

B₁₁₁, B₁₁₂, B₁₁₃, and B₁₁₄: The most stable core-shell borospherenes with an icosahedral B₁₂ core at the center exhibiting superatomic behaviors

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ABSTRACT

Boron allotropes are known to be predominately constructed by icosahedral B_{12} cages, while icosahedral- B_{12} stuffing proves to effectively improve the stability of fullerene-like boron nanoclusters in the size range between $B_{98}-B_{102}$. However, the thermodynamically most stable core-shell borospherenes with a B_{12} icosahedron at the center still remains unknown. Based on the structural motif of $D_{5h} C_{70}$ and extensive first-principles theory calculations, we predict herein the high-symmetry $C_{5v} B_{111}^+$ (3) which satisfies the Wade's n+1 and n+2 skeletal electron counting rules exactly and the approximately electron sufficient $C_s B_{111}$ (4), $C_s B_{112}$ (5), $C_s B_{113}$ (6), and $C_s B_{114}$ (7) which are the most stable neutral core-shell borospherenes with a B_{12} icosahedron at the center reported to date in the size range between $B_{68}-B_{130}$, with $C_s B_{112}$ (5) being the thermodynamically most favorite species in the series. Detailed orbital and bonding analyses indicate that these spherically aromatic species all contain a negatively charged icosahedral B_{12}^{2-} core at the center which exhibits typical superatomic behaviors in the electronic configuration of $1S^21P^61D^{10}1F^8$, with its dangling valences saturated by twelve radial B-B 2c-2e σ bonds between the B_{12} inner core and the B_{70} outer shell. The infrared (IR) and Raman spectra of the concerned species are computationally simulated to facilitate their future characterizations.

KEYWORDS

first-principles theory, borospherenes, structures, bonding, superatomic behaviors, spherical aromaticity

1 Introduction

As a prototypical electron-deficient element, boron is known to form at least sixteen distinct allotropes predominately constructed by three-dimensional (3D) icosahedral B₁₂ cages that in many cases are accompanied by other boron atoms lying outside the icosahedrons [1, 2]. Typical multi-center twoelectron $(nc-2e^{-})$ bonds (n ranging from one to the total number)of atoms in the molecule) are formed to compensate for the electron deficiency of boron in both 3D bulk boron allotropes and polyhedral molecules [3]. In contrast, size-selected boron clusters $(B_n^{-/0})$ in gas phases have been confirmed by joint photoelectron spectroscopy (PES) and first-principles theory investigations to possess planar or quasi-planar (2D) structures in a unexpectedly wide range of cluster size (n = 3-38, 41, 42), except cage-like borospherenes $D_{2d} B_{40}^{-/0}$ discovered in 2014 and C_3/C_2 B₃₉⁻ observed in 2015 [4–8]. The borospherene family has been extended in theory to include the B_n^q series (n = 36-42, q = n-40) in different charge states [9–12]. Seashell-like borospherenes C₂ B₂₈⁻ and C_s B₂₉⁻ were late observed in PES measurements as minor isomers competing with their 2D global minimum (GM) counterparts [13, 14]. Boron cluster monocations B_n^+ (n = 16-25) were shown to possess doublering tubular geometries in a joint ion-mobility measurements and density functional theory (DFT) investigation [15]. Extensive GM searches showed that complicated structural competitions exist in medium-sized B_n clusters, with B₄₆ being the smallest core-shell boron cluster ($B_4@B_{42}$) and B_{48} , B_{54} , B_{60} , and B_{62} being the first bilayer boron clusters predicted to date [16, 17].

