
A Theoretical Study of Vibrational Properties of Neutral and Cationic B_{12} Clusters

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ABSTRACT: Calculations based on density functional theory predict the ground state of B_{12} and B_{12}^+ to be a convex planar configuration with C_1 symmetry. A small ionization-induced structural change in B_{12} is also predicted. It is suggested that multicentered bonds together with delocalized charge density are dominant factors in stabilizing the planar configuration over 3D configuration for B_{12} and B_{12}^+ . The calculated vibrational frequencies lie in the range of 200–1328 cm^{-1} in which the high-frequency modes are associated with asymmetric stretching of the boron atoms located at the cluster surface. The infrared spectra of both neutral and cationic B_{12} show similar infrared active modes in the high-frequency region, but different modes in the low-frequency region due to dissimilar atomic charges in the cationic B_{12} . The combined effect of charge delocalization and reduced dimensionality is reflected in the calculated static dipole polarizability of these clusters. © 2005 Wiley Periodicals, Inc. *Int J Quantum Chem* 102: 656–664, 2005

Key words: clusters; boron; density functional theory; IR spectra

1. Introduction

The boron compounds show a wide variety of structures and compositions that include single atom, connected pairs, multiple chains, planar networks, and polyhedral groupings. This variety of structures is a consequence of the peculiar elec-

tronic structure of boron, which is characterized by an unpaired electron in the $(\text{He})2s^22p^1$ configuration. It can then lead to various hybridization like sp , s^2p , sp^2 , and sp^3 between boron atoms or by the interactions with other atoms [1]. Although boron chemistry is mainly based on the B_{12} icosahedra and B_6 octahedron units [2–8], recent studies have uncovered 2D structures for small boron clusters. For example, several studies on B_{12}^+ and B_{13}^+ have reported the stable planar and quasiplanar structures [9–15] which were found to be different from the conventional 3D cages obtained in boranes [5, 6].

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The primary focus of most of the previous theoretical studies on boron clusters [11–24] has been calculations of the structural and electronic properties in which calculations of the vibrational properties of the boron clusters were not performed. Specifically, various isomeric configurations of B₁₂ were considered for electronic structure calculations [11, 18, 19, 23], but analysis of the vibrational stability of any of the isomeric configurations was not performed yet. It is well known that calculations of the vibrational properties together with the IR spectra help experimentalists in identifying the cluster configurations.

In this work, we present the results of a theoretical study based on density functional theory (DFT) with a focus on calculations of the vibrational properties of the neutral and cationic B₁₂. Furthermore, we have analyzed molecular orbitals of several conformers of B₁₂ and B₁₂⁺ to establish a general pattern of physics and chemistry of boron clusters. It is expected that such an analysis will reveal an interplay between the degree of localization of molecular orbitals and the coordination number for the cluster atoms in predicting the stability of configurational isomers of B₁₂. It has recently been pointed out that the ground-state configuration of the neutral and ionized state of a given cluster may not be the same [25]. We will therefore investigate the ionization-induced structural changes in B₁₂. We will also calculate, for the first time, the static dipole polarizability of several isomeric configurations of B₁₂ and B₁₂⁺ to assess the variation in the polarizability with the structural arrangement of boron atoms. The presentation of this article is organized as follows: In Section 2, we briefly describe computational details. Results and discussion of the geometrical features, cluster stability, vibrational stability, static dipole polarizability, and a comparison of some of the results obtained using the basis sets 6-31G(*d,p*) and 6-311G(*df*) for B₁₂ and B₁₂⁺ clusters, are presented in Section 3. In Section 4, conclusions are given.

2. Computational Method

The electronic structure calculations were performed for several neutral and cationic structural isomers of B₁₂ using the Gaussian 98 code [26]. All calculations were carried out by solving the Kohn–Sham equations in the DFT framework. We have employed the generalized gradient approximations (GGA) using the functionals of Becke’s 3-parameter

hybrid exchange functional [27] and the Lee–Yang–Parr correlation functional (B3LYP) and a double-zeta basis set (6-31G(*d,p*)) in these calculations. Some of the isomers were selected for calculations using the 6-311G(*df*) basis set to test the reliability and accuracy of the results obtained using the 6-31G(*d,p*) basis set. All the structures in this work have been fully optimized by employing the gradient and updated Hessian. The convergence criteria for the gradient and energy were set to 10^{−4} hartree/Å and 10^{−9} hartree respectively. Calculations of the static dipole polarizability was performed by applying an external electric field of strength 0.001 a.u. along the *x*, *y*, and *z* axes separately. The stability of the isomeric configurations considered here was assessed by computing the vibrational frequencies under the harmonic approximation with analytical force constants.

