



Lowest-energy structures and photoelectron spectra of In_nP_n ($n = 1-12$) clusters from density functional theory

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ARTICLE INFO

Article history:

Received 13 March 2008
Received in revised form 6 May 2008
Accepted 6 May 2008
Available online 20 May 2008

Keywords:

Indium phosphide
Clusters
Geometry
Electronic structures

ABSTRACT

Lowest-energy structures of In_nP_n ($n = 1-12$) clusters have been determined from a number of structural isomers using all-electron density functional calculations. The In–P alternating hollow cage-like structures emerge at $n = 7$. Size-dependent cluster properties such as binding energy, HOMO–LUMO gaps, electron affinities, and photoelectron spectra have been computed and discussed. The simulated electron affinities and photoelectron spectra agree reasonably with experiments. With exceptionally low electron affinity and large HOMO–LUMO gap, In_3P_3 was identified as a magic-numbered cluster of relatively higher stability, in agreement with experimental observations.

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1. Introduction

The structures, bonding characteristics and electronic properties of small semiconductor clusters are interesting since they not only represent the intermediate state between microscopic atoms and macroscopic condensed matters but also provide us some clues to how to develop novel nanoscale electronic and photonic devices. So far, a number of experiments and theoretical studies have been reported for small clusters of III–V compounds such as GaAs [1–4], GaN [5–8] and AlP [9–12]. Among those semiconductor compounds, InP was one of the earliest III–V compounds being synthesized as early as 1910s. Since then, it attracted a lot of attentions as an important semiconductor materials [13] due to the following facts: (1) the lattice parameter of InP solid matches well with those narrow-band-gap semiconductor alloys like InGaAs and InGaAsP [14]; (2) the electron mobility in InP is high [15]; (3) InP-based millimeter-wave sources and amplifiers can operate at high frequencies with lower noise [16]; (4) p-type InP can be utilized in the high-frequency Schottky-barrier solar cells [17]; (5) InP-based materials are good candidates for optical fiber communications [18]. Thus, it would be important to elucidate the structural growth behavior of small InP clusters as function of cluster size

and to reveal the transition from microscopic molecule towards bulk solid of InP.

Previously, experimental works on the small InP clusters were mainly done with photodissociation and photoelectron spectroscopy techniques [19–23,12]. From these experiments, the absorption spectra, ultraviolet photoelectron spectra (PES), vertical detachment energies (VDE) and electron affinity (EA) were obtained. In the early 1990s, Mandich's group have measured the visible and near-infrared absorption spectra of a number of stoichiometric and nonstoichiometric In_xP_y clusters with $x + y = 5-14$ [19,20]. Later, Neumark's group has carried out a series of experiments to probe the electronic structures of In_nP_n^- clusters up to different sizes ($n \leq 4$ [21], $n \leq 13$ [22,23]) via measuring their anionic photoelectron spectra. The low-lying electronic states of diatomic InP molecule were also probed using the same technique [12].

On the theoretical sides, comprehensive search of the lowest-energy configurations of In_xP_y clusters using first-principles approaches were limited in very small sizes, that is, $x + y \leq 6$ [24,25]. For the larger sizes, Neumark and co-workers [23] have performed density functional theory (DFT) calculations on the In_nP_n ($n = 3, 4, 6, 9$) clusters with a few presumed configurations at level of B3LYP/LANL2DZ. In spite of the abundant experimental data on the photoelectron spectra on the In_nP_n clusters up to $n = 13$ [21–23], little is known about the structural growth behavior and electronic properties for the In_nP_n clusters with $n > 3$ from theoretical simulations. In this work, we have conducted a comprehensive search of the lowest-energy structures of the neutral In_nP_n

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and anionic In_nP_n^- ($n = 1-12$) clusters. The anionic photoelectron spectra of these clusters were then simulated. The size-dependent electronic properties such as HOMO–LUMO gap and EA will be discussed and compared with available experimental data.

2. Computational methods

Here first-principle calculations were performed using all-electron density functional theory implemented in the DMol package [26]. The exchange–correlation interaction was treated by the generalized gradient approximation with the Perdew–Burke–Erzerhof (PBE) parameterization [27]. Double numerical plus *d*-polarization (DNP) basis set was adopted [26]. Self-consistent field (SCF) calculations were carried out with a convergence criterion of 10^{-6} Hartree on the total energy. Full geometry optimizations were then performed using the Broyden–Fletcher–Goldfarb–Shanno (BFGS) algorithm without any symmetry constraint.

To search for the most stable structures of In_nP_n ($n = 2-12$) clusters, we have generated a number of possible isomers that are adopted from the other semiconductor compound clusters like GaAs [1] and ZnO [28], and from hand-made construction following chemical intuition. For each cluster size, 10 to 30 isomer structures were considered. To simulate the photoelectron spectra and to compute the EA of the indium phosphide clusters, we have also performed comprehensive search for the lowest-energy configurations of the anionic In_nP_n^- clusters using the same population of initial structures.

To validate the performance of the present theoretical scheme, we first investigated the indium phosphide solid and compared our results to the experiment data. The equilibrium lattice of 6.00 Å for the zinc blende crystal from our calculations is slightly higher than the experimental value 5.87 Å [29]. Within the equilibrium lattice, the computed binding energy of 3.404 eV/atom and band gap of 1.28 eV are in satisfactory agreement to the experiment data of 3.339 eV/atom [29] and 1.42 eV [29], respectively. Moreover, the theoretical Fermi energy for the InP solid is 4.402 eV, rather close to the experimental electron affinity of 4.38 eV [29]. All these agreements suggest that the computational scheme we chose would be reasonable for describing the interatomic bonding and electronic properties of InP clusters.

