

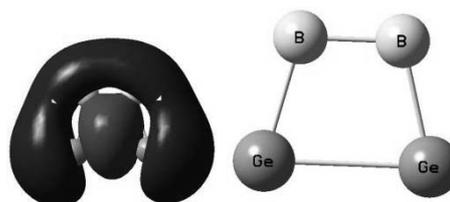
GEOMETRIES STABILITIES AND ELECTRONIC PROPRIETIES OF Ge_2B_2 CLUSTER: A DENSITY FUNCTIONAL STUDY

Run-Ning ZHAO

Institute of Applied Mathematics and Physics, Shanghai DianJi University, Shanghai201306, People's Republic of China

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The Ge_2B_2 clusters with different spin states have been systematically investigated by using the density functional method. The total energies, equilibrium geometries, and the electronic properties are discussed. Equilibrium geometries and the relative stabilities in terms of the calculated averaged atomic binding energies are discussed, indicating that the remarkable stable cluster corresponds to the ringlike trapezoid BBGeGe isomer which has the largest HOMO-LUMO gap. The electron density distributions of HOMO states of all Ge_2B_2 clusters exhibit that all ringlike isomers have strong π -type bonding interactions and the stabilities are determined by dominated π - π interactions. In addition, the charge-transfer mechanism is discussed.



INTRODUCTION

The germanium, silicon, carbon, and phosphorus-related molecules have attracted attention in many fields,^{1, 2} such as in astrophysical chemistry and microelectronic technology due to their applications in the microelectronic and photoelectronic materials. Silicon-, carbon-, nitrogen- or phosphorus-containing molecules have been detected experimentally,² the discovery of these molecules has drawn attention to the chemistry of heteroatomic systems and makes them quite reasonable to anticipate the discovery of more complex species.

Molecules with large delocalized π orbitals are ubiquitous throughout chemistry. Unfortunately, the interactions in the highly polarizable molecules are notoriously difficult to be studied because of dispersion dominated π - π interactions. Many experimental and theoretical studies have been the subjects on small N, P, and C doped silicon compounds (Si_mN_n ,³ Si_mP_n ,⁴ Si_mC_n ,⁵ SiCP_2 ,⁶). Particularly, the isoelectronic 18-valence-electron

AABB (A = C, Si; B = N, P) series; some clusters have odd electron counts; the low-lying triplet states are possible for those molecules with even electron counts. Open chain, ring, linear, and cage structures are all possible geometries of the clusters above; Several molecular species containing one or two Ge atoms, oxygen, sulfur, N, or hydrogen have been identified with IR or Raman spectroscopy and supported by theoretical calculations.^{7, 8}

Geometrical structures, electronic structures, and stabilities of mixed III-V group clusters and other clusters have been the topics of theoretical and experimental studies.^{9, 12} For the clusters like B_2Ge_2 , they can be commonly generated by laser vaporization synthesis in future, in which only the lowest lying isomers (especially the global minima) can be spectroscopically detected. Spectral characterization species of germanium boron is of great practical interest and of importance in material applications because the clusters possess the novel and important bonding

* Corresponding author: zhaorunning@126.com

properties,^{13, 14} it is important to know the bonding properties of boron to germanium atoms in germanium semiconductor materials. The bonding and properties of B–Ge clusters will depend strongly on factors other than electron count. No previous theoretical study and experimental study of the neutral germanium boron cluster are found. Thus, it is proper for us to present and describe the structures and relative energies of the isomers and then to focus their attention on the global minimum in the followed electron structural discussion. In order to achieve a detailed and systematical understanding of the cluster series, a detailed investigation on the geometric and electronic properties of Ge_2B_2 clusters is undertaken by using density functional method.

COMPUTATIONAL DETAILS

All calculations are carried out by using the GAUSSIAN 09,¹⁵ the optimized geometries and harmonic vibrational frequencies of various Ge_2B_2 isomers are obtained at the mPW2PLYP(d)/6-311++G(2df) level. With aim to examine all stable geometries as minima and to estimate zero-point energy corrections that are included into the calculated electronic energies, vibrational frequencies are calculated at the same level of theory.