3. Results and Discussion

STRUCTURES AND ENERGETICS

Several isomers of B₁₂ considered for DFT calculations in this work were taken from previous studies [11, 18, 19, 22]. They can be categorized into planar (2D) and 3D configurations. Figure 1 shows the optimized geometries of some of the low-energy isomers. The details of other configurations considered here can be obtained from one of the authors. The calculated results find the neutral isomers to be in the singlet spin state. Total energy of the 3D structures are always higher than that of the planar structures. The most stable configuration is a convex structure with C₁ symmetry (i.e., B₁₂-I), which is in contrast to the reported C_{3v} structure as the most stable configuration of B₁₂ [18, 19, 23]. The C₁ configuration (i.e., B₁₂-I) consists of three B₇ units which are reported [24] to be the most stable structure of B₇. The next low-energy isomer is the C₂ planar structure (i.e., B₁₂-II), while calculations at the CI/3-21G level of theory [19] find the D_{2h} structure to be the second-lowest energy isomer for B₁₂. Because the CI/3-21G study [19] did not assess the cluster stability by the frequency calculations, both C_{3v} and D_{2h} configurations of B₁₂ may be associated with imaginary frequencies.

The next configuration in terms of total energy is a cage-type C_{2h} structure (i.e., B₁₂-III). It is different from the conventional B₁₂ icosahedra and can be viewed as four B₇ units overlapping in the opposite site where each opposite face appears as the lowest

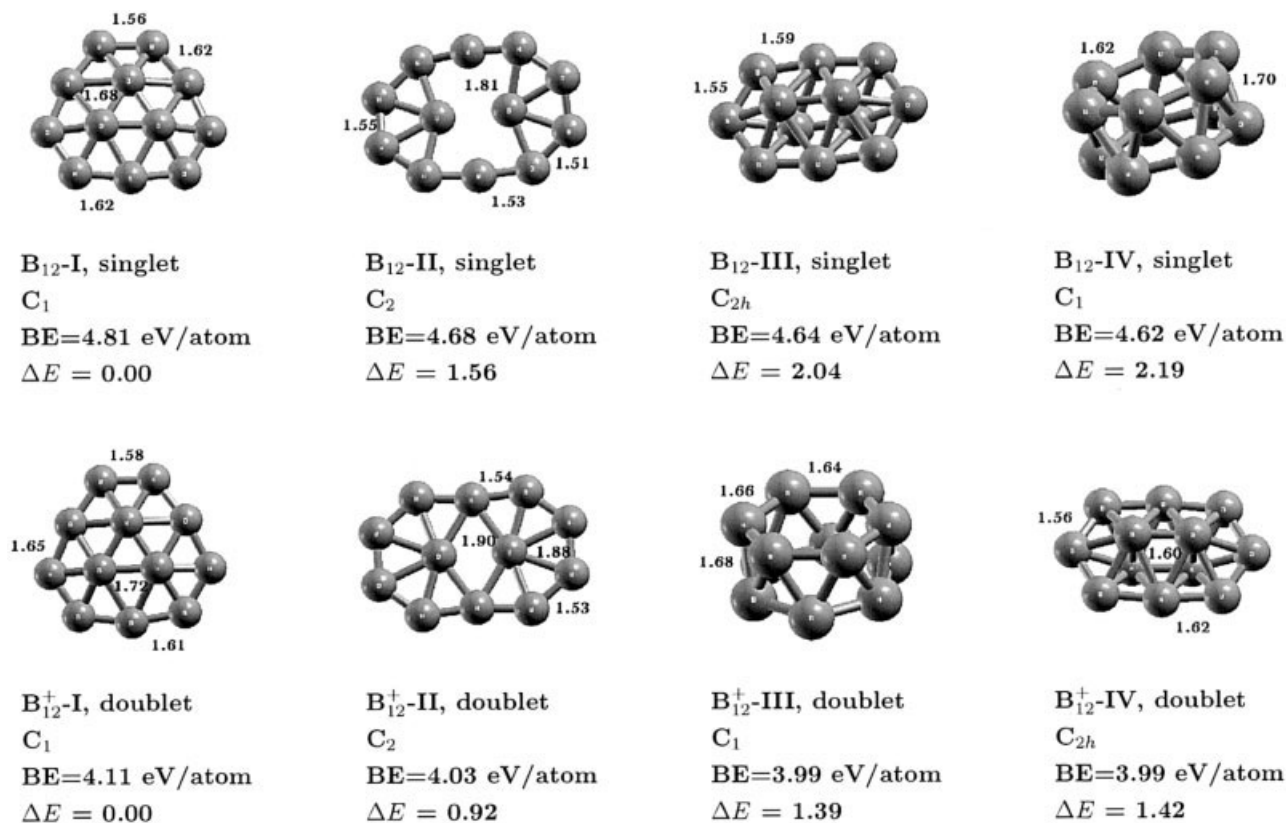


FIGURE 1. Isomeric configurations of B₁₂ and B₁₂⁺: energy differences (ΔE in eV) relative to the lowest-energy configuration, symmetry, spin multiplicity, and binding energy (eV/atom) obtained using the 6-31G(d,p) basis set.

