A DFT Study on The Minimum Energy Configurations and Stabilities of Cationic Boron Clusters B_n ($n = 2 - 13$)

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Abstract: We present optimized structures of cationic boron clusters consisting of 2 through 13 atoms. Our density functional theory (DFT) calculations are done with Gaussian03. The exchange–correlation potential is approximated within the generalized gradient approximation (GGA) by using the functional B3LYP. Cationic boron clusters form either planar or quasi–planar type atomic configurations. We studied systems with charge Q up to 4. It is observed that small cations become unstable after double, triple or quadruple ionizations. However, large–size cations are stable even for higher ionizions. Our frequency analysis reveals that all of the cationic clusters studied have positive vibrational frequencies indicating that no transition state is possible. A brief analysis of binding energy per atom, average bond length, the highest occupied molecular orbital (HOMO), and the lowest unoccupied molecular orbital (LUMO) gap values are also provided. We further present the most possible fragmentation channel as an additional stability analysis, and discuss conditions for the Coulomb explosion.

Keywords: Boron clusters, electronic structure, cluster stability, Coulomb explosion

1. INTRODUCTION

Boron is a light semiconductor with low density and high melting point. It shows metallic [Mailhiot et al. (1990)], and superconducting [Eremets et al. (2001), Ma et al. (2004)] behaviour under high pressure. It is as hard as diamond. In addition, it can build molecules of unlimited size by covalently bonding to itself. All these properties make boron very promising in device applications, and in many different areas like medicine, nonlinear optics, and polymer science [for details see Grimes (2004)].

To our knowledge, the first experimental investigation on small boron clusters was reported by Anderson et al. (1987). They produced cationic boron clusters with laser ablation technique and obtained some fragmentation channels. Later they reported chemical reactivity of cationic clusters with several species like D_2O and CO_2 [see Anderson et al. (1990), and Anderson et al. (1991)]. In addition, cationic boron clusters ranging in size from 2 to 52 were produced from hexagonal boron nitride with laser ablation by La Placa et al. (1992). Several theoretical analyses based on the *ab initio* methods deal with electronic and atomic properties of small boron clusters. The ground and excited states of neutral and cationic B_2 clusters were obtained by using the multi–reference single– and double (MRD)– excitation configuration interaction (CI) [Bruna et al. (1989)], and the unrestricted Hartree–Fock and the variational CI methods [Carmichael (1989)]. Moreover, Ray et al. (1992) computed the equilibrium geometry, binding and fragmentation energies of neutral and cationic boron clusters of size 2 through 8 atoms with the *ab initio* techniques via taking into account the correlation energy with a perturbative approach. In a detailed *ab initio* molecular orbital (MO) study, Kato et al. (1992) investigated the equilibrium geometry, electronic structure, energy of neutral and cationic boron clusters composed of 2–12 atoms. Subsequently, they studied several optimized planar and non–planar structures of neutral and cationic B_{12}, and B_{13} clusters by employing the *ab initio* MO theory [see Kato et al. (1993)]. They proved that all three–dimensional (3D) structures proposed for both neutral and charged B_{13} clusters are unstable. Boustani (1994) performed a systematic local spin density formalism study on small cationic boron clusters B_n^+ ($n = 2$–14). He figured out that these systems prefer planar or quasi–planar type configurations. Ricca et al. (1996) also studied the optimized geometries of cationic clusters using DFT and adopting the B3LYP functional. Their computations

confirmed the conclusion of Boustani that cationic boron clusters prefer planar or quasi–planar geometries.

Dissociation channels and the Coulomb explosion in atomic and molecular clusters have been widely studied theoretically and experimentally, since they provide invaluable information about stability of a system. Sattler et al. (1981) observed the Coulomb explosion through mass spectra of doubly charged metallic, ionic and van der Waals clusters. Depending on their size, doubly charged clusters were found to be either stable against the fragmentation or they dissociated into singly charged cations. Fragmentation channels of cationic sodium clusters in small size range [Iniguez et al. (1990)], and the Coulomb explosion in large metallic sodium clusters [Calvo (2006)] have been investigated by using the *ab initio* techniques. In the case of small sized doubly ionized potassium clusters, fragments dissociated after the Coulomb explosion were proven to carry equal positive unit charge [Brechignac et al. (1994)]. Singly, doubly and triply charged lithium clusters were studied with *ab initio* techniques by Rao et al. (1987). They observed that although singly charged clusters were stable against fragmentation, doubly and triply ionized systems were Coulombically fragmented.

