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A theoretical study of structural, vibrational, and electronic properties of neutral, positive, and negative indium arsenide clusters, In_nAs_n ($n = 1, 2, 3$)

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Abstract

First principles study of the small InAs_n clusters is performed to investigate the changes in structural, vibrational and electronic properties, when an electron is either added or removed from the corresponding neutral clusters. The calculated results reveal that the addition of an electron to the neutral clusters induce significant structural changes relative to the case when an electron is removed. The changes in vibrational properties can be explained in terms of the variation of the interatomic distances upon removing or adding the electron. The calculated values of electron affinity and ionization potential are comparable to those calculated in GaAs and InP clusters. © 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

The III–V binary compounds are of a great interest to the technological industry. These compounds have been extensively studied in their solid state. However, the fabrication techniques for the electronic devices generally use the thin layers of III–V compounds formed by sputtering of a III–group solid substrate in the group-V atmosphere. This deposition process is known to introduce

defects on the surface which can be viewed as small III–V clusters adsorbed on the surface. As a consequence, a detailed knowledge about the structural and the electronic properties of small III–V clusters with stoichiometric and non-stoichiometric configurations is required to improve the performance of devices based on III–V compounds.

The majority of the experimental and theoretical studies on small III–V clusters have, so far, focussed on GaAs. The other members of the III–V group have received a rather less attention in the scientific community. Our group has been active in calculations of structural and electronic properties of small III–V clusters with an emphasis on nitrides [1–4]. We also carried out a study on the structural and vibrational properties of the group III-phosphide and -arsenide clusters [5]. The main

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aim of that analysis was to put forward the analogies and difference in the behavior of these clusters with respect to the corresponding group III-nitride clusters. The lack of information about $(\text{InAs})_n$ clusters as well experimental as theoretical along with the recent studies [6–9] carried out about ionized phosphide clusters motivated this work. We now extend our investigation and report the results of the theoretical study on neutral and ionized In_nAs_n , $n = 1, 2, 3$. Specifically, we will focus on the variations in the physical and chemical properties, when an electron is either added or removed from the neutral clusters. Our previous calculations were performed using DMol program [10]. This code employs double zeta numerical basis sets with d polarization functions (DNP). However, these basis sets are not reliable enough to describe the negatively-charged clusters. This deficiency, moved us to use the Gaussian 98 code to perform our simulation, using the same theoretical framework and analytical basis sets having greater flexibility to describe the anionic clusters.

The paper is organized as follows. In Section 2 we briefly review the methodology used for the electronic structure calculations, and the electron density analysis. In Section 3 we present and discuss the results obtained. Finally, we summarize our conclusions in Section 4.

2. Methodology

The electronic structure calculations were performed on several neutral, negatively-, and positively-charged structural isomers of $(\text{InAs})_n$ ($n = 1–3$) clusters using the GAUSSIAN 98 code [11]. All calculations were carried out by solving the Kohn–Sham equations in the framework of the density functional theory (DFT). The generalized gradient approximation (GGA) functionals due to Becke [12] and of Perdew and Wang [13] to represent the exchange and correlation contributions, respectively (BPW91) were employed. The double zeta valence plus polarization (DZVP) basis sets optimized for the density functional theory orbitals were used for the indium and arsenic atoms [14].

All structural configurations considered in this work were fully optimized employing the gradient and updated Hessian. The convergence criteria of 10^{-6} hartree/Å for the gradient, and 10^{-8} hartree for the energy were used for the optimization. For the lowest energy isomer, the vibrational frequencies under harmonic approximation were also computed. The atomic and bonding properties were studied under the Atoms in Molecules Theory (AIM) [15]. In order to perform the AIM analysis we used the AIMPAC95 package [16] which employs the Promega algorithm for integration of the atomic properties. The precision of the integrations is always a matter of concern in topological analysis. In the cases studied here, the error in the total charge is less than 10^{-3} e.