energy configuration of B₁₀ in C_{2h} symmetry [18, 19, 23]. The double-ring isomer is the next low-energy structure (i.e., B₁₂-IV). Even though it is less stable relative to the convex C₁ structure of B₁₂, it is predicted to be extremely stable for large boron clusters [28]. The icosahedra unit, which is a fragment of a bulk [7, 8, 16], is found to be more than 3 eV higher in energy than the ground state of B₁₂.

The ionization-induced changes in ordering of the lowest-energy isomers of B₁₂ are found to be small. The ground state of B₁₂⁺ remains to be the convex C₁ structure, as also predicted by a previous study [12]. The next isomer is a C₂ planar structure at 0.92 eV above the C₁ isomer. The ordering of the next two lowest-energy isomers of B₁₂⁺ clusters are almost same as that in the neutral clusters. In this case, double-ring with C₁ symmetry and cage-type C_{2h} structure are nearly degenerate with energy difference (ΔE) of 0.03 eV. The optimized geometry of the B₁₂⁺ icosahedra is slightly distorted from its I_h symmetry and is found to be 2.78 eV higher in energy relative to the ground state. The ionization

introduces small changes in the bond lengths and bond angles of the ionized clusters as compared to their corresponding neutral species.

The stability of the isomeric configurations of B₁₂ can be assessed in terms of the binding energy per atom (BE) as: $E_b[B_n] = -(E[B_n] - nE(B))/n$, where E is the total energy of the system and n is the total number of atoms. For the lowest-energy structure of B₁₂, BE is 4.81 eV/atom. Our calculations shows that BE increases from B₆^{*} (3.95 eV/atom) to B₁₂. This is consistent with the increasing trend of BE with the cluster-size approaching to the cohesive energy of about 6.0 eV of the bulk boron [29]. The calculated binding energy per atom for the ground state of B₁₂⁺ is 4.11 eV/atom.

The vertical ionization potential is defined as the energy difference between the cationic and neutral clusters with both at the optimized geometry of the neutral cluster (i.e., $IP_{\text{vertical}} = E_{q=0} - E_{q=+1}$, where E is the total energy of the cluster and q is the

*Details of the results on B₆ can be obtained from the authors.

charge on the cluster). The adiabatic ionization potential is defined as the energy difference between the cationic and neutral clusters at their own respective optimized geometries. The calculated vertical and adiabatic IP values are 8.52 and 8.40 eV, respectively. The experimental IP value [10] is reported to be 8.20 eV. The high value of IP for B₁₂ is mainly due to the closed-shell electronic configuration in its ground state that provides a high stability of the cluster configuration.

CHEMICAL BONDING AND ELECTRONIC PROPERTIES

The chemical bonding of boron is known to be dominated by its electron-deficient character [21]. Thus, multi-center bonds such as the three-center triangular B—B—B unit become a key bonding feature in boron compounds to accommodate its electron deficiency [23]. It then results in the tendency of the boron atoms to prefer configuration based on a polyhedral unit (e.g., B₁₂ icosahedra unit) in which the triangular faces prevail. However, at the cluster level, calculations predict the preference of planar isomers over 3D isomers, including the icosahedra unit. To understand the difference in the preferred configurations at the cluster and bulk level, we have performed analysis of molecular orbitals for planar, double-ring, and icosahedra isomers of B₁₂.

The natural bond orbital (NBO) analysis [30] finds that the isomeric configurations considered here prefer sp² hybridization, as the case with B₆. For the lowest-energy configuration (i.e., B₁₂-I), the natural electron configuration for the atoms are (core)2s^{0.88}2p^{2.03}, (core)2s^{0.82}2p^{2.09}, and (core)2s^{0.55}2p^{2.66}, whereas for the 3D double-ring structure (i.e., B₁₂-IV), the natural electron configuration for the atoms is (core)2s^{0.76}2p^{2.22}. On the other hand, the natural electron configurations of the icosahedra isomer are (core)2s^{0.88}2p^{2.12}, (core)2s^{0.66}2p^{2.31}, and (core)2s^{0.67}2p^{2.30}. Also, Mulliken-partitioned atomic charge analysis suggests a negligible charge transfer among atoms in the B₁₂ isomers. Thus, the mixing of 2s and 2p orbitals among boron atoms in the clusters is expected to play an important role in forming the covalent bond that stabilizes the configurations shown in Figure 1. A comparison of some of the molecular orbitals (MOs) of the convex planar structure and double-ring configuration of the neutral B₁₂ is shown in Figure 2. A similar analysis was also performed for B₁₂⁺ isomers, which is not shown

