_{\infty h}$ (IV)	1.44	$D_{\infty h}$ (IV)	1.64
$C_{\infty v}$ (III)	1.86	$C_{\infty v}$ (II)	2.02

<sup>a</sup> The Roman numerals in parentheses refer to the labels of the corresponding isomers in Figure 1.



**Figure 1.** Schematic representation of the isomers of dimers and trimers considered in this work. The filled circles represent the P and As atoms, and the empty circles represent the Al, Ga, and In atoms.

structure, as it happened in the nitride dimers, the nonmetallic atoms are occupying the shorter axis of the rhombus (see Figure 1). The rhombic structure can be understood as the addition of two metallic atoms in opposite sides of the diatomic  $\text{X}_2$  molecule and can be best classified as metallic edge-capped  $\text{X}_2$ .

Among the family of group III–V dimers,  $\text{Ga}_2\text{As}_2$  has been the focus of several theoretical studies. The calculated GGA-DFT bond lengths and bond angles are in very good agreement with the values obtained using the MRSDCI method.<sup>3</sup> Likewise, our GGA-DFT values are in good agreement with the MRSDCI values for  $\text{Al}_2\text{P}_2$ <sup>10</sup> and  $\text{Ga}_2\text{P}_2$  dimers.<sup>13</sup>

It is important to note here that the X–X distance remained constant in phosphide ( $R_{\text{P–P}} = 2.08 \text{ \AA}$ ) and arsenide ( $R_{\text{As–As}} = 2.34 \text{ \AA}$ ) dimers in going from Al to Ga to In in the series. This fact indicates that the X–X bond is a covalent bond and its

strength is maintained in the series considered here. The P–P and As–As bond lengths in dimers are larger than those in the corresponding diatomic molecules, indicating a weakening of the X–X bond strengths in dimers relative to diatomics.

**3.  $M_3X_3$  Trimers.** For trimers, several structural configurations were considered for electronic structure calculations. As in the case of the dimers, our choice was mainly based on the previous theoretical studies of  $\text{Ga}_3\text{N}_3$ <sup>21</sup> and  $\text{Ga}_3\text{As}_3$ .<sup>5–7</sup> Sketches of the isomeric configurations considered in this work are collected in Figure 1, including linear, planar, and three-dimensional structures. The structural parameters of the most stable isomer for each of the trimer clusters are given in Table 4, and the relative energies of the next two lowest energy configurations with respect to the lowest energy isomer are collected in Table 5.

Among the possible structural isomers presented in Figure 1, the lowest energy structure in  $\text{Al}_3\text{P}_3$  and  $\text{Al}_3\text{As}_3$  is the hexagonal planar  $D_{3h}$  structure (isomer E), as was the case in  $\text{Al}_3\text{N}_3$ . It presents alternate Al and P (As) atoms, with the three P (As) atoms edge-capping the triangle formed by the Al atoms. In both  $\text{Al}_3\text{P}_3$  and  $\text{Al}_3\text{As}_3$ , the Al–X bond is dominating the stability of the structure with a relatively larger strength than the corresponding monomers. For example,  $R_{\text{Al–P}}$  ( $R_{\text{Al–As}}$ ) is found to be 2.24 (2.35)  $\text{Å}$ , in  $\text{Al}_3\text{P}_3$  ( $\text{Al}_3\text{As}_3$ ), in comparison to the value of 2.46 (2.57)  $\text{Å}$  in the AlP (AlAs) monomer.

