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Research paper

Analysis of the geometrical properties and electronic structure of arsenide doped boron clusters: Ab-initio approach

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ABSTRACT

Density functional theory (DFT) and coupled-cluster (CCSD(T)) theory have been applied to investigate the geometric, growth pattern, bonding, stability, dissociation, adsorption and electronic properties of arsenide doped boron clusters B_nAs (n = 1–9). Vertical ionization potential (VIP), vertical electron affinity (VEA), HOMO-LUMO energy gap (E_g), binding energy (E_b), chemical hardness (η), and radial distribution functions (RDFs) of B-As and B-B interactions have also been investigated and discussed for the most stable isomers. The results show that the As-dopant atom prefers to locate in peripheral regions for the studied sizes. Arsenic atom can obviously enhance the stability of B_nAs clusters.

1. Introduction

Group-III-arsenides, like BAs, AlAs and GaAs etc., have received considerable attention as potential advanced materials used in many potential applications in electro-optical industry [1–4] due to their desirable physical properties such as wide band gap [5], high melting points [6], dielectric constant [7], high thermal conductivity [8], low ionicity [9,10], short bond length and hardness [11]. Among group-III-arsenide, boron arsenide (BAs) are the most widely studied [12–26] because it has a large mass ratio of constituent atoms, an unusual atomic bonding and a heavy atom (As) having only a single isotope [27]. BAs is found to have a remarkable room temperature thermal conductivity which is comparable to those in diamond and graphite [27].

A large number of investigations on boron clusters and their derivatives doped by other elements have been reported [28–41]. One of the main reasons in these studies is to understand the change of physical properties as a function of size. According to the best of our knowledge, there is no systematic report on an As atom doped B clusters. Therefore it is of importance to accurately calculate the effect of an As atom on the geometries, stabilities, and bonding characteristics of boron clusters by doping of arsenide atom. More interestingly, in order to achieve systematic understanding of the growth pattern and the nature of chemical bonding in large clusters, it is necessary to have a good understanding of small clusters.

In this study, we have investigated the geometry, structural stabilities and electronic properties of the B_nAs (n = 1–9) clusters. In addition, the geometry optimization of the pure boron clusters was calculated by using the same level of theory and basis set to ascertain the effects of the doped arsenide atom on the pure B clusters at the same time. In this regards, we have analysed the optimized average bond lengths, the low-lying isomers with relative energies, binding energy, second-order energy difference, fragmentation energy, vertical ionization potential (VIP), vertical electron affinity (VEA), the highest occupied molecular orbital (HOMO), the lowest unoccupied molecular orbital (LUMO) and the frontier molecular orbital energy gap (HOMO–LUMO difference in energy gap, E_g), chemical hardness (η), the atomic charges of the As atom and radial distribution functions (RDFs) of B-As and B-B binary interactions of the B_nAs (n = 1–9) clusters using density functional theory (DFT) calculations.

2. Computational details

The geometries of low-lying isomers of B_nAs (n = 1–9) clusters are performed using DFT with Becke's three-parameter exchange and Lee–Yang–Parr nonlocal correlation functional (B3LYP) [42].

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Before the optimization, in order to get the low-lying energy isomers of B_nAs (n = 1–9) clusters, we considered lots of possible initial geometries obtained by adding or substituting one As atom on the pure B_n and B_{n+1} clusters, which were presented in the previous studies [35,43–46], as well as by adding one B atom to the stable $B_{n-1}As$ clusters. All initial geometries, therefore, were optimized by successively increasing the number of boron by using 3-21G basis set to obtain reliable initial structures. After that, 6-311 + G (2df) basis set was used for further detailed optimization process. The calculations have been performed using the Gaussian09 program package [47]. All optimized geometries are confirmed to be real minima or transition states via frequency computations, which is also used to calculate the zero-point energies (ZPE), at this level of theory. Then, we carry out single point energy (SPE) calculations with coupled-cluster single, double and triple excitation (CCSD(T)) method [48] to get more reliable electronic energies. Although the CCSD(T) method accurately reproduces experimental activation energies [49,50] and electronic properties [51] of various structures, a T1 diagnostic test [52] was also carried out as an additional verification on the quality of the CCSD(T) to estimate possible multireference characters of all of the optimized B_nAs (n = 1–9) clusters. For the lowest-lying isomers of BAs, B_2As and B_6As clusters, we found T1 diagnostic values of 0.067, 0.054 and 0.053, respectively, greater than the threshold value of 0.044 [53], suggesting that a higher-level multireference method is necessary. We have found the T1 diagnostic values for the other clusters in the 0.016–0.036 range, indicating that the clusters are accurately described by the coupled-cluster approach. The 6-311 + G(2df) basis set is also chosen as a compromise between the quality of the theoretical method and the computational cost in the CCSD (T) calculations. The calculations are carried out for singlet-triplet and doublet-quadruplet energy states for considered clusters with even and odd numbers of valance electrons, respectively. All the structures are visualized using the Gauss View 5.0.9 package [54].