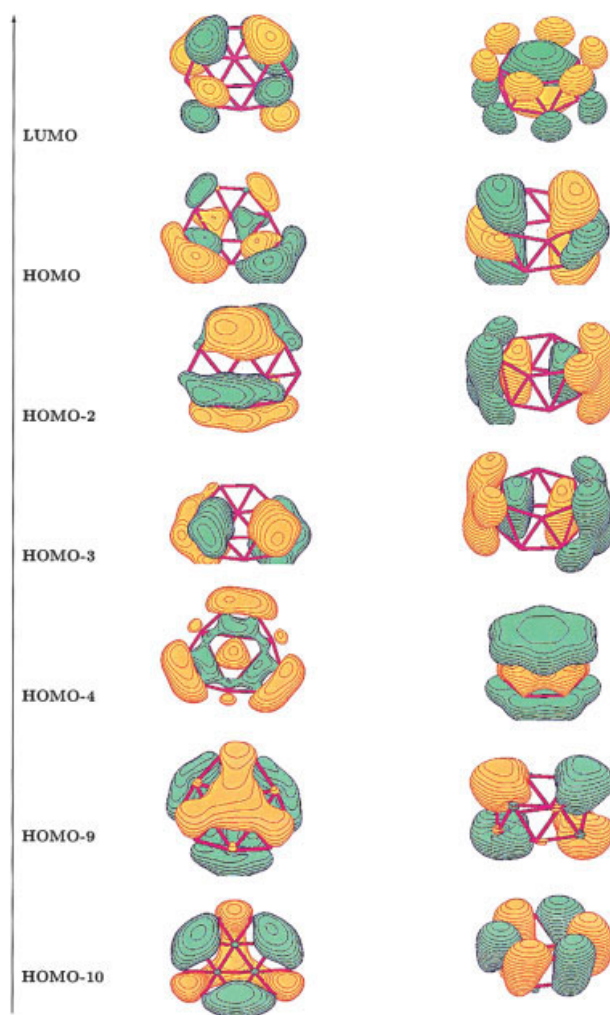


FIGURE 2. Some of the molecular orbitals (MOs) of convex planar and double-ring configurations of B₁₂. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

here. In Figure 2, we use the notation HOMO-*n* to represent the (30-*n*)th occupied molecular orbital in B₁₂, because there are 30 occupied molecular orbitals associated with 12 boron atoms in each cluster.

In the convex planar structure (i.e., B₁₂-I), the lowest unoccupied molecular orbital (LUMO) shows a localized π bonding, while both highest occupied molecular orbital (HOMO) and HOMO-1 orbital show double-degenerate localized σ bonds. The double degeneracy of the σ bond leads to a delocalization of the cluster charge density. Besides, the double degeneracy of HOMO-2 and HOMO-3 orbitals, which is effectively due to the delocalized π bonds, is found to be benzene-like in nature [23]. The multicentered, delocalized σ bonds are present

in HOMO-4 and HOMO-10 orbitals. It is noteworthy that the fully delocalized π bonding present in the HOMO-9 orbital shows that the aromaticity that was found in benzene is also present in this neutral boron cluster.

The double-ring isomer (i.e., B₁₂-IV) with a diameter of 3.2 Å is composed of two rings of 6 atoms each, 1.62 Å apart, arranged in a staggered configuration. Each ring is rotated by an angle of $\pi/6$ with respect to the other ring in order to form the staggered configuration. Such a staggered double-ring formation facilitates the sp² hybridization, thereby making it comparatively stable among 3D structures. The charge density of HOMO and LUMO given in Figure 2 shows a strongly localized π and σ bond, respectively. The HOMO shows a π bond between the atoms of each ring, while the LUMO shows a lateral p-p overlap between the atoms of both rings. The HOMO and (HOMO-1) orbitals are doubly degenerate, giving rise to an effective delocalization. The double degeneracy of HOMO-2 and HOMO-3 orbitals shows a localized σ bonding, as compared to the delocalized π bonding observed in the convex planar isomer. The delocalized π bonding is also seen in HOMO-4 and HOMO-9 orbitals, and the HOMO-10 orbital shows the localized σ bonding.

Thus, a comparison of the molecular orbitals of the convex planar and double-ring isomers suggests that the order of π and σ orbitals is reversed for HOMO and LUMO, respectively. This fact, together with a relatively larger degree of delocalized orbitals in the planar configuration, appears to be the dominant cause for the preference of the planar configuration in the ground state of neutral and cationic B₁₂ clusters. We also note here that the high strain energy due to a smaller diameter of the ring may contribute in making the double-ring isomer less competitive in becoming the lowest-energy configuration of B₁₂.