Initially, total energy calculations predicted a three-dimensional structure with  $C_{2v}$  symmetry (i.e., isomer L; see Figure 1) to be the lowest energy isomer for  $\text{Ga}_3\text{X}_3$  and  $\text{In}_3\text{X}_3$  trimers. The isomer L can be described as an edge-capped trigonal bipyramid where P (As) atoms form a triangle with a Ga (In) atom in the symmetry plane, and the other two Ga (In) atoms are located above and below the plane, respectively. However, the frequency analysis of this isomer L revealed the presence of an imaginary frequency for phosphide and arsenide trimers. To find the minimum on the energy surface, the nonequivalent metallic atom in the isomer L was displaced into a face-capped position, leading to a lower energy structure (i.e., isomer M; see Figure 1) with  $C_s$  symmetry and no imaginary frequencies in the vibrational spectrum. The isomer M is then predicted to be the most stable isomer for the phosphide and arsenide trimers, and their geometrical parameters are collected in Table 4. In this isomer, the nonmetallic triangle plays a very important role. Furthermore, the M–M bond distance decreases as we move from  $C_{2v}$  to  $C_s$  (from 3.71 to 2.81  $\text{Å}$  in  $\text{Ga}_3\text{P}_3$ , from 3.84 to 2.77  $\text{Å}$  in  $\text{Ga}_3\text{As}_3$ , from 4.01 to 3.22  $\text{Å}$  in  $\text{In}_3\text{P}_3$ , and from 4.11 to 3.20  $\text{Å}$  in  $\text{In}_3\text{As}_3$ ), thereby becoming nearly equal to the corresponding  $M_2$  diatomic molecule distances ( $Ga_2 = 2.79 \text{ \AA}$ ,  $In_2 = 3.17 \text{ \AA}$ ). Hence, this M–M bond contributes to stabilizing the isomer M ( $C_s$  symmetry) with respect to the isomer L ( $C_{2v}$  symmetry). It also indicates the increasing importance of the metallic–metallic bond in going down the group of the periodic table that was already demonstrated in our previous works.<sup>16,21</sup> For the gallium and indium  $C_s$  structure (isomer M), the M–X distance in a given cluster shows a wide range of values (for example, 2.47–2.80  $\text{Å}$  in  $\text{Ga}_3\text{P}_3$ , 2.57–2.91  $\text{Å}$  in  $\text{Ga}_3\text{As}_3$ ). However, the short X–X distance is maintained constant while going from Ga to In. This fact indicates that the X–X bond is a covalent bond and its strength is maintained when the metallic atom is varied. An analogous behavior was observed in  $M_2X_2$  dimer clusters, as reported above. The M–X bond, with varying distances and very low angles, does not behave as a covalent bond, but its ionic character cannot be established without an analysis of the electronic structure, which is beyond the scope of this work. Unlike phosphide and arsenide trimers, our

**TABLE 4: Spin Multiplicity, Bond Lengths (Å), and Bond Angles (deg) of the Lowest Energy Isomer of M<sub>3</sub>X<sub>3</sub> (M = Al, Ga, In; X = N, P, As) Trimers<sup>a</sup>**

	2S + 1	R <sub>M-X</sub>	R <sub>X-X</sub>	R <sub>M-M</sub>	A <sub>M-X-M</sub>	A <sub>X-M-X</sub>	A <sub>X-X-X</sub>
Al <sub>3</sub> N <sub>3</sub> , D <sub>3h</sub> GGA/DNP <sup>16</sup>	1	1.79		2.54	90	150	
Al <sub>3</sub> P <sub>3</sub> , D <sub>3h</sub> GGA/DNP (this work)	1	2.24		2.75	76	164	
HF/6-31G* <sup>8</sup>		2.21		2.85	80	160	
Al <sub>3</sub> As <sub>3</sub> , D <sub>3h</sub> GGA/DNP (this work)	1	2.35		2.81	74	167	
Ga <sub>3</sub> N <sub>3</sub> , C <sub>2v</sub> GGA/DNP (this work)	3	2.20	1.21	2.67	72 (M-M-M)	174 (X-X-X)	
Ga <sub>3</sub> P <sub>3</sub> , C <sub>s</sub> GGA/DNP (this work)	1	2.47–2.80	2.27, 2.23	2.81	121, 120, 62	49, 50, 51	61, 59
Ga <sub>3</sub> As <sub>3</sub> , C <sub>s</sub> GGA/DNP (this work)	1	2.57–2.91	2.53, 2.51	2.77	116, 121, 58	52, 55, 54	60, 60
HF/TZ+P <sup>6</sup>	1	2.53–3.11	2.52, 2.47	3.04			
In <sub>3</sub> N <sub>3</sub> , C <sub>2v</sub> GGA/DNP <sup>16</sup>	3	2.41	1.2	3.05	72 (M-M-M)	177 (X-X-X)	
In <sub>3</sub> P <sub>3</sub> , C <sub>s</sub> GGA/DNP (this work)	1	2.69–2.99	2.29, 2.23	3.22	125, 118, 66	45, 46, 47	62, 59
In <sub>3</sub> As <sub>3</sub> , C <sub>s</sub> GGA/DNP (this work)	1	2.78–3.09	2.55, 2.51	3.20	119, 120, 63	49, 50, 51	61, 59

<sup>a</sup> The values for the nitride trimers are taken from our previous study.