3. Results and discussion

Fig. 1 presents a schematic representation of several isomeric configurations considered in this study for the geometry optimization. The choice of these isomers is based on our previous analysis on III–V clusters [1,3,5]. Since the lowest energy isomer for the cationic and anionic clusters may be different from that of the neutral cluster, we have performed the geometry optimization in both

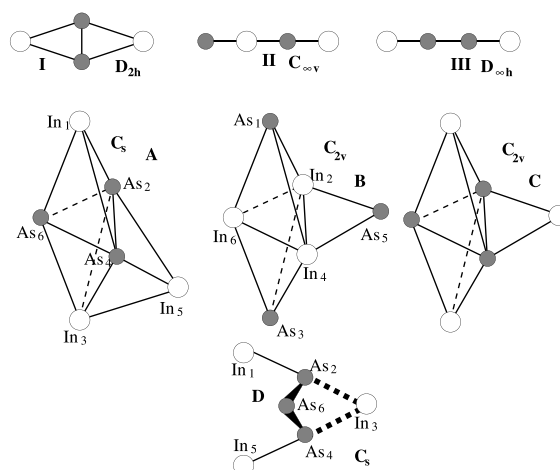


Fig. 1. Schematic representation of the isomeric configurations of In_2As_2 and In_3As_3 . The filled circles represent As and the empty circles represent In atoms.

anionic and cationic clusters as well. We have computed all geometrical and topological parameters for all isomers as well in the neutral clusters as in the ionized ones. Most of these values have been omitted for the sake of brevity but they are available from the authors upon request (mco-stale@mtu.edu).

3.1. Monomers: $InAs$, $InAs^+$, and $InAs^-$

The electronic state is $^3\Sigma$ for the neutral monomer, and $^2\Sigma$ for both ions. The values of the bond length (2.79 Å) and the vibrational frequency (171 cm^{-1}) obtained for the neutral molecule are in very good agreement with our previous results obtained using DMol program [5]. Due to the lack of experimental results, this agreement can be used as a benchmark for the quality of our simulation.

For the cationic case, the ionized electron comes out from a bonding orbital predicting its instability relative to the neutral monomer by 7.5 eV. It is also manifested in an increase of the internuclear distance (2.81 Å) and decrease of the frequency value (129 cm^{-1}) indicating that the bond in cationic state is weaker than the corresponding one in the neutral monomer.

The anion was found to be 1.65 eV more stable than the neutral one with a smaller bond length (2.60 Å) and a higher stretching frequency (219 cm^{-1}). This is consistent with the fact that the lowest unoccupied molecular orbital (LUMO) of the neutral monomer has the bonding character and is occupied by the additional electron in the anionic monomer.

3.2. Dimers: In_2As_2 , $In_2As_2^+$, and $In_2As_2^-$

For the neutral and ionized dimers, we have considered linear and planar isomers (see Fig. 1) for the geometry optimization. All isomers are found to be in a singlet electronic state for the neutral dimers and a doublet for the ionized ones. The lowest energy isomer has the D_{2h} rhombus structure for the neutral and charged clusters.

In the linear configurations considered here, the In–As–As–In isomer is more stable (2.06, 0.69 eV relative to D_{2h} - In_2As_2 and $In_2As_2^+$, respectively)

than As–In–As–In (5.46, 1.99 eV, relative to D_{2h} - In_2As_2 and $In_2As_2^+$, respectively) for the neutral and cationic dimer, however, this energy ordering is reversed for the anionic dimer (1.36 eV in $C_{\infty v}$ and 1.56 eV in $D_{\infty h}$ relative to D_{2h}). This inversion is due to an increase in the As–As bond distance (2.24, 2.18, and 2.31 Å, in neutral, cationic, and anionic dimers) upon accommodating an extra electron in the anionic state.

In the rhombus cationic dimer, the loss of an electron results in the increase of the In–As (from 2.88 to 3.15 Å) bond distance, with a corresponding decrease in the As–As distance (from 2.33 to 2.24 Å). Employing a molecular orbital description, it appears that the ionized electron comes from an As–As anti-bonding molecular orbital. The vibrational frequencies of the normal modes associated with the movement of the As–As bond reflect the same behavior (see Table 1). The breathing a_g mode increases its value of 317–357 cm^{-1} in going from the neutral to the cationic dimer.