The 6-311++G(2df) basis sets is proven to be reliable and accurate for the geometries, stabilities, and electronic properties of molecule.^{16, 17} It is well-known that the mPW2PLYP(d) method is suitable for the calculation of clusters with nonzero or large HOMO-LUMO gaps containing a similar scaled perturbative correction and is typically reliable for treating dispersion dominated interactions,¹⁸ such as the compounds dominated by π - π interactions; the calculated HOMO properties of Ge_2B_2 clusters give additional support to the use of the mPW2PLYP(d) method in the present context as shown below. In order to test the reliability of our calculations, the GeB molecule is calculated at the mPW2PLYP(d)/6-311++G(2df) level, the calculated results of the bond length, electronic state, and frequency for GeB diatom are respective 2.202 Å, $^2\Sigma_g^-$, and 483.2 cm^{-1} ; The calculated bond length, electronic state, and frequency of Ge_2 dimer (2.293 Å, $^3\Sigma_g^-$, 294.0 cm^{-1}) are in good agreement with previous high-level MRCI calculations (2.384 Å, $^3\Sigma_g^-$, 290.0 cm^{-1}) and ECP-DZP calculations (2.361, $^3\Sigma_g^-$, 325 cm^{-1}) as

well as experimental result (2.439 Å),^{8, 9, 20} The calculated bond length of B_2 is 1.519 Å with electronic state and frequency being respective $^5\Sigma_u$ and 1096.1 cm^{-1} which is in good agreement with previous value,^{8, 21} Consequently, the mPW2PLYP(d)/6-311++G(2df) method is reliable and accurate enough to be applied to describe the properties of Ge_mB_n clusters. The calculated binding energies for B_2 , Ge_2 , and BGe are respective 3.04, 2.61, and 1.46 eV, reflecting that B-B interaction is stronger than Ge-Ge and B-Ge interactions in strengths and B-B interaction dominates the stabilities of B_2Ge_2 clusters.

In this paper, equilibrium geometries of Ge_2B_2 clusters are optimized, and their stabilities are examined by the calculated harmonic vibrational frequency. A relaxation along the coordinates of the found imaginary vibrational mode is carried out until the local minimum is actually obtained. In addition, the spin electronic configuration of the geometry is considered.

RESULTS AND DISCUSSION

1. Geometries and Stabilities

The geometries and stabilities of BGeGeB clusters are optimized by using the mPW2PLYP(d) method at the 6-311++G(2df) level. The obtained results are listed in Table 1 and Fig. 1. On the basis of obtained results, the stable geometries can be divided into three types, linear ($\text{GB}n$), planar Y-type (GAN), and cyclelike (BAN and $\text{BB}n$) geometries.

As far as the linear Ge_2B_2 clusters are concerned, four stable linear geometries are obtained. The calculated bond lengths and optimized geometries are listed in Table 1 and Fig. 1. As seen from the optimized geometries related to these clusters, one can find that the B atoms can interact with Ge atoms with different ways and forms different linear geometrical forms. According to the calculated total energies, one finds that two B atoms in the GB1 and GB2 isomers localize at the center positions and interact with their neighboring Ge atom, respectively; the electronic state of GB1 is $^1\Sigma$. For the GB3 isomer, the calculated Ge-B bond lengths are shorter than those of GB1 and GB2. As can be seen from Fig. 1, one can find that the GB4 isomer is composed of B_2 and Ge_2 dimers, the calculated B-B and Ge-Ge bond lengths are respective 2.322 and 1.714 Å,

which are longer than those of B₂ and Ge₂ dimers; Overall, the trend in stability for the linear GB*n* isomers is GB1 > GB4 > GB2 > GB3. In addition, the linear geometries with B-B bonding are more

stable than those of the nonlinear geometries because of the stronger B-B interaction which dominates the stability of cluster.