The proposal of a perfect cage-like I_h B₈₀ isovalent with I_h C₆₀ (B₈₀~C₆₀) aroused considerable interests in all-boron fullerene clusters [18-21]. However, Ih B80 late proved to be much less stable than its amorphous C1 B80 counterparts in incomplete core-shell configurations [19-21]. Amorphous core-shell B₆₈, B₇₄, and B₈₄ clusters with a partially encapsulated icosahedral B₁₂ core have also been predicted [20, 22]. Larger boron nanoclusters in complete core-shell configurations are expected to favor icasohedral-B12 stuffed structures in thermodynamics. It turned out to be true that icosahdral-B12 stuffing effectively improved the stability of core-shell D_{3d} B₉₈, C_{3v} B₉₉, C_{2h} B₁₀₀, C_s B₁₀₁, and D_{3d} B₁₀₂ which appeared to be systematically more stable than their fullerene-like counterparts at DFT-PBE level, with Cs B101 being the most stable species in the series [23]. These core-shell boron clusters all contain an icosahedral-B12 stuffed B84 (B12@B12@B60) network based on the structural motif of I_h C₆₀. Late density functional theory (DFT) investigations presented a slightly different relative energy order for these boron clusters, with an amorphous core-shell C1 B102 being 0.029 eV/atom more stable than Cs B101 at DFT-PBE level [24]. However, to the best of our knowledge, core-shell boron clusters based on the structural motifs of larger carbon fullerenes like C70 and C80 have not been explored in literature and the thermodynamically most stable core-shell borospherenes with a B12 icosahedron at the center still remains unknown in both experiments and theory to date.

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Based on the structural motif of the experimentally known D_{5h} C_{70} and extensive first-principles theory calculations, we predict herein the spherically aromatic core-shell C_{5v} B_{111}^+ (3), C_s B_{111} (4), C_s B_{112} (5), C_s B_{113} (6), and C_s B_{114} (7) which all contain a icosahedral- B_{12} stuffed B_{94} network ($B_{12}@B_{12}@B_{70}$) with the negatively charged B_{12}^{2-} core at center behaving like a superatom with the electronic configuration of $1S^21P^61D^{10}1F^8$. The approximately electron sufficient B_{111} (4), B_{112} (5), B_{113} (6), and B_{114} (7) according to Wade's n+1 and n+2 skeletal electron counting rules appear to be the most stable neutral core-shell species reported to date in the size range between $B_{68}-B_{130}$.

2 Theoretical procedures

Preliminary structural optimizations were performed on core-shell B108, B109, B110, B111, B112, B113 and B114 clusters using the CP2K software suite [25], with 12, 36, 69, 144, 232, 328 and 418 initial structures manually constructed based on the structural motif of D_{5h} C₇₀, respectively. Similar structural optimizations were implemented on core-shell C_{2h} B₁₂₀, C_s B₁₂₁, Ci B122, D5d B124, Cs B125, C2 B126, C2h B128 and C2 B130 in the structural motif of Ih C80. Low-lying structures were then fully optimized with frequencies checked at DFT-PBE0 [26], TPSSh [27] and B3LYP [28] levels of theory with the basis set of 6-31G(d) [29] using the Gaussian 09 suite [30]. More reliable relative energies were calculated for the two lowest-lying isomers at PBE0/6-311G(d) [26, 29]. Natural bonding orbital (NBO) analyses were performed using the NBO 6.0 program [31]. Born-Oppenheimer molecular dynamics (BOMD) simulations were performed on the B_{112} (5) at 600, 800, and 1,000 K for 30 ps to check the dynamic stability of the system, using the software suite CP2K program [25]. Nucleus-independent chemical shifts (NICS) [32, 33] were calculated at the cage center of the B_{12} icosahedron to assess the spherical aromaticity of core-shell systems. Chemical bonding analyses on B_{111}^+ (3) and B_{112} (5) were conducted using the adaptive natural density partitioning (AdNDP 2.0) method [34, 35] at the PBE0/6-31G level [26, 29]. The IR and Raman spectra of B_{111}^+ (3) and B_{112} (5) were computationally simulated at PBE0/6-31G(d).

3 Results and discussions

3.1 Structures and stability

Based on the fullerene-like $D_{5h} B_{70}$ (1) constructed by substituting all carbon atoms of D_{5h} C₇₀ by boron, the high-symmetry core-shell C_{5v} B₉₄ (2) (B₁₂@B₁₂@B₇₀) network can be generated by incorporating an icosahedral- B_{12} centered $I_h B_{24}$ unit ($B_{12}@B_{12}$) inside $B_{70}(1)$ (Fig. 1). Unfortunately, the infinite $B_{94}(2)$ is unstable in nature. It possesses one closo B₁₂ isocohedron at the center, two nido B₆ pentagonal pyramids on the top and bottom, five nido B6 pentagonal pyramids on the lower waist, and five nido B7 hexagonal pyramids on the upper waist. It is therefore 50 electron deficient according to the Wade's n+1 and n+2 skeletal electron counting rules [36, 37], similar to the situation in the icosahedral-B₁₂ stuffed Ih B84 (B12@B12@B60) [23]. The 50 electron deficient B_{94} (2) can be made electron sufficient by adding 17 capping B atoms (with 51 valence electrons) on the cage surface while detaching one valence electron from the system to form the high-symmetry $C_{5\nu} B_{111^+}$ (3) monocation (Fig. 1) which follows the Wade's skeletal electron counting rules exactly. $C_{5\nu} B_{111^+}$ (3) with the smallest vibrational frequency of $v_{\rm min} = 192.1 \text{ cm}^{-1}$ at PBE0/631G(d) turned out to be a true minimum on the potential energy surface as the most stable isomer of the monocation obtained in this work (Fig. S1 in the Electronic Supplementary Material (ESM)).