In the anionic dimer, the analysis of the vibrational frequency of the D_{2h} isomer, however, has revealed the presence of one imaginary frequency, b_{3u} . In order to find the true minimum, we have, therefore, analyzed the movement of the atoms associated with the b_{3u} mode. Since the b_{3u} mode corresponds to the displacement of the In atoms out of the plane, we allowed the displacement of In atoms during the geometry optimization. The resulting bent rhombus configuration (bending angle is 142°) with no imaginary frequency and the lowest energy for the anionic dimer has the C_{2v} symmetry ($\Delta E_{D_{2h}-C_{2v}} = 0.05$ eV). For this isomer, there is a decrease of the In–As (from 2.88 to 2.78 Å) bond distance together with an increase of the As–As (from 2.33 to 2.49 Å) bond distance when compared to the neutral D_{2h} isomer. This fact is in accordance with the description of the LUMO of the neutral dimer. It has an antibonding contribution for the arsenic-arsenic bond, as it was the case with the highest occupied molecular orbital (HOMO). The repulsion of this newly occupied orbital increases the energy of the In–As bonding orbital, which was responsible for the rigidity of the planar molecule, thus allowing for a bending which lowers the total energy. The symmetry

Table 1

Symmetry labels and frequencies (ω) in cm^{-1} of the normal modes of vibration for the neutral, cationic, and anionic dimers and trimers in their most stable isomers

In_2As_2	Mode	Neutral (D_{2h})	Cation (D_{2h})	Mode	Anion (C_{2v})
	b_{3u}	39	26	a_1	35
	b_{2u}	77	25	b_1	96
	a_g	119	84	a_1	130
	b_{3g}	150	40	a_2	131
	b_{1u}	176	114	b_2	192
	a_g	317	357	a_1	251
In_3As_3	Mode	Neutral (C_s)	Cation (C_s)	Mode	Anion (C_{2v})
	a'	38	31	b_1	47
	a''	43	30	a_1	74
	a''	71	81	b_2	75
	a'	78	74	a_1	91
	a'	102	82	b_2	111
	a'	118	107	a_1	125
	a''	133	132	b_1	135
	a'	147	141	a_2	136
	a'	174	157	b_2	148
	a''	213	219	a_1	162
	a'	220	210	b_1	230
	a'	286	294	a_1	243

change when an electron is added is in agreement with the experimental [6,7] and theoretical [8,9] studies in aluminum and gallium phosphide dimers.

The vibrational frequencies for the negatively-charged dimer are also collected in Table 1. As the case with the neutral and positively-charged dimers, the low-frequency modes ($\omega < 130 \text{ cm}^{-1}$) correspond to out-of-plane bending movements in the negatively-charged dimer. The a_2 mode corresponds a torsion of the As–As bond and the b_2 mode involves the stretching movement of In–As bond, and the highest frequency mode a_1 corresponds to the vibration of As–As bond. The frequencies values of these two last modes are directly comparable with the b_{1u} and a_g modes in the neutral dimer, respectively due to the similar movement of atoms. Accordingly, the b_2 mode (192 cm^{-1}) is greater than the b_{1u} one (176 cm^{-1}), and the value of the a_1 mode (251 cm^{-1}) is smaller than the a_g mode (317 cm^{-1}). The differences in the vibrational frequencies of the anionic and neutral dimer can be understood in terms of the respective bond distances given previously.

3.3. Trimers: In_3As_3 , In_3As_3^+ , and In_3As_3^-

Based on our previous experience with the III–V clusters [3,5], we only consider the non-planar configurations for the InAs trimers. In Fig. 1, the isomer A is described as a face-capped trigonal bipyramid with the C_s symmetry group. It is the most stable isomer for the neutral and the cationic trimers, followed by isomers C ($\Delta E_{C-A} = 0.56 \text{ eV}$) and D ($\Delta E_{D-A} = 1.14 \text{ eV}$) in the neutral case, and isomers D ($\Delta E_{D-A} = 0.89 \text{ eV}$) and C ($\Delta E_{C-A} = 0.95 \text{ eV}$) for the cation. However, the isomer C is the most stable for the anionic trimer, being 0.21 and 0.58 eV below isomers A and D, respectively.

