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Journal of Molecular Structure: THEOCHEM 851 (2008) 167–174

THEO CHEM

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Density functional theory studies on the structure, electronic state and photoelectron spectroscopy of $(GaP)_n^-$ ($n = 7$–9) clusters

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Received 21 August 2007; received in revised form 5 November 2007; accepted 6 November 2007

Abstract

The equilibrium geometries, electronic states, vibrational frequencies and energies of $(GaP)_n$ and $(GaP)_n^-$ ($n = 7$–9) have been calculated by hybrid B3LYP and B3PW91 functionals at 6-31+G(d) level. The results reveal that the lowest lying electronic states' geometries of the neutral have the same molecular symmetry as the corresponding anions'. $(GaP)_7$ is shown to have a singlet ground state ($^1A_1$) with C_{3v} symmetry. $(GaP)_8$ is found to be a closed-shell molecule with S_4 symmetry. $(GaP)_9$ takes on a singlet ground state ($^1A'$) with C_{3v} symmetry. The charge-induced structural changes in these clusters have been discussed. Moreover, natural bond orbital (NBO) analysis implemented to gain insight into the bonding pattern of these clusters indicates these clusters have a partial ionic character. Natural electron configuration shows the extra electron is mostly localized on the metal atoms. In addition, three types of energy separations reported in this work are the adiabatic electron affinity (AEA), the vertical detachment energy (VDE), and the vertical electron affinity (VEA). Herein, adiabatic electron affinities (AEAs) and vertical detachment energies (VDEs) for all of interest are excellent consistent with experiments, as strongly supports the optimized structures. And the order of AEAs and VDEs of the $(GaP)_n^-$ are both $(GaP)_9 < (GaP)_8 < (GaP)_7$. $(GaP)_9$ exhibits the lowest adiabatic electron affinity of all the clusters studied, indicating a particularly stable neutral species.

Keywords: Density functional theory; $(GaP)_n$ and $(GaP)_n^-$ clusters; Natural bond orbital (NBO) analysis; Vertical detachment energies; Adiabatic electron affinities

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1. Introduction

The group III–V semiconductor materials have attracted considerable interest due to their potential applications in fast microelectronic devices and light-emitting diodes [1]. Though these materials have been studied extensively in the solid sate and thin film forms, research at the micro- and nanocluster levels is relatively lacking. Representing a link between the solid state and the isolated molecular world, theoretical and experimental studies of these clusters have drawn increasing attention during recent years [2–31]. Experimentally, a number of III–V semiconductor clusters, particularly Ga_xAs_y, Ga_xP_y, and In_xP_y, were observed via anion photodetachment spectroscopy [2–7]. Prior to the work of Neumark and co-workers, Weltner and his associates [8–10] had investigated the IR absorption spectra of GaX, GaX_2, Ga_2X, and InX (X = P, As, and Sb), as well as Ga_2As_3 cluster, isolated in a 4 K argon matrix. Theoretically, Balasubramanian and co-workers [11–21] have studied the low-lying electronic states of Ga_xP_y, Ga_xAs_y, Al_xP_y, etc. clusters with fewer atoms at the complete active space self-consistent field (CASSCF) and multi-reference singles–doubles configuration interaction (MRSDCI) levels of theory. Costales and co-workers [22] have investigated the structural and vibrational properties of $(MX)_n$ ($n = 1$–3) clusters for different combinations of metallic M (M = Al, Ga, In) and non-metallic X (X = P, As) using the density functional theory (DFT). Archibong and

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doi:10.1016/j.theochem.2007.11.018

co-workers [23–26] have investigated the photoelectron spectra of $Ga_xP_y^-$ ($x + y \leqslant 5$) experimentally and theoretically. Andreoni [27] employed the Car-Parrinello molecular dynamics method to study the structure, stability and melting point of $(GaP)_n$ clusters with $n = 2$–5. Tozzini et al. [28] reported that spontaneous formation and stability of small GaP fullerene cage with *ab initio* molecular dynamics simulations starting from a bulk fragment. Recently, the structure and electronic state of Ga_nP and Ga_nP_2 ($n = 1$–7) clusters have been studied by Li group [29].

Elucidating the electronic structures of $Ga_xP_y^-$ clusters is essential to understanding the photoelectron spectroscopy (PES) and properties of gallium phosphide nanoparticles. In our previous work [30,31], we investigate the electronic structure and property of $Ga_xP_y^-$ and Ga_xP_y ($x + y \leqslant 8$) species using DFT calculations. We are interested in probing the electronic structure of gallium phosphide clusters that reproduce the observed photoelectron spectra. In some cases, the predicted properties help experimentalists to interpret their results. To the best of our knowledge, the information relative to the geometric structure of larger stoichiometric $(GaP)_n^-$ is still little understood. Here we report the results of a theoretical study of $(GaP)_n^-$ and $(GaP)_n$ ($n = 7$–9) clusters based on density function theory (DFT). Part of our objective is to furnish theoretical verifications of vertical detachment energies (VDEs) of $(GaP)_n^-$ and adiabatic electron affinities (AEAs) of the neutral in the literature [2]. Most importantly, we have found the ground state geometries of $(GaP)_n$ and $(GaP)_n^-$ ($n = 7$–9). A match between the predicted and observed properties identifies the correct structures. In addition, vertical electron affinities (VEAs) of the neutral were predicted.