Besides chemical bonding, the coordination number of boron atoms is expected to play an important role in determining the cluster stability. In bulk, the coordination number of boron atoms is 5 [31]. On the other hand, the calculated (average) coordination number of boron atoms in planar and double-ring configurations is 4 as compared to that of 5 in the icosahedra configuration. However, the values of BD (i.e., 2-center bond based on Lewis structure) calculated from the NBO analysis [29] are 9 and 1 for planar and icosahedra isomers, respectively. This distinct difference in the values of BD suggests that the icosahedra configuration (which is

a fragment of a bulk) is not energetically preferred despite of having a high coordination number for boron atoms.

It is well known that stability of a given cluster is reflected in the HOMO-LUMO gap. The HOMO-LUMO gap for neutral and cationic lowest-energy structure of B₁₂ are 3.61 and 1.51 eV. In general, ionized B₁₂ clusters have a smaller gap relative to the corresponding neutral isomers. Given that the larger HOMO-LUMO gap generally refers to a higher value of the chemical hardness [32], ionized boron clusters appear to be chemically more reactive than the corresponding neutral clusters.

VIBRATIONAL FREQUENCIES

The neutral and cation isomers of B₁₂ considered in this work are at local minima on the potential energy surface and their corresponding 3N-6 vibrational modes are shown in Figure 3, which excludes the translational and rotational modes frequencies. We are not aware of any previous theoretical study on the vibrational properties of B₁₂ and B₁₂⁺. It is to be noted here that B₁₂⁺ is reported to be in transition state at the level of local spin density theory [11].

The calculated vibrational frequencies of B₁₂ lie in the range of 200–1328 cm⁻¹. The distribution of the vibrational frequencies of both neutral and cation isomers shows the similar trend. The frequencies in the cation isomers are generally lower than the corresponding neutral isomers. The lowest frequencies in the ground state of neutral and cationic isomers are 200.2 cm⁻¹ and 107.7 cm⁻¹, respectively. The highest frequencies in the ground state of neutral and cationic isomers are 1327.5 cm⁻¹ and 1304.7 cm⁻¹, respectively. The lower-frequency region of both neutral and cationic B₁₂ is associated with the bending modes, while the higher-frequency region (>1000 cm⁻¹) is dominated by the stretching modes. The highest-frequency mode of the ground state of B₁₂ and B₁₂⁺ is associated with an asymmetric stretching of boron atoms located at the cluster surface.

From computational standpoint of view, the prediction of IR intensities can be accomplished by using the mixed second derivatives of energy with respect to geometric motion and an external electric field by permitting estimation of changes in the dipole moment as a function of vibrations. The intensity (km/mol) of an IR absorption band is proportional to the square of change in molecular electric dipole moment μ in normal coordinates (i.e., $I_i = \text{const} \times (\partial\mu/\partial Q_i)^2$) [33].

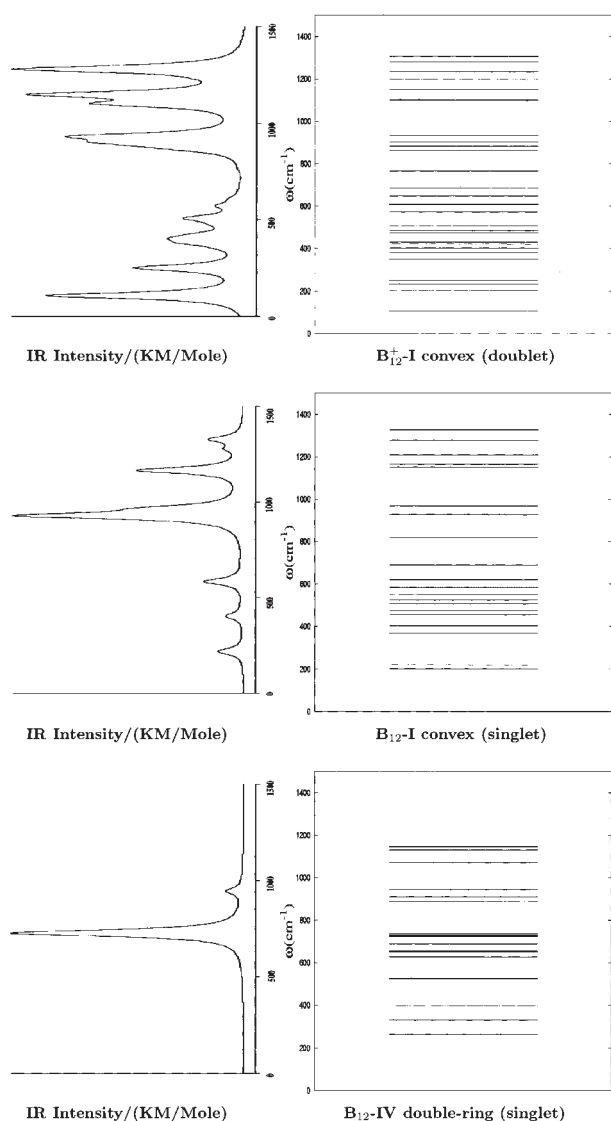


FIGURE 3. The vibrational frequencies and the corresponding IR spectra of the B₁₂ and B₁₂⁺ clusters.