Stability of semiconductor clusters with various sizes has been studied from the points of view of fragmentations and the Coulomb explosion. Islam et al. (1989) reported detailed *ab initio* calculations on the fragmentation attitudes of ionized carbon clusters with several configurations, and predicted some magic numbers with a well–defined periodicity. They further discussed fragmentation of singly and doubly ionized cations, and possibility of the Coulomb explosion. A recent study of Tendero et al. (2006) also discusses fragmentation energies for neutral and positively charged small carbon clusters. The authors have shown that the fragmentation energy oscillates with cluster size, and the Coulomb explosion occurs in doubly charged cationic clusters consisting of 2, 3, and 4 atoms. Due to its importance in technological applications, stability of silicon clusters has also been investigated extensively as a function of cluster size by Qin et al. (2009).

The physical and chemical properties of boron clusters can be extracted from their stability analysis. In one of the earliest studies, Anderson et al. (1987) experimentally investigated stability of small cationic boron ions ranging in size 2 to 8 atoms with collision induced dissociation. In dissociation channels having the lowest energies, singly ionized boron atom B_1^+ appeared as the major fragment at studied collision energies. Subsequently, they examined fragmentation attitudes of cationic boron clusters up to 13 atoms using the same experimental method; and compared some of their results with those of Hanley et al. (1988) obtained through the *ab initio* method up to 6 atoms. They could observe only binary fragmentations at low collision energies. However, with increasing cluster size, 3 or 4 fragments were ejected at high collision energies. Niu et al. (1997) theoretically investigated fragmentation attitudes of singly and doubly ionized cationic boron clusters up to 6 atoms. They could not observe the Coulomb explosion in doubly charged clusters.

Planar boron clusters up to size 15 have already been realized experimentally in the gas phase by Zhai et al.

(2002). Some experimental and theoretical studies indicate that transition from planar geometry to 3D structures starts at B_{20}, which is a double–ring tubular structure [see Wang et al. (1995), Li et al. (2003), and An et al. (2006)]. This transition point is still a controversial issue.

In this study we shall deal with multi–charged small cationic boron clusters. The paper is organized as follows. The methodology of our calculations is presented in the next section. In section 3 we discuss our results and compare them with the literature wherever possible. Finally our conclusions are given in section 4.

2. COMPUTATIONAL METHOD

We solved the Kohn–Sham equations by employing the first principle calculations within the DFT framework. The exchange–correlation potential was approximated by the GGA using three–parameter hybrid exchange functional of Becke (1993), and the nonlocal correlation functional of Lee, Yang, and Parr (1998) (LYP). Geometry optimization and vibrational frequency computations were performed with software package Gaussian (2003). Our calculations were done through three stages. First, using a smaller basis set (3-21G), we obtained wavefunctions and a reliable initial geometry for each cluster. Then, in order to check if an open shell structure was possible, we optimized the wavefunctions through a larger basis set (6-311+G*) by allowing electrons diffuse into the shells with larger energy. Finally we reoptimized the geometries, and performed the vibrational frequency computations to find the equilibrium structures and transition states of clusters. We did not impose any constraint on the symmetry during the optimization and frequency computations.

We consider planar or quasi–planar n–atom cationic boron clusters B_n^Q, with $2 \leq n \leq 13$, and $1 \leq Q \leq 4$. Our recipe for obtaining the equilibrium configuration of a charged cluster is as follows. Atomic positions of the optimized neutral cluster were chosen as the initial coordinates of atoms in a single–charged cationic system. Then we optimized this configuration as we had done for the neutral state, and obtained equilibrium geometry of the single–charged cluster. We followed the same procedure as Q value was increased. We also found the ground state spin multiplicity of the cationic clusters. We further computed the frequencies of vibrational modes in order to verify the equilibrium configurations. Since negative or imaginary frequencies refer to transition states, we eliminated configurations having these frequencies, and by perturbing the atomic positions we found true equilibrium geometries for which all frequencies are positive.