Figure 1 Optimized structures of the core-shell borospherenes $C_{5\nu} B_{111}^+$ (3), $C_s B_{111}$ (4), $C_s B_{112}$ (5), $C_s B_{113}$ (6), and $C_s B_{114}$ (7) at PBE0/6-311G(d) level, compared with the manually constructed $D_{5h} B_{70}$ (1) and $C_{5\nu} B_{94}$ (2) based on the structural motif of $D_{5h} C_{70}$. Atoms on the icosahedral B_{12} core are highlighted in red.

More generally, B_{94} (2) can approach near the electron sufficiency by adding 17, 18, 19, and 20 boron atoms on the cage surface to generate the neutral core-shell C_s B₁₁₁ (4), C_s B₁₁₂ (5), C_s B₁₁₃ (6), and C_s B₁₁₄ (7), respectively (Fig. 1). B₁₁₁ (4) contains 12 penta-coordinate apex B atoms over 12 B5 pentagons and 5 hexa-coordinate apex B atoms in 5 B₆ hexagons in an overall C_s symmetry, B₁₁₂ (5) possesses 12 penta-coordinate apex B atoms over 12 B5 pentagons and 6 hexa-coordinate apex B atoms in 6 B₆ hexagons (including 5 in the middle waist and 1 at the bottom), B_{113} (6) can be constructed by adding two equivalent hexa-coordinate B capping atoms to B_{111^+} (3) in two B_6 hexagons on the top, while B_{114} (7) can be obtained from B_{111}^+ (3) by addition of three hexa-coordinate B atoms in three B₆ hexagons on the top. The approximately electron sufficient C2h B120, Cs B121, Ci B122, D5d B124, Cs B125, C2 B126, C2h B128 and C2 B130 with a B104 (B12@B12@B80) network in the structural motif of I_h C₈₀ (Fig. S2 in the ESM) are also considered here to compare with the previously reported most stable C₁/C_s B₁₀₁ and C₁/D_{3d} B₁₀₂ [23, 24].

The calculated cohesive energies per atom (E_c) defined as $(E_c = (E_t - nE)/n$ are summarized in Table 1, Fig. 2, Fig. S3, and Table S1 in the ESM, where E_t is the total energy of the B_n cluster and E the energy of a boron atom. As clearly shown in Fig. 2 and Fig. S3 in the ESM, the E_c of the core-shell B₆₈₋₁₃₀ clusters exhibits three obvious and consistent local minima at C_1 B₁₀₁, C_s B₁₁₂ (5), and D_{5d} B₁₂₄ at PBE0/6-311G(d), TPSSh/ 6-311(d), and B3LYP/6-311G(d) levels, respectively, evidencing the relative stability of the core-shell species concerned in this work. The closely lying C1 B101 and C1 B102 around the first minimum reported by Zhao et al. appear to be 0.007/0.003 and 0.011/0.007 eV/atom more stable than the $C_s B_{101}$ and $D_{3d} B_{102}$ proposed by Jemmis et al. based on the structural motif of $I_h C_{60}$ at PBE0/TPSSh, respectively, with C1 B101 being slightly more stable than C1 B102 by 0.010/0.009 eV/atom at PBE0/TPSSh. The close-lying $C_s B_{111}$ (4), $C_s B_{112}$ (5), $C_s B_{113}$ (6), and $C_s B_{114}$ (7) around the second minimum with the cohesive energies of E_c = 5.671/5.397, 5.678/5.404, 5.676/5.402, and 5.670/5.395 eV/atom at PBE0/TPSSh turn out to be the most stable core-shell borospherenes reported to date in the size range between $B_{68}-B_{130}$, with $C_s B_{112}$ (5), the lowest-lying isomer of the neutral with the smallest vibrational frequency of $v_{\min} = 65.2 \text{ cm}^{-1}$ (Fig. S4 in the ESM), being the most stable core-shell species in thermodynamics in the series. Our B_{111} (4), B_{112} (5), B_{113} (6), and B_{114} (7) are 0.031/0.030, 0.038/0.037, 0.036/0.035, and