The IR spectra of the lowest-energy configuration of neutral (i.e., B₁₂-I), cation (i.e., B₁₂⁺-I), and neutral double-ring (i.e., B₁₂-IV) is shown in Figure 3. The neutral lowest-energy configuration has its IR active modes located in the region around 928 cm⁻¹ and 1165 cm⁻¹, which are expected to be in A₁ and E mode if the convex planar structure is to be in C_{3v} symmetry [34]. The cationic ground-state structure has multiple IR active modes in the regions 108, 251, 933, 1149, and 1280 cm⁻¹. The maximum peak is located at 1280 cm⁻¹, which is associated with asymmetric stretching of three apex boron atoms. The IR active regions in both neutral and

cationic ground state are quite similar with each other in the high-frequency region. Due to dissimilar atomic charges, the cationic isomer has another IR active mode region in the lower-frequency range. On the other hand, the neutral double-ring structure has only one unique IR active mode in its IR spectra at about 730 cm⁻¹, and is mainly associated with three stretching modes that lie closely to each other at 723 cm⁻¹, 724 cm⁻¹, and 730 cm⁻¹. These three IR active modes are expected to be in A₁, B₁, and B₂ mode if the double-ring is to be in C_{2v} symmetry [34]. At I_{max} of about 730 cm⁻¹, diameter of both the rings are found to expand and contract in an opposite way that acts like a “breathing mode” due to its unique geometrical structure.

STATIC DIPOLE POLARIZABILITY

Measurements of static dipole polarizability are frequently used by experimentalists to characterize the nature of atomic, molecular, and cluster species. Physically, it describes the response of the electronic cloud of the given cluster in the presence of an external static electric field. Instead of giving an exhaustive description of different characters in each isomers, we are presenting some of the features predicted by calculations in this study. In general, the calculated dipole moments of the neutral and cationic B₁₂ show a close relationship with the structural symmetry of the cluster. The convex planar structure (i.e., B₁₂-I), which does not have a center of symmetry, has nonzero dipole moments, whereas cage-type (i.e., B₁₂-III) and double-ring (i.e., B₁₂-IV) structures have zero dipole moments.

A direct comparison with the parallel (α_{xx}), transverse (α_{yy}), and perpendicular (α_{zz}) components of the static dipole polarizability of different isomers in the B_n series reported in the previous studies [35–37] is not possible because of the different orientations of *x*, *y* and *z* axes chosen in calculations. Thus, we have calculated the directional averaged static polarizability, $\alpha_{\text{avg}} = (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})/3$, to extract a general trend with the increase in the cluster size. Table I shows the calculated dipole moments and the static polarizability tensor along the *x*, *y*, and *z* directions with the total dipole moment and directional averaged static polarizability of the low-energy configurations of B₁₂ and B₁₂⁺.

The directional averaged static polarizability per atom (i.e., α_{avg}/n , where *n* is the total number of boron atoms in the cluster) shows overall decrease from 17.63 a.u. to 12.23 a.u. in going from B₃³⁷ to B₁₂. From Table I, we observe that the ionization of the

TABLE I

Calculated dipole moment (μ_i in debye), components of the static polarizability tensor (α_{ij} in a.u.), and directional averaged static polarizability (α_{avg} in a.u.) for low-energy configurations of B_{12} and B_{12}^+ .

Property	$B_{12}, Q = 0$				$B_{12}, Q = +1$			
	B_{12} -I	B_{12} -II	B_{12} -III	B_{12} -IV	B_{12}^+ -I	B_{12}^+ -II	B_{12}^+ -III	B_{12}^+ -IV
μ_x	-0.0004	0.0000	0.0000	0.0002	1.0654	0.0000	0.0000	-0.0019
μ_y	0.0017	0.0000	0.0000	-0.0001	0.1008	0.0000	0.0000	0.0002
μ_z	2.0752	0.0011	0.0000	0.0000	1.2516	-0.0017	0.0000	-0.0039
μ_{Tot}	2.0752	0.0011	0.0000	0.0002	1.6467	0.0017	0.0000	0.0044
α_{xx}	186.24	172.45	91.47	135.25	187.43	173.65	84.55	129.86
α_{yy}	185.76	236.95	183.63	135.03	206.20	230.76	168.64	126.15
α_{zz}	68.36	69.70	129.43	110.35	65.92	60.91	126.34	104.45
α_{avg}	146.79	159.70	134.84	126.88	153.18	155.11	126.51	120.15