3. RESULTS

Small sized cationic boron clusters B_n consisting of 2–13 atoms have been experimentally proven to have either planar or quasi–planar geometry. Top views of the optimized geometries for these systems we obtained are illustrated in Fig. 1. Optimized configurations of cations with sizes 2, 3, and 4 resemble their corresponding neutral systems. However, cationic B_5 systems transform into pentagon. B_6 and B_7 cations are formed in hexagonal geometry. On the other hand, heptagonal and octagonal structures are
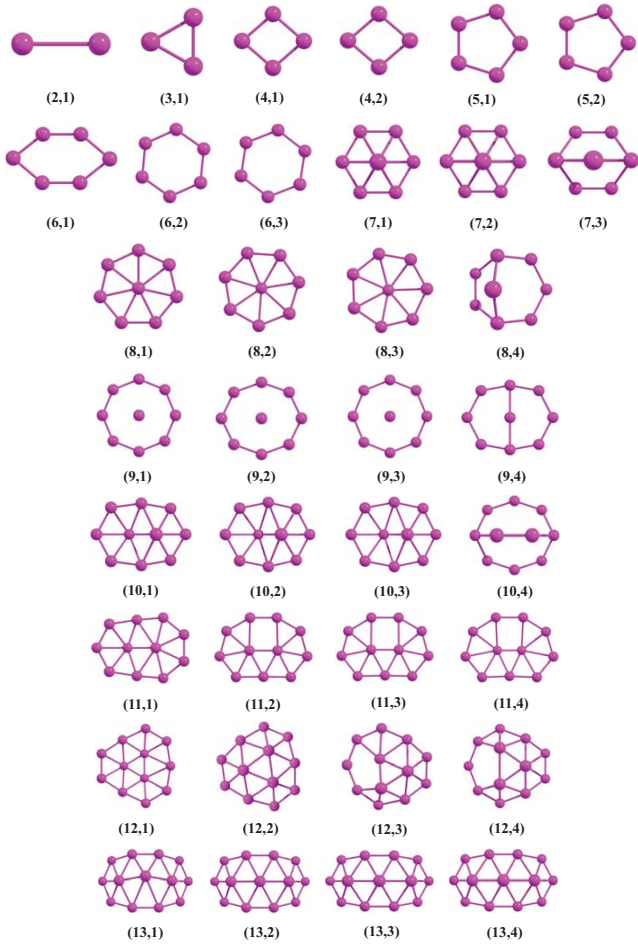
Fig. 1. (Color online) Top views of optimized structures of cationic boron clusters. Numbers in the parentheses are, respectively, the size and charge of the clusters.

observed for, respectively, B_8 and B_9 cations. Similar to neutral B_{10}, singly, doubly, and triply ionized B_{10} clusters have optimized geometries comprising hexagonal units. Most of the bonds between two inner atoms and atoms along the periphery of quartetly ionized B_{10} are broken. Indeed, two inner atoms move away, in the perpendicular direction of the plane, from the cluster. Atomic structure of four times ionized B_{10} looks like a cap. In fact this is a common situation for cationic clusters having atom or atoms within their interior region. The atom at the center moves away perpendicularly from the triply ionized B_7, and quartetly ionized B_8. Cationic B_9 clusters form in exact planar geometries. Although optimized structures of neutral B_9 and its cations are similar, a symmetrical lateral expansion is observed in quartetly ionized B_9. Singly ionized B_{11} has a geometry consisting of hexagonal and heptagonal units, but the rest up to charge $Q = 4$ have geometries similar to the neutral system. Cationic B_{11} clusters have almost planar type atomic arrangements as their neutral state. Optimized structures of neutral B_{12}, and its singly and doubly ionized cations are composed of hexagonal units. Considerable distortions occur in the structures of triply and quartetly ionized B_{12}, as is seen in Fig. 1. Atomic structures of B_{12} cations are all convex. On the other hand, cationic B_{13} clusters have cap–like optimized geometries comprising hexagonal units.

We determined variation of the average bond length (ABL) as a function of cluster size n. Although a systematic trend does not appear in the ABL as n changes, it systematically increases with Q for a given n, meaning that as the cluster loses electron it relaxes into a new expanded geometry.

The binding energy per atom (BE) in a cluster can be calculated through the relation

$$E_b = \frac{1}{n}\Big[QE_1^+ + (n-Q)E_1 - E_n^Q \Big]. \qquad (1)$$

Here E_1^+ (E_1) is the energy of singly charged (neutral) boron atom, E_n^Q is the energy of multi–charged boron cluster, and $n > Q$. We computed energy of a free boron atom and its cationic ions by employing the Gaussian03 and GGA together with the same functionals for the exchange–correlation potential. The ground state spin multiplicity (M), total energy, BE, ABL, and HOMO–LUMO energy gaps for spin up (α) and spin down (β) electrons of cationic boron clusters are presented in table 1. We observed that B_2^{+2}, B_3^{+2}, B_4^{+3}, B_5^{+3}, B_6^{+4} and B_7^{+4} are unstable.