We have organized the rest of the paper as follows. The computational methods used in this work are presented in Section 2. In Section 3, we discuss our results from different aspects. Finally, we present our conclusions in Section 4.

2. Computational details

All electron calculations were performed on neutral and negatively charged $(GaP)_n$ ($n = 7$–9) clusters, in the framework of DFT, using Gaussian 03 program [32]. The Becke's three-parameter exchange functional (B3′) [33] and two correlation functional of Lee–Yang–Parr (LYP) [34] and Perdew–Wang 91 (PW91) [35] were employed here. The choice of DFT has been fully justified for semiconductor system studies [29–31,37,38]. For anionic systems, diffuse basis set is expected to play an important role in determining the structural configuration. For this reason, the 6-31+G(d) basis set was used for P and Ga atoms in the present calculations. All of the isomers analyzed in this study have been fully geometrically optimized by analytical B3LYP/6-31+G(d) and B3PW91/6-31+G(d) methods. Restricted methods were used for all closed-shell systems, while unrestricted methods were employed for the open-shell species. Moreover, the vibrational frequencies of all structures were calculated in order to determine the ground state. The structural configurations for the geometry optimization are designed mostly on the basis of the previous investigations on $(AlN)_n$ clusters [37]. Meanwhile, it is found that isomers of Ga_xP_y with direct Ga–Ga and P–P bondings are more stable in our previous studies [31]. So to locate the lowest energy isomer, we should consider all kinds of configurations involving four-, five-, six-, seven-, and eight-membered rings.

Furthermore, adiabatic electron affinities (AEAs) of $(GaP)_n$ clusters and vertical detachment energies (VDEs) of $(GaP)_n^-$ radical anions were calculated and have been compared with the available experimental values. The AEA is defined as the energy difference between the neutral cluster and its corresponding radical anion at their lowest electronic states, that is $\mathrm{AEA} = E_{(\text{optimized neutral})} - E_{(\text{optimized anion})}$, where both the neutral cluster and its radical anion are fully optimized. The VDE is defined as the energy difference between the optimized anion cluster and the corresponding neutral molecular without relaxation, that is $\mathrm{VDE} = E_{(\text{neutral at optimized anion geometry})} - E_{(\text{optimized anion})}$. The vertical electron affinity (VEA) has also been computed, defined as the energy difference between the neutral and anionic clusters with both at the optimized neutral geometry, that is $\mathrm{VEA} = E_{(\text{optimized neutral})} - E_{(\text{anion at optimized neural geometry})}$. Although the vertical electron affinity is not currently measured through any experiment, it provides a lower bound to the AEA in the same way as the VDE is an upper bound to it [36].

To test the accuracy of the present method to describe gallium phosphide compounds, the smallest GaP diatomic cluster was calculated at the DFT-B3LYP/6-31+G(d) level and its obtained properties were compared with recent theoretical and experimental results. The Ga–P bond lengths in the $^2\Sigma^+$ ground state of GaP^- and $^3\Sigma^-$ ground state of GaP are predicted to be 2.137 and 2.462 Å, respectively. Those values agree well with the theoretical results of 2.152 and 2.476 Å at the B3LYP/6-311+G(2df) level [23]. The AEA of GaP is calculated to be 2.03 eV (including correction for the zero-point energy) at the B3LYP/6-31+G(d) level, which is within the experimental value of 1.96 ± 0.075 eV reported by Neumark and co-workers [2]. Additional calculations on GaN and Ga_2 diatomic clusters at the B3LYP/6-31+G(d) level also show satisfactory agreement with available data [20,39]. For example, the Ga–N bond lengths in the $^2\Sigma^+$ ground state of GaN^- and $^3\Sigma^-$ ground state of GaN are predicted to be 1.774 and 2.028 Å, respectively. Those values are consistent with the theoretical results of reference [20]. The AEA of GaN is calculated to be 1.601 eV, which agrees with the theoretical result of 1.44 ± 0.5 eV [20]. In the $^4\Sigma_g^-$ ground state of Ga_2 anion, the Ga–Ga bond length is predicted to be 2.498 Å, which agrees well with the theoretical results of 2.562 Å at the complete active space self-consistent field (CASSCF)/second-order configuration interaction (SOCI) level