Table 1 Calculated cohesive energies per atom (E_{c} eV/atom) and HOMO-LUMO energy gaps (ΔE_{gap} , eV) of the optimized core-shell boron clusters B_n (n = 68-130) at PBE0 /6-311G(d) and TPSSh/6-311G(d) levels

Cluster(Symmetry)	PBE0		TPSSh	
	$-E_{c}$	$\Delta E_{\rm gap}$	$-E_{c}$	$\Delta E_{\rm gap}$
$B_{68}(C_1)$ [18]	5.527	1.557	5.261	1.047
$B_{80}(C_1)$ [19]	5.529	1.368	5.262	0.820
$B_{84}(C_1)$ [17]	5.533	1.603	5.267	0.958
$B_{100}(C_{2h})$ [23]	5.588	0.721	5.321	0.321
$B_{101}(C_1)$ [24]	5.640	1.242	5.367	0.805
$B_{102}(C_1)$ [24]	5.630	1.240	5.358	0.722
$B_{106}(C_{5v})$	5.611	1.139	5.343	0.357
$B_{108}(C_s)$	5.642	1.609	5.372	1.058
$B_{109}(C_s)$	5.658	1.643	5.383	0.883
$B_{110}(C_s)$	5.666	1.751	5.390	1.007
$B_{111}(C_s)$	5.671	1.286	5.397	0.691
$B_{112}(C_s)$	5.678	1.826	5.404	1.251
$B_{113}(C_s)$	5.676	1.210	5.402	0.659
$B_{114}(C_s)$	5.670	1.518	5.395	0.923
$B_{120}(C_{2h})$	5.610	1.154	5.342	0.808
$B_{121}(C_s)$	5.628	1.430	5.358	1.018
$B_{122}(C_i)$	5.627	1.087	5.356	0.778
$B_{124}(D_{5d})$	5.665	0.864	5.389	0.428
$B_{125}(C_s)$	5.660	1.266	5.384	0.702
$B_{126}(C_2)$	5.643	1.209	5.369	0.695
$B_{128}(C_{2h})$	5.611	1.333	5.340	0.743
$B_{130}(C_2)$	5.593	1.640	5.320	1.68

0.030/0.028 eV/atom more stable than the previously reported C_1 B₁₀₁ [24] at PBE0/TPSSh, respectively. In fact, as demonstrated in Fig. 2 and Table 1, C_s B₁₀₈, and C_s B₁₀₉, and C_s B₁₁₀ in the structural motif of D_{5h} C₇₀ are already slightly more stable than C_1 B₁₀₁ at both PBE0 and TPSSh. The D_{5d} B₁₂₄, C_s B₁₂₅, and C_2 B₁₂₆ species around the third minimum obtained in this work also appear to be systematically more stable than the previously reported C_1 B₁₀₁ [24] (by 0.025/0.022, 0.020/0.017, and 0.003/ 0.002 eV/atom at PBE0/TPSSh, respectively), with D_{5d} B₁₂₄ as the third local minimum constructed from the highly stable cage-like D_{5d} B₁₀₀ [38] in the structural motif of I_h C₈₀ being 0.013/0/015 eV/atom less stable than C_s B₁₁₂ (5) at PBE0/TPSSh.