neutral cluster decreases the polarizability. The ground state of the neutral cluster (i.e., B_{12} -I) has a significantly less polarizability ($\alpha_{\text{avg}} = 146.79$ a.u.) as compared to that of the chainlike structure ($\alpha_{\text{avg}} = 241.60$ a.u.) reported in a previous study [37]. It is interesting to note that delocalization of the charge distribution in a given cluster configuration plays an important role in reducing the static dipole polarizability. The large difference in α_{avg} between the chainlike and convex planar structure may therefore be attributed to the localized π -electron population along chain direction [37] as compared to delocalized π and σ bonds in the convex planar configuration of B_{12} .

BASIS SETS: A COMPARISON OF SOME RESULTS OBTAINED USING 6-31G(*d,p*) AND 6-311G(*df*) BASIS SETS

To test the reliability and accuracy of the 6-31G(*d,p*) basis set used in this study, we also performed DFT calculations for the first two low-energy geometries of B_{12} and B_{12}^+ , using the 6-311G(*df*) basis set. Table II collects some of the results in terms of binding energy, ΔE , ω_{lowest} , ω_{highest} , and HOMO-LUMO gap of B_{12} and B_{12}^+ clusters showing no significant difference in either energetics or frequencies obtained using the 6-31G(*d,p*) and 6-311G(*df*) basis sets. Furthermore, the calculated values of vertical IP and adiabatic IP using the 6-311G(*df*) basis set come out to be 8.81 and 8.68 eV, respectively. The 6-31G(*d,p*) basis set yields values of 8.52 and 8.40 eV for vertical IP and adiabatic IP, respectively.

4. Conclusion

The ground state of B_{12} and B_{12}^+ is predicted to be the convex planar C_1 configuration in contrast to the convex planar C_{3v} configuration reported by previous studies. The ionization-induced structural changes in B_{12} are found to be very small. It is shown that the basic building block of the bulk crystal is energetically not preferred for the B_{12} cluster despite of its high coordination number for the boron atoms. The B_{12}^+ isomers are found to be less stable than the corresponding neutral species. A very high IP value and a large HOMO-LUMO gap show the very high stability of the neutral cluster. A combination of delocalized charge density and multicentered bonds facilitates the planar structure to be more energetically preferable than other isomers in B_{12} . The calculated vibrational frequencies lie in the range of 200–1328 cm^{-1} . The IR spectra of both neutral and cationic B_{12} show similar IR active modes in the higher-frequency region, but different modes in the lower-frequency region due to dissimilar atomic charges in the cationic B_{12} . A combination of charge delocalization and reduced dimensionality of structural configurations appears to play an important role in determining the static dipole polarizability of B_{12} clusters. These results can be used as a baseline for future research on electrooptical properties in nano devices based on boron. It is also observed that the use of the 6-311G(*df*) basis set does not introduce a significant change in the structural energetics, electronic properties, and vibrational properties of B_{12} and B_{12}^+ .

TABLE II
Comparison of some results obtained using 6-31G(d,p) and 6-311G(df) basis sets
for low-energy isomers of B₁₂ and B₁₂⁺.

Isomer	Property	6-31G(d,p) basis set	6-311G(df) basis set
B ₁₂ -I, C ₁	<i>E</i>	-297.971543	-298.042294
	ΔE	0.00	0.00
	BE	4.81	4.75
	HOMO-LUMO gap	3.61	3.60
	ω_{lowest}	200.2	200.02
	ω_{highest}	1327.5	1321.68
B ₁₂ -II, C ₂	<i>E</i>	-297.914032	-297.989053
	ΔE	1.56	1.45
	BE	4.68	4.63
	HOMO-LUMO gap	2.75	2.79
	ω_{lowest}	62.9	58.83
	ω_{highest}	1635.76	1634.16
B ₁₂ ⁺ -I, C ₁	<i>E</i>	-297.662832	-297.723387
	ΔE	0.00	0.00
	BE	4.11	4.02
	HOMO-LUMO gap	1.51	1.52
	ω_{lowest}	107.7	102.24
	ω_{highest}	1304.7	1300.7
B ₁₂ ⁺ -II, C ₂	<i>E</i>	-297.629154	-297.692217
	ΔE	0.92	0.85
	BE	4.03	3.95
	HOMO-LUMO gap	1.95	1.94
	ω_{lowest}	68.34	64.37
	ω_{highest}	1609.76	1605.29

Units: total energy, *E* (hartree), energy difference relative to the ground state, ΔE (eV), binding energy, BE (eV/atom), HOMO-LUMO gap (eV), lowest and highest vibrational frequency (ω_{lowest} , ω_{highest} in cm⁻¹).