Table 1

The calculated bond lengths, bond angles, total energies, binding energies of the stable BGeGeB cluster at the mPW2PLYP(d)/6-311++G(2df) level (units: Bond length, Å; Bond angle, degree; E_T, hartree; E_b, eV; α, ∠B1Ge1G2; β, ∠Ge1Ge2B2; γ, ∠Ge1B1B2)

sym B(1)-Ge(1)	Ge(1)-Ge(2)	Ge(2)-B(2)	B(1)-B(2)			α	β	γ	E _T	E _b
BBGeGe GA1 C _s	1.915	3.044	1.915	1.683	108.4				-4200.173600	3.158
BBGeGe GA2 C _{2v}	2.071	2.340	2.071	1.602	157.3				-4200.127372	2.844
BBGeGe GA3 C _s	1.964	2.435	1.964	1.577	156.3	156.3			-4200.122009	2.807
BGeGeB BA1 C _{2h}	2.043	2.767	2.043	3.001	47.4	47.4	85.2		-4200.242649	3.628
BGeBGe BA2 C _{2h}	2.253	2.767	2.253						-4200.091761	2.601
BGeGeB BB1 C _{2v}	1.981	2.529	1.981	1.564	75.9	75.9	104.9		-4200.255376	3.714
BBGeGe BB2 C ₁	2.112	2.541	1.996	1.627			140.6		-4200.206205	3.380
GeBBGe GB1 C _{∞v}	1.954	1.954	1.562						-4200.212295	3.421
GeBBGe GB2 C _i	2.002	2.002	1.661						-4200.094411	2.619
GeBGeB GB3 C _{∞v}	1.926	3.806	1.874						-4200.078874	2.514
GeGeBB GB4 C _{∞v}	2.322	1.714							-4200.126720	2.839

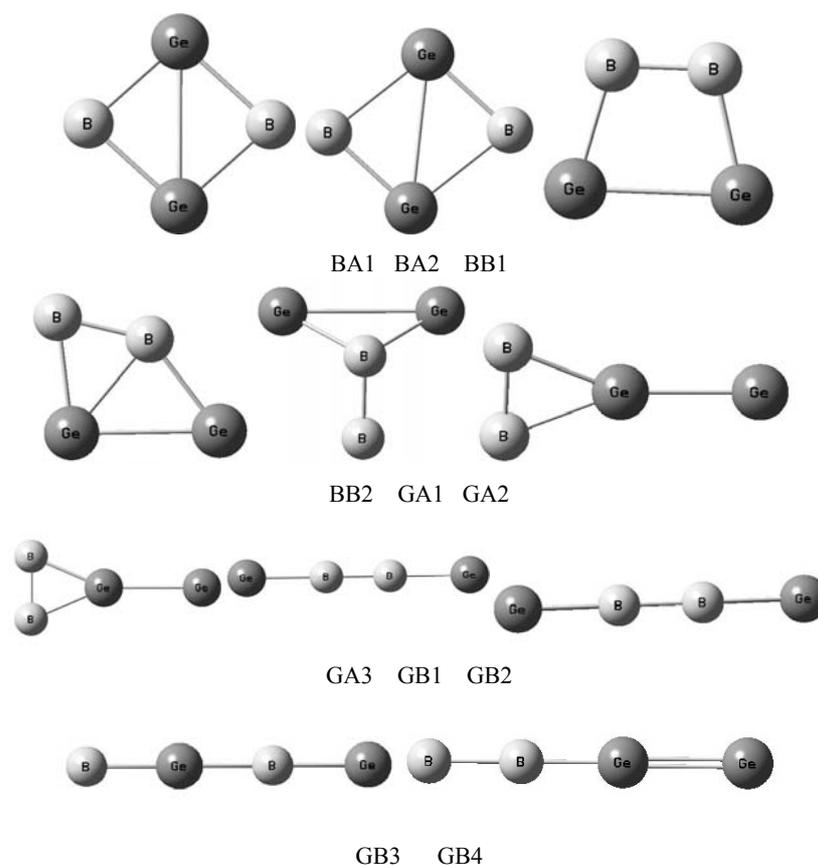


Fig. 1 – The optimized geometries of the stable Ge₂B₂ clusters.