Table 1. The ground state spin multiplicity (M), total energy (in Hartree), BE, HOMO–LUMO energy gap values for cationic boron clusters with $2 \leq n \leq 13$, and $1 \leq Q \leq 4$.

Size	Q	M	Total Energy (H)	BE (eV)	ABL (Å)	HOMO-LUMO α (eV)	β (eV)
B_2	1	2	-49.0892	1.16	2.166	2.732	4.802
B_3	1	1	-73.9376	2.46	1.577	2.643	2.643
B_4	1	2	-98.8109	3.28	1.546	3.657	2.690
	2	1	-98.2120	1.38	1.586	2.349	2.349
B_5	1	1	-123.6929	3.82	1.551	4.250	4.250
	2	2	-123.1253	2.48	1.588	4.450	2.241
B_6	1	2	-148.5203	3.93	1.570	2.231	3.112
	2	1	-148.0023	3.04	1.576	3.194	3.194
	3	2	-147.2460	1.06	1.624	3.329	1.795
B_7	1	1	-173.4178	4.28	1.661	3.259	3.259
	2	2	-172.8681	3.39	1.688	3.586	1.812
	3	1	-172.1073	1.68	1.641	2.897	2.897
B_8	1	2	-198.2792	4.42	1.690	1.406	2.526
	2	1	-197.7711	3.79	1.724	2.688	2.688
	3	2	-197.0267	2.35	1.759	2.622	1.454
	4	1	-196.0918	0.26	1.681	2.390	2.390
B_9	1	3	-223.1170	4.46	1.533	4.371	2.957
	2	2	-222.6123	3.91	1.633	1.367	2.373
	3	1	-221.9256	2.80	1.590	2.444	2.444
	4	2	-221.0261	1.05	1.678	2.374	1.817
B_{10}	1	2	-247.9819	4.57	1.680	3.519	2.108
	2	1	-247.4841	4.08	1.723	2.515	2.515
	3	2	-246.7804	3.04	1.745	2.477	2.335
	4	1	-245.9256	1.59	1.658	2.599	2.599
B_{11}	1	1	-272.8628	4.69	1.699	2.364	2.364
	2	2	-272.3754	4.28	1.692	2.156	2.432
	3	1	-271.6988	3.40	1.720	1.876	1.876
	4	2	-270.8377	2.06	1.749	1.855	2.008
B_{12}	1	2	-297.7077	4.71	1.676	3.772	1.514
	2	3	-297.2185	4.33	1.675	4.182	2.295
	3	2	-296.5447	3.53	1.746	2.162	2.355
	4	1	-295.7083	2.36	1.724	2.836	2.836
B_{13}	1	1	-322.5519	4.73	1.669	1.969	1.969
	2	2	-322.0844	4.42	1.711	1.945	1.862
	3	1	-321.4452	3.76	1.730	1.902	1.902
	4	2	-320.6239	2.71	1.752	2.159	1.782

Dissociation of clusters is typically induced by a femtosecond laser irradiation of a target cluster. Another method is to collide the clusters with an energetic electron beam, highly charged ions or atoms. Clusters can also fragment into neutral or charged species at high temperatures. General relation for the energy difference between a cluster and its fragments, or the parent and daughters, is defined as

$$\Delta E_n^Q = \sum_{j,m} E_m^j - E_n^Q, \qquad j \le Q, \qquad 1 \le m < n. \quad (2)$$

The charge and mass conservation laws yield $\sum j = Q$ and $\sum m = n$. If ΔE_n^Q is negative, the parent cluster is not stable against that fragmentation channel. In this case the energy is released and the fragmentation is spontaneous. This process is called as the Coulomb explosion. On the other hand, positive ΔE_n^Q means that the parent cluster is stable against that particular dissociation channel, and one must supply external energy to the parent for realization of the process.

We investigated fragmentation of boron clusters as a function of cluster size and their charge state. The dissociation channel we considered in this report is