The isomer B is described as a edge-capped trigonal bipyramid with the C_{2v} symmetry. In this isomeric configuration, the equatorial plane is formed by a triangle of In atoms instead of arsenic atoms. On the other hand, the triangle consisting of arsenic atoms plays a very important role in the A and C isomers. For the neutral trimer, the isomer B has a relatively much higher energy than the most stable isomer A (22.10 eV), suggesting that the As–As bond is preferred over the In–In bond in the neutral InAs trimer.

The HOMO of the neutral isomer A consists of a mainly non-bonding molecular orbital which is localized over the As₆ atom (see Fig. 1). The loss of an electron produces a rearrangement of the atoms: In₃ (from 3.05 to 3.38 Å) and In₁ (from 3.06 to 3.58 Å) increase their distances to As₂ and As₄, which in turn move away from each other (from 2.53 to 2.60 Å). All other parameters are almost equal in the neutral and cationic species, except for a small displacement of In₅ towards the rest of the atoms. On the other hand, addition of an electron to the neutral trimer changes the symmetry of the most stable isomer to C_{2v} (i.e. isomer C). In this isomer, the arsenic triangle opens up increasing the As₄–As₂ bond distance to 3.72 Å, In₅ moves into a symmetric position, and In₁ and In₃ move to the right, being almost equidistant to As₆ (2.92 Å) and In₅ (3.10 Å). The molecular orbital picture appears to provide an explanation of the predicted structural changes as follows: LUMO in the neutral C_s isomer is a bonding orbital localized over the In₃–In₅ interaction. When an electron is added, this orbital becomes HOMO in the anionic C_s isomer with positive orbital energy. On the other hand, in the C_{2v} isomer, the extra electron is delocalized over all the molecule (see below the topological charge values) yielding a more stable configuration with HOMO orbital energy being negative.

Analysis of the normal vibrational modes reflects that the lowest frequency modes are associated with the bending and torsion of the bipyramid induced by the vibration of the Indium capped. The next modes are related with the stretching of the In₃–In₅ bond and the In–As bonds. The highest frequency modes involve the vibrational movement of the As–As bond in the triangle. Comparing the vibrational frequency values for the neutral and cationic clusters (Table 1) we can see that the variation in the frequencies is small. This small variation is in agreement with the variation in the bond distances going from neutral to cationic trimer. In the anionic trimer, however variations in the frequencies with respect to the neutral trimer are larger. It is a consequence of a larger change in the bond distances. We note that the highest mode a₁ (243 cm⁻¹) in the anionic trimer is smaller than the a' (296 cm⁻¹) in the neutral trimer due to the expansion of the arsenic triangle upon accepting an extra electron.

3.4. Atomic and bonding properties

In the neutral InAs monomer, there is a small charge transfer of about 0.37 e from In to As, in accordance with the chemical intuition and Pauling electronegativities for In (1.7) and As (2.0) atoms. The atomic charges in neutral dimer and trimer are very similar to those in the neutral monomer, exception being the small charge of As₆ (–0.29 e) in the trimer due to its low coordination. In the cationic clusters, the electron removed is evenly distributed among all atoms. In a similar way, the electron added is evenly distributed among the atoms in the anions, the exception being again As₆ in the trimer.

The topological structures of the InAs clusters considered here are almost the same as drawn in Fig. 1, the only exception being trimers. In the neutral trimer, the topological molecular graph shows that the In₃ is not bonded with the As₂ and As₄ atoms. When one electron is lost, the As₆–In₁ bond breaks, and the In₁ atom moves toward the equatorial plane in the opposite direction. The isomer C represents the molecular graph for the anionic trimer, except that the As₂–As₄ bond is broken: the arsenic triangle opens up when the electron is added. This molecular graph allows us to see this isomer as an irregular octahedron, with In and As atoms playing very similar roles.