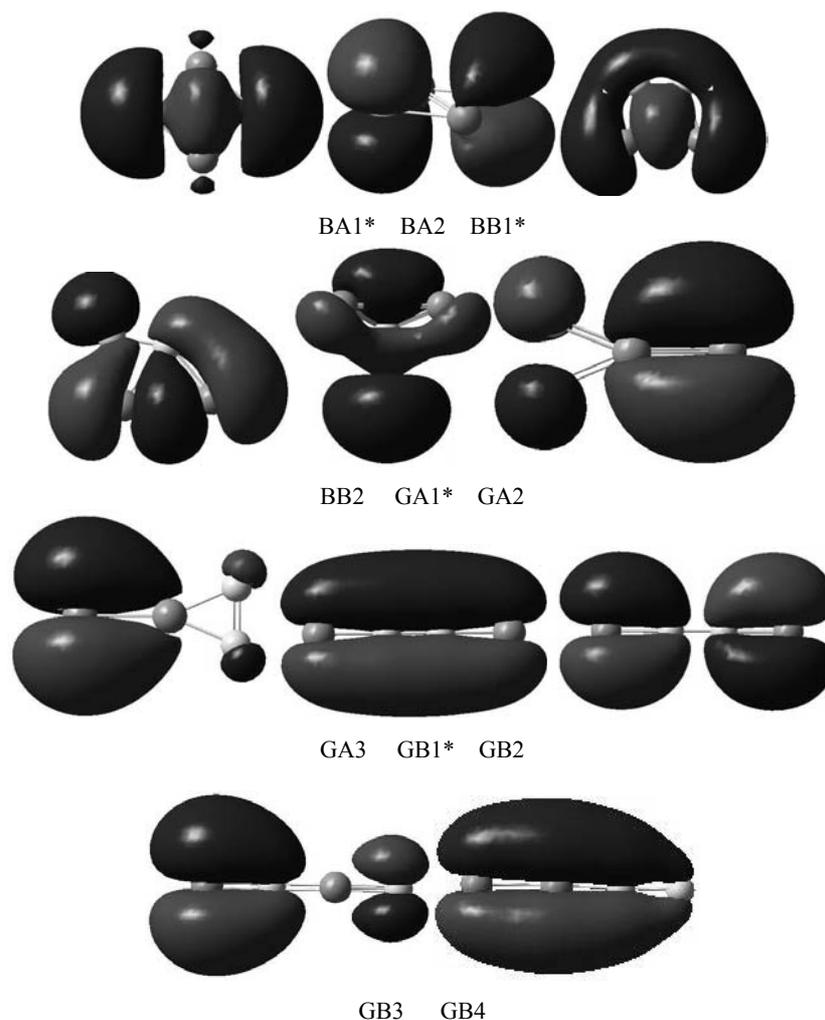


Fig. 2 – The HOMO states for the stable Ge_2B_2 clusters, where the top (or left) Ge or B atom represents as Ge(1) or B(1) and the bottom (or right) Ge or B atom represents Ge(2) or B(2). Stars indicate the lowest-energy structures of all calculated minima.

The Y-type geometries are optimized, three stable GA1, GA2, and GA3 isomers are finally obtained (shown in Fig. 1), and the geometries can be described as B_2 dimer interacting with Ge_2 dimer with different forms. For the GA1 isomer, the B-B and Ge-Ge bond lengths are respective 1.683 and 3.044 Å, indicating that the interactions of B_2 and Ge_2 enhance the stability of GA1 with electronic state being $^1\text{A}'$. As far as C_{2v} GA2 and C_s GA3 isomers are concerned, their electronic states are $^1\text{A}_1$ and $^3\text{A}'$, respectively; Singlet GA2 is analogue to that of triplet GA3 in geometry. Furthermore, Ge-Ge bond length in GA2 is shorter than that of GA3 while B-B bond length in GA2 is longer than in GA3. GA2 is lower in total energy by 0.146 eV than GA3, moreover, GA2 is higher in total energy than GA1; consequently, the singlet GA1 is the most stable geometry of all T-type isomers.

The rhombus-type GeBGeB isomers are considered and optimized, two stable geometries

are obtained. Our calculated results show that BA1 isomer is more stable than BA2 isomer and its electronic state is $^1\text{A}_g$.