$$B_n^Q \longrightarrow B_{n-1}^{Q-1} + B_1^+. \quad (3)$$
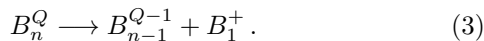
In this channel small fragment B_1 always carries a unit charge, and other fragment B_{n-1}^{Q-1} is either neutral or charged depending on the value of Q. We show calculated fragmentation energies as a function of n for the channel (3) in Fig. 2. The highest curve shows the dissociation energies of singly ionized boron clusters. In this process, smaller fragment B_1 carries a positive unit charge, and larger fragment B_{n-1} remains neutral. Since the fragmentation energy is always positive, singly ionized boron clusters are stable against this reaction. In other words, the cations need that much external energy for realization of this reaction. The lower (green) curve represents dissociation energies of doubly ionized boron clusters. In this case both fragments B_1 and B_{n-1} carry positive unit charge. The energies for doubly ionized clusters B_4, B_5, B_6, and B_9 are negative, meaning that these clusters are not stable against this process. Hence, this channel is the Coulomb explosion. Fragmentation energies for this channel are positive for the remaining doubly ionized clusters. Triply and quartely ionized boron clusters involve B_1^+ as smaller fragment and, respectively, B_{n-1}^{+2} and B_{n-1}^{+3} as larger fragments. As is seen, the energies are all negative, and more energy is released with increasing Q. Clusters with $Q = 3$ and 4 are not stable against the reaction channel and this behaviour directly proves the well-known Coulomb explosion for multi-charged boron clusters.

Obviously there are many possible fragmentation channels for multi-charged B_n clusters. Here we considered the most probable fragments that can be observed in a dissociation channel. This channel is the one for which ΔE_n^Q is minimum. Experiments and theoretical calculations have proven that neutral or ionized single boron atom are one of the main fragments in the dissociation channels of boron clusters [see Anderson et al. (1987), and Hanley et al. (1988)].
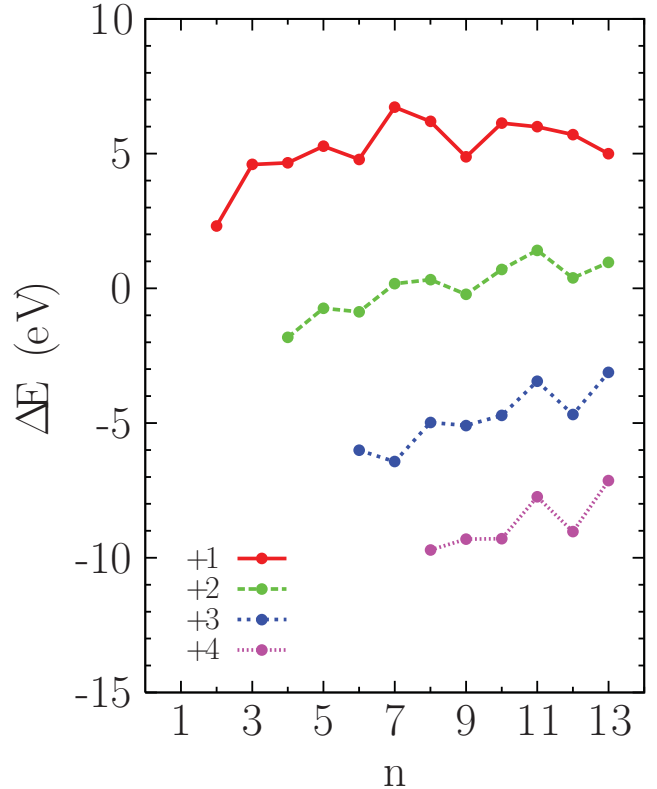

Fig. 2. (Color online) Fragmentation energy (in eV) as a function of cluster size for the channel (3).

4. CONCLUSION

In this study we have obtained the equilibrium geometries of multi-charged cationic boron clusters with size $n = 2$–13. The ABL and its dependence on n have been determined for each charge Q. Variation of the ABL is quite similar for singly, doubly and triply charged cations. Besides, ABL is found to increase with Q for a given n. Binding energy calculations show that larger cations remain stable as they loose electron, in contrast to smaller ones. Stability of a particular cluster decreases with increasing number of ionization.

We have also investigated one of the most possible fragmentation channels, and the dissociation energy of multi-ionized boron clusters. Energies of the dissociation channel we discussed here are the minimum energy differences between the parent cluster and its fragments. We especially concentrated on binary fragmentations which are preferred by the most probable reaction channels or at low collision energies in charge induced dissociation experiments. In this channel, singly ionized boron monomer B_1^+ is ejected as the small fragment. If larger fragment B_{n-1} carries more charge than the smaller one, the Coulomb explosion process is definitely possible. Besides, when both fragments carry equal charge, the Coulomb explosion occurs for clusters with $n = 4$, 5, 6, and 9. A zig-zag variation in the fragmentation energy with n appears for the channel. In any Coulomb explosion process more energy is released with increasing Q. In the case of stable clusters, the fragmentation energy decreases, or the clusters become less stable, with increasing Q. Hence, the clusters dissociate much easier as their charge increases.

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