Both ρ and $\nabla^2\rho$ in the bond critical points follow an exponential relationship with the distance for a given pair of atoms. In this way, the short bonds have a higher density, which is associated with a higher bond strength. We found three different kinds of bonds: In–As, In–In, and As–As. The first two have a positive $\nabla^2\rho$ value near 10⁻² e/bohr⁵. However, $\nabla^2\rho$ in the As–As bond point is negative, indicating a sharing interaction, for small bond lengths (dimers and As₂–As₄ of the cationic trimer). On the other hand, $\nabla^2\rho$ is positive for the larger bond lengths (all other trimer As–As bonds), corresponding to non-sharing interactions. This behavior can be understood by comparing with the $\nabla^2\rho$ values for the As₂ molecule as a function of the interatomic distance: it is negative for distances between 2.17 and 2.51 Å, positive elsewhere. The values for all of the As–As bonds in the clusters studied fulfill this same condition, and

in fact have Laplacian values very close to those of the diatomic molecule at the same distance.

3.5. Electronic properties

The calculated electron affinity and the ionization potential for the monomer, dimer, and trimer are listed in Table 2. We define the electron affinity to be $EA = E(\text{neutral}) - E(\text{anion})$ and the ionization potential to be $IP = E(\text{cation}) - E(\text{neutral})$. For all cases, anionic clusters are more stable than the neutral clusters.

Due to the lack of the experimental studies on the InAs clusters, we will compare the calculated values with the experimental results of photoelectron spectroscopy on GaAs and InP clusters. The vertical electron affinity in $(\text{GaAs})_n$ with $n = 1, 2, 3$, is measured to be about 2.1 eV [17], while that in $(\text{InP})_n$ is estimated to be about 1.88, 1.75, and 1.40, with $n = 1, 2, 3$, respectively [18]. Our calculated EA results for $(\text{InAs})_n$ are 1.76, 2.12 and 2.01 comparing well with the values reported for InP and GaAs clusters. The calculated value of the ionization potential are 7.52, 7.39 and 6.74 eV for monomer, dimer and trimer, respectively. These values also compare well with those reported for GaAs clusters. The calculated value of the ionization potential is 7.5 eV for Ga_2As_2 and Ga_3As_3 [19]. It is important to note that the adiabatic and vertical values for the ionization potential in the monomer are the same, and in the dimer and the trimer the adiabatic values are smaller than the vertical ionization potential. It is due to the change in the internuclear distance is only 0.02 Å when one electron is removed out from the neutral monomer. However, the loss of one electron in both dimer and trimer produces larger changes in the structural parameters,

thereby yielding lower values of the adiabatic ionization potential.

The HOMO–LUMO gap has been computed for all isomers. In the anionic clusters, the gap decrease when the size increase (1.85–1.35 eV), while, in the cationic clusters, the HOMO–LUMO gap increase from 0.86 eV in the monomer to 1.51 eV in the trimer.

4. Conclusions

In this work, we have found that the addition of one electron to the neutral cluster produces greater structural changes than the loss of one electron. In this way, the most stable isomers of anionic clusters belong to a different symmetry than those of the neutral one. However, the cationic dimer and trimer have the same symmetry as the neutral clusters. These changes are a consequence of the reorganization of the electron density when the clusters are ionized. This rearrangement resulted in the the formation of the new bonds In–As and In–In in the anionic trimer, and the shortening of the In–As bond distance in the anionic dimer. Therefore, the anionic clusters more stable than the neutral ones, and the latter are more stable than the cationic ones. In the same way, the addition of one electron is an exothermic process, and the loss is an endothermic process as indicate the electron affinity and ionization potential values. Employing the Atoms in Molecules Theory, we have found that the In–As bond is a polar and non sharing interaction, and the In–In bond is a non sharing interaction. However, depending on the internuclear distances, the As–As is either sharing (small bond lengths) or non-sharing (larger bond lengths). The topological charges indicate that these clusters have a partial ionic character. Moreover, the loss or gain of the electron is contributed equally for all atoms in the cluster.

Table 2

Adiabatic and vertical values (eV) for the electron affinity (EA) and the ionization potential (IP) for the monomer, dimer and trimer

	Monomer	Dimer	Trimer
Adiab. EA	1.65	1.68	1.45
Vert. EA	1.76	2.12	2.01
Adiab. IP	7.52	6.67	6.33
Vert. IP	7.52	7.39	6.74

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