3. Results and discussions

For the diatomic InP molecule of singlet spin state, our calculations predicted a In–P bond length of 2.714 Å and a vibrational frequency of 238.8 cm^{-1} . Previously, accurate quantum chemical calculations at MRDCI/RECP level gave 2.71 Å and 248 cm^{-1} [30], while experimental vibrational frequency was 255 cm^{-1} [12]. Again, such agreement demonstrates the validity of our computational approach in small InP clusters. The lowest-energy structures obtained for neutral and anionic In_nP_n ($n = 2-12$) clusters are shown in Fig. 1. Normal mode analysis of these ground-state structures shows no imaginary frequency, indicating that they are all true minima on the potential energy surface instead of the saddle points.

The lowest-energy structure of In_2P_2 is a planar rhombus with P–P bond length of 2.082 Å and In–P bond length of 2.795 Å. Same rhombus configuration was found in previous calculations by Costales [24] and Zhang [25], while the bond lengths were 2.08 Å (P–P) and 2.80 Å (In–P) at PW91/DNP level [24], and 2.063 Å (P–P) and 2.765 Å (In–P) at B3LYP/LAND2DZ level [25], respectively. The lowest-energy structure of the In_2P_2^- cluster remains rhombus. From our calculations, the P–P bond length in the anionic In_2P_2^- cluster changes to 2.261 Å and In–P length to 2.688 Å, close to previous theoretical results of 2.219 Å and 2.66 Å [25], respectively.

The most stable configuration found for In_3P_3 is a face-capped trigonal bipyramid. This is in agreement with previous works by Costales [24] and Zhang [25]. When the cluster carries one extra electron, its lowest-energy structure transforms into a distorted octahedron (see Fig. 1). Similar charge-induced structural change in the anionic In_3P_3^- cluster was observed in Zhang's recent calculations [25].

The lowest-energy configuration of In_4P_4 is a squashed cube (C_{2v}) with In–In bond length of 3.479 Å and P–P bond length of 2.126 Å, while the anionic In_4P_4^- is a distorted octahedron capped with an InP dimer. Previously, Meloni et al. [23] proposed a bi-capped octahedron structure as the lowest-energy configuration for In_4P_4 and optimized it using B3LYP method implemented in the Gaussian98 package. To make a direct comparison, we take the structures reported in Meloni's paper as the initial ones to re-optimize using our own computational scheme at PBE/DNP level. Upon optimization, the total energy of Meloni's structure is higher than our lowest-energy structure by 8.38 eV from our calculations.

The most stable structure of In_5P_5 is a tetracapped trigonal prism with some distortion, while the structure of the anionic In_5P_5^- cluster changes to a bicapped square antiprism. Within our knowledge, there was no previous first-principles calculation on the In_5P_5 cluster.

The lowest-energy structure of In_6P_6 is a superstructure consisting of a tetrahedron, a dimer, and a bicapped tetrahedron, which is 5.56 eV lower than the distorted C_1 structure reported by Meloni et al. [23] and re-optimized by our PBE/DNP calculations. With one extra electron, the most stable structure of the anionic In_6P_6^- cluster becomes a hexagonal prism (D_{3d}) with alternating indium and phosphorus atoms, similar to the equilibrium structure of Al_6P_6 cluster [9].

Starting from In_7P_7 , the lowest-energy structures of In_nP_n clusters prefer hollow cages up to $n = 12$. The most stable structure of In_7P_7 is a cage consisting of four square faces, four pentagonal faces, and one hexagonal faces. Following the cage-like growth pattern, the lowest-energy configuration of In_8P_8 is a near-spherical cage with four square faces, four pentagonal faces, and two hexagonal faces. The most stable configuration of In_9P_9 is a C_{3h} cage with alternating In–P arrangement without any In–In and P–P bond, which consists of five hexagonal faces and six square faces. This is different from the structure of In_9P_9 cluster proposed by Meloni et al. [23], whose energy is higher than ours by 2.57 eV re-optimized at our PBE/DNP level of theory. The lowest-energy structure of $\text{In}_{10}\text{P}_{10}$ is a hollow cage consisting of six hexagonal faces and six square faces. The most stable configuration of $\text{In}_{11}\text{P}_{11}$ is a C_s cage including seven hexagonal faces and six square faces. The lowest-energy structure of $\text{In}_{12}\text{P}_{12}$ is a high-symmetry cage (T_h) consisting of eight hexagonal faces and six square faces. On this cage, the In and P atoms are arranged in a perfectly alternating way so that each In atom is bonded with three P atoms and each P atom bonded with three In atoms. Excepted at $n = 8$, most of the anionic In_nP_n^- ($n = 7-12$) clusters adopt the same configurations as their neutral ones. For In_8P_8^- , a prolate double-caged structure (S_4) instead of a spherical-like cage was found to be most stable.

From our calculations, we found that the average In–P bond length generally decreases when the cluster size increases. For example, the average In–P bond length of In_2P_2 is 2.795 Å, while that of In_7P_7 and $\text{In}_{12}\text{P}_{12}$ is 2.594 Å and 2.575 Å respectively, rather close to the equilibrium In–P bond length of 2.598 Å computed for the InP solid. In other words, the cage configurations obtained for In_nP_n ($n = 7-12$) clusters can be considered to be somewhat bulk-like, not only from the In–P alternating arrangement like that in the zinc blende crystal, but also from the reduced average bond length. It is also interesting to compare the lowest-energy configurations of In_nP_n clusters with their counterpart, i.e., Al_nP_n [9].

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