For the BB1 and BB2 isomers, the geometries can be described as B_2 interacting with Ge_2 , and the cyclelike BB1 and BB2 geometries are formed. On the basis of the calculated results, one can find that B-B bond length in BB1 is longer than in BB2 isomer while Ge-Ge bond length in BB1 is longer than in BB2 isomer. According to the optimized geometries, one finds that B-B interactions in BB1 and BB2 play the dominant roles. It is should mentioned that BB1 is lower in total energy by 1.338 eV than BB2; BB1 is the most stable geometries with electronic state being $^1\text{A}_1$.

It is well known that for the singlet state isomers the calculated S^2 is zero and no spin contamination is involved. On the basis of our calculated results, however, the GA3, BA2, BB2, and GB3 involve in higher spin state; the

calculated S^2 (spin contamination) for BA2 and BB2 being respective 6.01 and 2.11 can be negligible while the calculated S^2 (spin contamination) for GA3 and GB3 being respective 2.71 and 3.27 are bigger than the expected values. Fortunately, the most stable GA1, BA1, BB1, and GB1 isomers are singlet spin states without spin contamination.

2. HOMO Properties

According to the contour maps of HOMO states of all GeBBGe clusters (Fig. 2), one finds that the electronic density distribution of HOMO states for the most stable GeBBGe clusters mainly delocalizes around B and Ge atoms, indicating that the hybridizations between B and Ge atoms, or between B and B atoms, and or between Ge and Ge atoms, are enhanced. Their shapes of the HOMO and bonding properties of various GeBBGe clusters are obviously different, and they depend on the geometrical forms.

Furthermore, the Ge-Ge, Ge-B, and B-B bondings in the Ge₂B₂ clusters are delocalized π -type bonds or partly σ -type bonds. For the linearlike clusters, the bondings in GB1 and GB4 clusters are completely delocalized π -type bonds while the bondings in GB2 and GB3 clusters are composed of two delocalized π -type bonds, the different bondings in linearlike clusters result in different isomers with different energies and stabilities, and their HOMO orbitals are degenerate orbitals. As far as Y-type isomers are concerned, the Ge-Ge bondings in GA2 and GA3 isomers are delocalized π -type bonds while the delocalized π -type bonds around Ge-B-Ge is formed in GA1

isomer. As seen from the HOMO shapes of the rhombus-type GeBGeB isomers, the chemical bondings of BA1 are composed of π -type and σ -type bonds while the bondings in BA2 are the delocalized π -type bonds. As for the HOMO shapes of BB1 and BB2 clusters, the bondings in BB1 are mainly delocalized π -type bonds while the bondings in BB2 are dominant by several localized π -type bonds. In general, the Ge₂B₂ molecules have large delocalized π -type bonds; In order to understand the properties of Ge₂B₂ molecules, the interactions in these high polarizable molecules dominated by covalent π - π interactions are urgently required to be studied.

3. APT atomic populations

The calculated APT (atomic polarizability tensor) charges are listed in Table 2. For the linearlike molecule, the negative charges are mainly localized at the B(1) atom which comes from germanium atoms or the other B(2) atom. As far as the Y-type isomers are concerned, the negative charges in GA1 molecule of Y-type isomers localize at B(1) atom which are transferred from Ge(1) and Ge(2) atoms as well as B(2) atom while the negative charges in GA2 and GA3 isomers are localized at Ge1 atom which are transferred from Ge(2) atoms and partly from the B atoms. For the rhombus-type GeBGeB isomers, the negative charges in BA1 are transferred from B atoms to germanium atoms while the negative charges of B atoms in BA2 are transferred from germanium atoms. For the BB1 and BB2 isomers, the negative charges of B atoms are transferred from germanium atoms.

Table 2

The calculated APT charges, electronic state, frequencies (cm⁻¹) and HOMO, LUMO (hartree), and HOMO-LUMO gaps (eV) of the BGeGeB cluster