**TABLE 5: Relative Energies of the Next Two Stable Isomers, with Respect to the Lowest Energy Isomer in Trimer Clusters<sup>a</sup>**

	ΔE (eV)		ΔE (eV)
Al <sub>3</sub> P <sub>3</sub>		Al <sub>3</sub> As <sub>3</sub>	
C <sub>s</sub> (M)	0.16	C <sub>s</sub> (M)	0.25
C <sub>2v</sub> (K)	0.43	C <sub>2v</sub> (K)	0.26
Ga <sub>3</sub> P <sub>3</sub>		Ga <sub>3</sub> As <sub>3</sub>	
C <sub>2v</sub> (L)	0.23	C <sub>2v</sub> (L)	0.43
C <sub>2v</sub> (K)	0.54	C <sub>2v</sub> (K)	0.47
In <sub>3</sub> P <sub>3</sub>		In <sub>3</sub> As <sub>3</sub>	
C <sub>2v</sub> (L)	0.17	C <sub>2v</sub> (L)	0.17
C <sub>2v</sub> (K)	0.82	C <sub>2v</sub> (K)	0.60

<sup>a</sup> The letters in parentheses refer to the labels of the corresponding isomers in Figure 1.

previous study predicted a planar configuration (with a N<sub>3</sub> subunit and C<sub>2v</sub> symmetry) to be the lowest energy isomer for both gallium and indium nitride trimers. This difference between nitride and phosphide and arsenide trimers can be explained by the fact that, unlike nitrogen atoms, the arsenic and phosphorus atoms do not tend to form azide-like structures. This is a manifestation of the well-known rule of chemical bonding theory, by which the atoms lose the ability to form multiple bonds as we go down in a column of the periodic table. Furthermore, heavier atoms are likely to gain the ability to form single bonds with coordination index larger than 4, due to the presence of available d-type orbitals. Hence, in the isomer M of gallium and indium phosphide and arsenide trimers, we can see the existence of two nonmetallic atoms with 5-fold coordination in the Figure 1.

Comparing our results for the M<sub>3</sub>X<sub>3</sub> trimers to those of previously reported calculations, we find that they agree well with few exceptions. Ga<sub>3</sub>As<sub>3</sub> is the most studied system among the group III–V trimers. A dynamical-simulated-annealing (DSA) calculation using the Car–Parrinello method<sup>9</sup> predicted a capped trigonal bipyramidal structure to be the lowest energy isomer, whereas an edge-capped bipyramid with C<sub>1</sub> symmetry (i.e., isomer N in Figure 1) was found to be the lowest energy isomer at the Hartree–Fock level of theory.<sup>26</sup> On the other hand, calculations employing fourth-order Moller–Plesset perturbation theory (MP4) at the HF-optimized configurations<sup>6</sup> showed the preference of the isomer M (with C<sub>s</sub> symmetry) over the isomer N (with C<sub>1</sub> symmetry). In the present GGA-DFT calculations,

the isomer N is found to be 0.47 eV higher in energy than the lowest energy isomer M for Ga<sub>3</sub>As<sub>3</sub>.

For Al<sub>3</sub>P<sub>3</sub>, MP4 calculations for the HF-optimized configuration<sup>8</sup> find the hexagonal planar D<sub>3h</sub> structure to be the lowest energy isomer (E<sub>D<sub>3h</sub></sub> – E<sub>C<sub>s</sub></sub> ≈ –0.18 eV), as predicted by our GGA-DFT calculations. However, a larger basis set coupled with second-order Moller–Plesset perturbation theory (MP2) calculations<sup>8</sup> predicted a capped trigonal bipyramidal C<sub>s</sub> structure to be the lowest energy isomer (E<sub>D<sub>3h</sub></sub> – E<sub>C<sub>s</sub></sub> ≈ 0.34 eV) for Al<sub>3</sub>P<sub>3</sub>. Since the energy difference between D<sub>3h</sub> and C<sub>s</sub> structures in our study is found to be small (E<sub>D<sub>3h</sub></sub> – E<sub>C<sub>s</sub></sub> ≈ –0.16 eV), it therefore appears that an unambiguous assignment cannot be made to the most stable isomer of Al<sub>3</sub>P<sub>3</sub>. Our GGA-DFT results for Ga<sub>3</sub>P<sub>3</sub> are in agreement with the results of total energy calculations using simulated annealing<sup>9</sup> in predicting the lowest energy isomer.