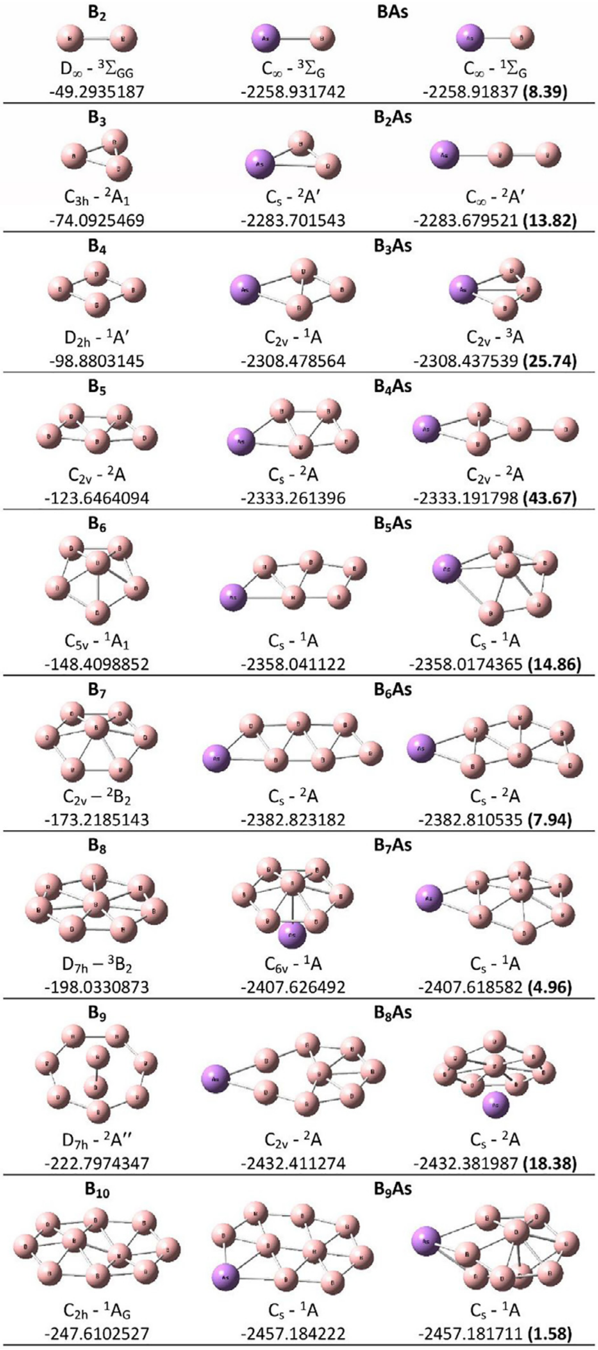

Fig. 1. The low-lying isomers for B_{n+1} and B_nAs (n = 1–9) clusters with relative energies (kcal/mol) at CCSD(T)/6-311 + G(2df)//B3LYP/6-311 + G(2df) without parentheses, at B3LYP/6-311 + G(2df) in parentheses.

3. Results and discussion

3.1. Equilibrium geometries

The obtained results for the lowest-energy structures of the B_nAs (n = 1–9) and pure boron clusters with their corresponding total energies, relative energies (for B_nAs), point group symmetries and electronic states are shown in Fig. 1. The first isomer of the BAs cluster has a linear geometry with $^3\Sigma_G$ electronic state, whereas the second isomer has $^1\Sigma_G$ electronic state. The energy difference between the two isomers is found to be 8.39 kcal/mol, as shown in Fig. 1. In B_2As cluster, the most stable isomer has a triangular geometry with the C_s point group and $^2A'$ electronic state. The second isomer (C_{∞},$^2A'$) can be grown from the isomers of the BAs stoichiometry by adding one boron atom. Moreover, the second isomer has 13.82 kcal/mol higher energy than the first isomer. The global minimum of the B_3As cluster has a planar geometry with the C_{2v} point group and the As atom is bonded by B atoms with triangular geometry. The second isomer in this series is reminiscent of the first isomer with C_{2v} point group, whereas it has triplet state (^3A). Moreover, it has a 25.74 kcal/mol higher energy than the global minimum (see in Fig. 1). For B_4As cluster, the first isomer has a "W-shaped planar" geometry with the C_{2v} point group and $^2A'$ electronic state. The second isomer (C_{2v},^2A) can be grown from the first isomer of the B_3As cluster by adding one boron atom, and it has 43.67 kcal/mol higher energy than the first isomer. Up to n = 5, the As doped B_n clusters prefer to grow from the first isomer of the pure boron clusters by adding one arsenide atom. The global minimum of the B_5As has a planar geometry with C_s point group and ^1A electronic state. Moreover, it is a 14.86 kcal/mol lower energy than the second isomer with quasi-planar geometry. The pure boron cluster has a quasi-planar geometry with C_{5v} point group at n = 6, whereas the both isomers of B_6As cluster prefer to planar geometries with C_s point group. It seems obvious that first isomer can be grown from the most stable isomer of the B_5As cluster. The second isomer is also a 7.94 kcal/mol higher energy than the global minimum. The first isomer of the B_7As cluster has an umbrella type geometry with the C_{6v} point group and ^1A electronic state. It can be grown from the lowest isomer of the pure B_7 cluster with one As atom bonded to the B atom in the center of B_7 cluster. Moreover, first time, the As atom prefers to remain on the peripheral position on the below of the cluster. So, it seems that a