Sys	S	state	B(1)	B(2)	Ge(1)	Ge(2)	Freq	HOMO	LUMO	Egap
BBGeGe GA1	0	¹ A'	-1.095	0.368	0.362	0.362	104.8	-0.28586	-0.02797	7.017
BBGeGe GA2	0	¹ A ₁	0.063	0.063	-0.501	0.375	41.6	-0.24392	-0.04425	5.433
BBGeGe GA3	1	³ A'	0.021	0.021	-0.431	0.389	81.1 -	0.31008	-0.02808	7.673
BGeBGe BA1	0	¹ A _g	0.763	0.763	-0.763	-0.763	230.2	-0.29886	-0.01728	7.662
BGeBGe BA2	2	⁵ A _g	-0.371	-0.371	0.371	0.371	110.6	-0.27885	-0.00308	7.504
BGeGeB BB1	0	¹ A ₁	-0.249	-0.249	0.249	0.249	189.2	-0.30761	0.00009	8.373
BBGeGe BB2	1	³ A	-0.138	-0.233	0.312	0.059	160.7	-0.30279	-0.00228	8.177
GeBBGe GB1	0	¹ Σ	-0.256	-0.255	0.255	0.256	48.7	-0.25235	-0.05490	5.373
GeBBGe GB2	0	¹ A _g	-0.049	-0.049	0.049	0.049	82.4	-0.22699	-0.06070	4.525
GeBGeB GB3	1	³ π	0.536	0.176	0.338	0.021	-61.5	-0.29049	-0.02644	7.185
GeGeBB GB4	0	¹ Σ	0.424	-0.617	0.014	0.179	38.3	-0.27713	-0.05961	5.919

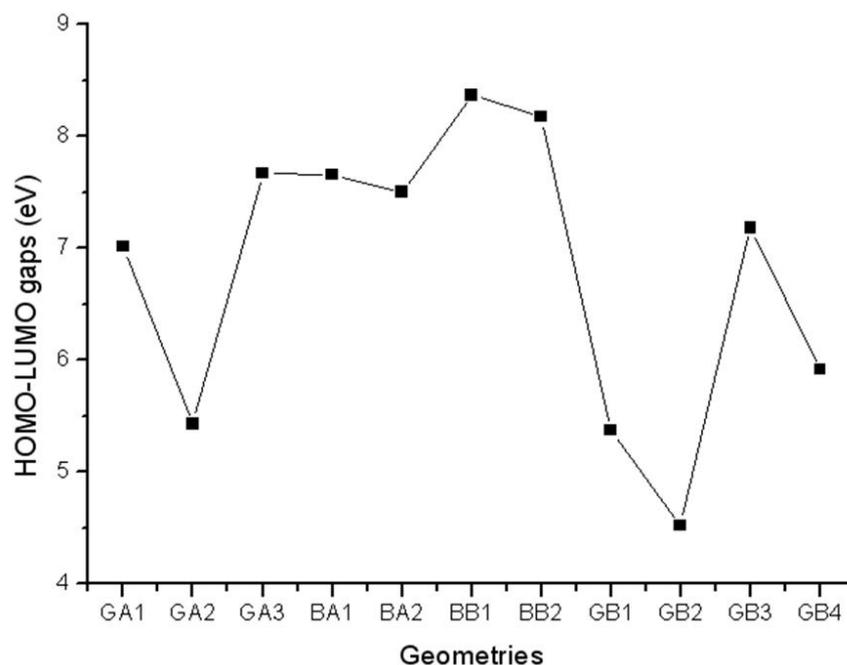


Fig. 3 – Geometry dependence of the HOMO-LUMO gap of the stable Ge_2B_2 clusters.

4. HOMO-LUMO gaps

The HOMO and LUMO energies as well as the corresponding highest occupied molecular orbital and lowest unoccupied molecular orbital (HOMO-LUMO) gaps of BGeGeB clusters are tabulated in Table 2 and reflected in Fig. 3. Based upon the calculated results, one can find that the Ge_2B_2 clusters have large HOMO-LUMO gaps at the ranges of 4.5-8.4 eV, indicating that Ge_2B_2 clusters are good semiconductor-related materials. On the basis of the calculated results, one can find that the cyclelike Ge_2B_2 clusters with HOMO-LUMO gaps at the range of 7.5-8.4 eV are bigger than the linearlike and Y-type Ge_2B_2 clusters with HOMO-LUMO gaps at the range of 4.5-7.5 eV, reflecting that the cyclelike Ge_2B_2 clusters have stronger chemical stabilities than the others and is suitable for the important wide band-gap semiconductor which has attracted much attention owing to its wide applications. Furthermore, we can predict that the HOMO-LUMO gaps for the charged Ge_2B_2 clusters with the large HOMO-LUMO gaps can be detachable experimentally because of their stronger chemical stability, especially for the cyclelike Ge_2B_2 clusters. It should be mentioned that the cyclelike Ge_2B_2 clusters have largest HOMO-LUMO gaps and have the most stable chemical stabilities. Consequently, the cyclelike Ge_2B_2 clusters are special stable in ionization and