**B. Vibrations.** Analysis of the normal vibrational modes of monomers, dimers, and trimers is carried out in this subsection. The study of the normal modes was used to assess the stability of the lowest lying isomers for the phosphide and arsenide trimers.

In Table 1 the vibrational frequencies of the monomers are collected. As we expected, a decrease in the relative bond strength can be seen as we go down in either the group III (from Al to Ga to In) or the group V (i.e. N to P to As) atoms of the monomers considered here.

To analyze the calculated frequencies of dimers, the atomic coordinates of M<sub>2</sub>X<sub>2</sub> were chosen in such way that the cluster lies on the yz plane with the X atoms located along the y axis and the M atoms along the z axis. In the phosphide and arsenide dimers, the analysis of normal modes reveals that the lowest frequency b<sub>3u</sub> mode corresponds to the out of plane bending, and the highest frequency a<sub>g</sub> mode involves mainly the vibration of the X–X bond, with frequency values somewhat smaller than the corresponding values in X<sub>2</sub> molecules (Table 6).<sup>27</sup> This is due to the fact that the X–X bond vibration is slightly coupled with the vibration of the M–X bonds. The frequency of the b<sub>1u</sub> mode in dimers is nearly equal to the frequency in the corresponding monomers. Its vibrational movement is mainly due to the symmetric stretching of the M–X bond.

The more intense IR active mode of a given cluster is likely to be associated with the mode that generates a larger charge

**TABLE 6: Symmetry Label and Frequency ( $\omega$ ) in  $\text{cm}^{-1}$  of the Normal Modes of Vibration of the Lowest Energy  $\text{M}_2\text{X}_2$   $D_{2h}$  Isomers**

mode	$\text{Al}_2\text{P}_2$	$\text{Ga}_2\text{P}_2$	$\text{In}_2\text{P}_2$	$\text{Al}_2\text{As}_2$	$\text{Ga}_2\text{As}_2$	$\text{In}_2\text{As}_2$
$b_{3u}$	92	67	53	67	47	37
$b_{2u}$	164	122 <sup>a</sup>	100 <sup>a</sup>	133 <sup>a</sup>	93 <sup>a</sup>	75 <sup>a</sup>
$a_g$	277	166	122	257	158	116
$b_{3g}$	289	253	239	191	159	146
$b_{1u}$	341 <sup>a</sup>	272 <sup>a</sup>	247 <sup>a</sup>	272 <sup>a</sup>	200 <sup>a</sup>	172 <sup>a</sup>
$a_g$	572	564	550	330	321	312

<sup>a</sup> Infrared-active modes of high intensity.

**TABLE 7: Symmetry Label and Frequency ( $\omega$ ) in  $\text{cm}^{-1}$  of the Normal Modes of Vibration of the Lowest Energy  $\text{M}_3\text{X}_3$  Isomers ( $D_{3h}$  for  $\text{Al}_3\text{X}_3$  and  $C_s$  for the rest)**

mode	$\text{Al}_3\text{P}_3$	$\text{Al}_3\text{As}_3$	mode	$\text{Ga}_3\text{P}_3$	$\text{In}_3\text{P}_3$	$\text{Ga}_3\text{As}_3$	$\text{In}_3\text{As}_3$
$e''$	75	25	$a'$	51	40	49	36
$a_2''$	143	112	$a''$	64	59	52	43
$e'$	200	157	$a'$	109	84	92	75
$e'$	313	204	$a''$	111	106	79	71
$a_1'$	331	225	$a'$	154	117	132	100
$a_1'$	374	301	$a''$	167	136	154	117
$a_2'$	498	415	$a''$	230	216	141	129
$e'$	596 <sup>a</sup>	502 <sup>a</sup>	$a'$	242 <sup>a</sup>	222 <sup>a</sup>	170 <sup>a</sup>	144 <sup>a</sup>
			$a'$	272 <sup>a</sup>	244 <sup>a</sup>	201 <sup>a</sup>	173 <sup>a</sup>
			$a''$	385	378	215	212
			$a'$	391	370	231	218
			$a'$	498	486	294	286