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References

- Semiconductors—Basic Data, 2nd rev ed. Madelung, O., Ed.; Springer-Verlag: Berlin–Heidelberg–New York, 1996.
- Lipscomb, W. L. Boron Hydrides; W. A. Benjamin: New York, 1963.
- Muetterties, E. L. (Ed.) Boron Hydride Chemistry, Academic: New York, 1975.
- Muetterties, E. L. (Ed.) The Chemistry Of Boron and Its Compounds, John Wiley: New York, 1967.
- Jemmis, E. D.; Balakrishnarajan, M. M.; Pancharatna, P. D. Chem Rev 2002, 102, 93.
- Jemmis, E. D.; Balakrishnarajan, M. M.; Pancharatna, P. D. J Am Chem Soc 2001, 123, 4313.
- Perkins, C. L.; Trenary, M.; Tanaka, T. Phys Rev Lett 1996, 77, 4772.
- Hubert, H.; Devouard, B.; Garvie, L. A. J.; O'Keeffe, M.; Buseck, P. R.; Petuskey, W. T.; McMillan, P. F. Nature 1998, 391, 376.
- Hanley, L.; Anderson, S. L. J Phys Chem 1987, 91, 5161.
- Hanley, L.; Whitten, J. L.; Anderson, S. L. J Phys Chem 1988, 92, 5803.
- Boustani, I. Int J Quantum Chem 1994, 52, 1081.
- Ricca, A.; Bauschlicher Jr, C. W. Chem Phys 1996, 208, 233.
- Gu, F. L.; Yang, X.; Tang, A. C.; Jiao, H.; Scheleyer, P. V. R. J Comput Chem 1998, 19, 203.
- Aihara, J. I. J Phys Chem A 2001, 105, 5486.
- Fowler, J. E.; Ugalde, J. M. J Phys Chem A 2000, 104, 397.
- Kawai, R.; Weare, J. H. J Chem Phys 1991, 95, 1151.
- Ray, A. K.; Howard, I. A.; Kanal, K. M. Phys Rev B 1992, 45, 14247.
- Boustani, I. Chem Phys Lett 1995, 240, 135.
- Boustani, I. Phys Rev B 1997, 55, 16426.

20. Niu, J.; Rao, B. K.; Jena, P. *J Chem Phys* 1997, 107, 132.
21. Alexandrova, A. N.; Boldyrev, A. I.; Zhai, H. J.; Wang, L. S.; Steiner, E.; Fowler, P. W. *J Phys Chem A* 2003, 107, 1359.
22. Ma, J.; Li, Z. H.; Fan, K. N.; Zhou, M. F. *Chem Phys Lett* 2003, 372, 708.
23. Zhai, H. J.; Kiran, B.; Li, J.; Wang, L. S. *Nature Materials* 2003, 2, 827.
24. Alexandrova, A. N.; Boldyrev, A. I.; Zhai, H. J.; Wang, L. S. *J Phys Chem A* 2004, 108, 3509.
25. Costales, A.; Kandalam, A. K.; Pandey, R. *J Phys Chem A* 2003, 107, 4508.
26. Frisch, M.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*. Gaussian, Inc.: Pittsburgh, PA, 1998.
27. Becke, A. D. *J Chem Phys* 1993, 98, 5468.
28. Chacko, S.; Kanhere, D. G.; Boustani, I. *Phys Rev B* 2003, 68, 035414.
29. Lide, D. R. *CRC Handbook of Chemistry and Physics*; CRC Press: Boca Raton, FL, 1995.
30. Carpenter, J. E.; Weinhold, F. *J Mol Struct (Theochem)* 1988, 169, 41.
31. Gersten, J. I.; Smith, F. I. *The Physics and Chemistry of Materials*; John Wiley: New York, 2001.
32. Pearson, R. G. *Chemical Hardness*; Wiley-VCH: Weinheim–New York, 1997.
33. Koch, W.; Holthausen, M. C. *A Chemist's Guide to Density Functional Theory*, 2nd ed.; Wiley-VCH: Weinheim–New York, 2002.
34. Cotton, F. A. *Chemical Applications of Group Theory*, 3rd ed.; John Wiley: New York, 1990.
35. Reis, H.; Papadopoulos, M. G. *J Comp Chem* 1999, 20, 679.
36. Reis, H.; Papadopoulos, M. G.; Boustani, I. *Int J Quantum Chem* 2000, 78, 131.
37. Abdurahman, A.; Shukla, A.; Seifert, G. *Phys Rev B* 2002, 66, 155423.