dissociation process and the Ge_2B_2 BB1 contributes to forming the most stable B_n -doped germanium nanoclusters, and makes them more attractive for the cluster-assembled nanomaterial.

5. Relative Stabilities

In order to investigate the relative stabilities of the most stable BGeGeB clusters, it is significant to calculate the average atomic binding energies (E_b) for BGeGeB clusters. The average atomic binding energies of BGeGeB clusters are defined as:

$$E_b = 2 E_T(\text{B}) + 2 E_T(\text{Ge}) - E_T(\text{Ge}_2\text{B}_2)/4$$

where $E_T(\text{Ge})$, $E_T(\text{B})$, and $E_T(\text{Ge}_2\text{B}_2)$ denote the total energies for the most stable Ge, B, and Ge_2B_2 clusters, respectively. The calculated $E_T(\text{Ge})$ and $E_T(\text{B})$ with zero-point energies are -2075.279997 and -24.574680 hartree, respectively. The calculated E_b values of the most stable BGeGeB isomers are plotted as the curves of E_b against the corresponding the geometries in Fig. 4 and also summarized in Table 1. It should be mentioned that the features are intuitively viewed and the peaks of the curve in Fig. 4 correspond to those clusters have enhanced local stabilities. As seen from Fig. 4, one can find that the GA1, GB1, BA1, and BB1 are more stable than their neighboring clusters and the BB1 geometry is the most stable one.

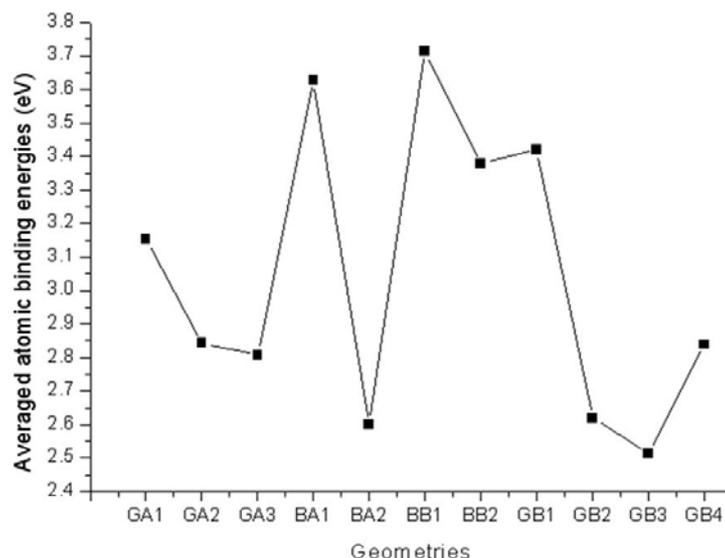


Fig. 4 – Geometry dependence of the averaged atomic binding energy of the stable Ge₂B₂ clusters.

CONCLUSION

Boron-germanium clusters have been systematically studied by using mPW2PLYP(d) method with 6-311++G(2df) basis sets. The geometrical stabilities of the Ge₂B₂ clusters are discussed based upon the calculated averaged atomic binding energies and reveal that the trapezoid singlet BBGeGe isomer is the most stable geometry and has the largest HOMO-LUMO gap, reflecting that trapezoid singlet BBGeGe isomer can be used to form the most stable B_n-doped germanium nanoclusters which has been important wide band-gap semiconductor material and has attracted much attention owing to its wide applications. On the basis of the calculated HOMO contour maps, it is indicated that all the ringlike isomers have strong π -type bonding interactions and the stabilities are mainly determined by dispersion dominated π - π interactions. The predicted structures and electronic properties are expected to be informative for the identification of Ge₂B₂ cluster.

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