<sup>a</sup> Infrared-active modes of high intensity.

separation within the cluster. In dimers, it corresponds to the  $b_{1u}$  mode due to the vibration of the most polar bond, the M–X bond in  $\text{M}_2\text{X}_2$ . The frequency values for the  $b_{1u}$  mode are 341, 272, 247, 272, 200, and 172  $\text{cm}^{-1}$  for  $\text{Al}_2\text{P}_2$ ,  $\text{Ga}_2\text{P}_2$ ,  $\text{In}_2\text{P}_2$ ,  $\text{Al}_2\text{As}_2$ ,  $\text{Ga}_2\text{As}_2$ , and  $\text{In}_2\text{As}_2$ , respectively. The trend of these values is in accordance with the electronegativity difference between the metallic (M) and the nonmetallic (X) atoms in dimers.

The lowest energy isomer for the aluminum trimers is predicted to be a planar  $D_{3h}$  configuration. Here, the lower frequency modes (i.e.  $e''$  and  $a_2''$ ) correspond to out-of-plane bending, whereas the  $e'$  modes are associated with the in-plane bending. The lower frequency  $a_1'$  mode is associated with the symmetric stretching of the M–X bond, and the higher frequency  $a_1'$  mode is a bending mode that opens the Al–X–Al angle in trimers. The  $a_2''$  and  $e'$  modes correspond to an asymmetric stretching of the Al–X bonds that produces an aluminum ring torsion inside the nonmetallic triangle. The highest frequency  $e'$  mode is predicted to be the most intense IR active mode, because it produces a larger splitting of charge in Al trimers (Table 7).

The lowest energy configurations of  $\text{Ga}_3\text{P}_3$ ,  $\text{Ga}_3\text{As}_3$ ,  $\text{In}_3\text{P}_3$ , and  $\text{In}_3\text{As}_3$  trimers have  $C_s$  symmetry. Due to the low symmetry of the this isomer, all modes are active in IR and Raman spectroscopies. The lowest frequency modes are the bending and torsion of the bipyramid induced by the movement of the face-capped metallic atoms. The next modes involve the stretching of the M–M and the M–X bonds. The highest frequency modes involve the vibrational movement of the bonds in the nonmetallic triangle. This ordering is in perfect agreement with the relative strength of M–M, M–X, and X–X bonds previously discussed. We note here that the frequency values for  $\text{Ga}_3\text{P}_3$  and  $\text{In}_3\text{P}_3$  are close to each other. Similarly, the values for  $\text{Ga}_3\text{As}_3$  and  $\text{In}_3\text{As}_3$  are close to each other. This similarity in frequency values therefore reflects that the nonmetallic triangle (either P or As) dominates the structural behavior in Ga and In trimers, in the same way that the linear  $\text{N}_3$  unit dominated the GaN and InN trimers.

#### IV. Summary

In this work, we have studied the structural and vibrational properties of the group III phosphide and arsenide clusters, paying attention to putting forward the analogies and the differences of their properties with respect to the nitride clusters. For monomers and dimers, the nitrides, phosphides, and arsenides have the same lowest energy isomer, and the trend in their structural and vibrational properties can be explained in terms of chemical intuition. Al trimers show a behavior analogous to that in  $\text{Al}_3\text{N}_3$ . With Ga and In trimers, however, phosphide and arsenide trimers show a preference for a single-bonded triangular  $\text{X}_3$  unit, instead of the multiple-bonded linear (azide-like)  $\text{N}_3$  units of the Ga and In nitrides. The existence of low-lying d orbitals favors the single-bonded structures and the increase in coordination index, which leads to three-dimensional structures.

**Acknowledgment.** Financial support from Accelrys Inc., San Diego, CA, is acknowledged here. A.C. and R.F. wish to thank the Spanish Secretaría de Estado de Universidades, Investigación y Desarrollo, for the award of their postdoctoral fellowships, and the Spanish DGICYT, for the grant BQU2000-0446.

#### References and Notes

- (1) Lemire, G. W.; Bishea, G. A.; Heidecke, S. A.; Morse, M. D. *J. Chem. Phys.* **1990**, *92*, 121.
- (2) Jin, C.; Taylor, K. T.; Conceicao, J.; Smalley, R. E. *Chem. Phys. Lett.* **1990**, *175*, 17.
- (3) Balasubramanian, K. *Chem. Phys. Lett.* **1990**, *171*, 58.
- (4) Meier, U.; Peyerimhoff, S. D.; Grein, F. *Chem. Phys.* **1991**, *150*, 331.
- (5) Lou, L.; Wang, L.; Chibante, L.; Laaksonen, R. T.; Nordlander, P.; Smalley, R. *J. Chem. Phys.* **1991**, *94*, 8015.
- (6) Al-Laham, M. A.; Raghavachari, K. *Chem. Phys. Lett.* **1991**, *187*, 13.
- (7) Lou, L.; Nordlander, P.; Smalley, R. *J. Chem. Phys.* **1992**, *97*, 1858.
- (8) Al-Laham, M. A.; Trucks, G. W.; Raghavachari, K. *J. Chem. Phys.* **1992**, *96*, 1137.
- (9) Andreoni, W. *Phys. Rev. B.* **1992**, *45*, 4203.
- (10) Liao, D. W.; Balasubramanian, K. *J. Chem. Phys.* **1992**, *96*, 8938.
- (11) Piquini, P.; Canuto, S.; Fazzio, A. *Int. J. Quantum Chem.* **1994**, *28*, 571.
- (12) Tomasulo, A.; Ramakrishna, M. V. *J. Chem. Phys.* **1996**, *105*, 10449.
- (13) Feng, P. Y.; Balasubramanian, K. *Chem. Phys. Lett.* **1996**, *258*, 387.
- (14) Quek, H.; Feng, Y.; Ong, C. Z. *Phys. D.* **1997**, *42*, 309.
- (15) Korambath, P.; Karna, S. P. *J. Phys. Chem.* **2000**, *104*, 4801.
- (16) Kandalam, A. K.; Blanco, M. A.; Pandey, R. *J. Phys. Chem. B* **2001**, *105*, 6080.
- (17) Taylor, T. R.; Asmis, K. R.; Xu, C.; Neumark, D. M. *Chem. Phys. Lett.* **1998**, *297*, 133.
- (18) Kolenbrander, K.; Mandich, M. L. *J. Chem. Phys.* **1990**, *92*, 4659.
- (19) Xu, C.; de Beer, E.; Arnold, D. W.; Arnold, C. C.; Neumark, D. M. *J. Chem. Phys.* **1994**, *101*, 5406.
- (20) Asmis, K. R.; Taylor, T. R.; Neumark, D. M. *Chem. Phys. Lett.* **1999**, *308*, 347.
- (21) Kandalam, A. K.; Pandey, R.; Blanco, M. A.; Costales, A.; Recio, J. M.; Newsam, J. M. *J. Phys. Chem. B* **2000**, *104*, 4361.
- (22) Delly, B. *J. Chem. Phys.* **1990**, *92*, 508.
- (23) Becke, A. D. *Phys. Rev. A.* **1988**, *38*, 3098.
- (24) Wang, Y.; Perdew, J. P. *Phys. Rev. B.* **1991**, *43*, 8911.
- (25) Costales, A.; Kandalam, A. K.; Martín Pendás, A.; Blanco, M. A.; Recio, J. M.; Pandey, R. *J. Phys. Chem. B* **2000**, *104*, 4368.
- (26) Graves, R. M.; Scuseria, G. E. *J. Chem. Phys.* **1991**, *95*, 6602.
- (27) The computed frequency values are 330, 155, 108, 2283, 780, and 429  $\text{cm}^{-1}$  for  $\text{Al}_2$ ,  $\text{Ga}_2$ ,  $\text{In}_2$ ,  $\text{N}_2$ ,  $\text{P}_2$ , and  $\text{As}_2$ , respectively. These values are in very good agreement with the available experimental data 350, 2358, 781, and 429  $\text{cm}^{-1}$  for  $\text{Al}_2$ ,  $\text{N}_2$ ,  $\text{P}_2$ , and  $\text{As}_2$ , respectively (from Huber, K. P.; Herzberg, G. *Constants of Diatomic Molecules*; Van Nostrand: New York, 1970).