We address here that the three local minima at C_1 B₁₀₁, C_8 B₁₁₂ (5), and D_{5d} B₁₂₄ on the $E_{c} \sim n$ curves in Fig. 2 correspond to core-shell borospherenes in the structural motifs of $I_h C_{60}$, D_{5h} C_{70} , and $I_h C_{80}$, respectively. The prediction of B_{111} (4), B_{112} (5), and B_{113} (6), and B_{114} (7) as the most stable core-shell borospherenes reported to date in the size range between B68-B130 clearly indicates that the slightly elongated ellipsoidal D_{5h} B₇₀ (1) constructed from D_{5h} C₇₀ provides the right cavity and most suitable structural motif to form core-shell borospherenes with an icosahedral-B₁₂ core at the center, while the perfect spherical I_h B₆₀ built from I_h C₆₀ and I_h B₈₀ obtained from I_h C₈₀ appear to be either slightly too small or too big in size to host an icosahedral B12 core comfortably inside. The most stable B112 (5) has the largest calculated HOMO-LUMO gap of ΔE_{gap} = 1.826/1.251/1.667 eV at PBE0/TPSSh/B3LYP in the core-shell boron clusters between B₆₈-B₁₃₀ (Table 1 and Table S1 in the ESM), well demonstrating its high chemical stability in the B_n series. The previously proposed quasi-planar $C_2 \alpha - B_{112}$ [39] and newly constructed hexa-ring tubular D₂ B₁₁₂ depicted in Fig. S4 in the ESM prove to be much less stable than B_{112} (5) (by 15.11 eV and 16.88 eV at PBE0/6-31G(d), respectively).

As indicated in Fig. S5 in the ESM, the thermodynamically stable $C_s B_{112}$ (5) also appears to be dynamically stable, as evidenced by the small calculated average root-mean-square-deviations of RMSD=0.11, 0.11, and 0.11 Å and maximum bond length deviations of MAXD = 0.64, 0.62, and 0.61 Å at 600, 800, and 1,000 K, respectively. The basic structural configuration of $C_s B_{112}$ (5) as the initial "seed" has been well maintained during the BOMD simulations, with no isomers with lower energies observed.

3.2 Bonding analyses

Detailed NBO and AdNDP bonding analyses were performed on closed-shell B₁₁₁⁺ (**3**) and B₁₁₂ (**5**) to better interpret their high stability. With the calculated natural charges of q = -1.81and -2.00 |e|, respectively, the icosahedral B₁₂ core in B₁₁₁⁺ (**3**) and B₁₁₂ (**5**) can be practically viewed as an icosahedral B₁₂²⁻ dianion, with its dangling valences saturated by twelve radial B-B 2c-2e bonds between the B₁₂ inner core and B₇₀ outer shell. To better interpret the bonding patterns of these core-shell borospherenes, we performed first an AdNDP analysis on the perfect icosahedral I_h B₁₂H₁₂²⁻ which is the best known closo borohydride dianion with high chemical stability [**3**]. As shown in Fig. 3(a), I_h B₁₂H₁₂²⁻ possesses 12 equivalent 2c-2e B–H σ -bonds with the occupation numbers of ON = 1.98 |e|. Its



Figure 2 Calculated cohesive energy per atom (E_c , eV/atom) as a function of optimized core-shell boron clusters B_n (n = 68-130) at (a) PBE0/6-311G(d) and (b) TPSSh/6-311G(d).



Figure 3 AdNDP bonding patterns of (a) $I_h B_{12}H_{12}^{2-}$ and (b) $C_s B_{112}(5)$, with the occupation numbers (ONs) indicated.

remaining 26 skeletal electrons are evenly distributed in 13 delocalized 12c-2e bonds on the B₁₂ icosahedron, including 1 12c-2e S-type bond, 3 12c-2e P-type bonds, 5 12c-2e D-type bonds, and 4 12c-2e F-type bonds with ON = 1.92-2.00 |e|. Such a bonding pattern has its origin from the superatomic electronic configuration $1S^21P^61D^{10}1F^8$ of I_h B₁₂H₁₂²⁻ (Fig. S6 in the ESM) which has a quadruply degenerate HOMO (g_u).

The AdNDP bonding pattern of B₁₁₂ (5) depicted in Fig. 3(b) well reflects the superatomic behaviors of its icosahedral B₁₂²⁻ core. It possesses in the first and second rows 12 2c-2e B-B σ bonds in radial directions to saturate the dangling valences of the B_{12}^{2-} core, 25 2c-2e B-B σ bonds between 20 B₆ hexagonal holes (except the B-centered hexagon at the bottom), 90 3c-2e σ bonds on 12 B₆ pentagonal pyramids and 5 B₇ hexagonal pyramids on the middle waist, 10 5c-2e π bonds on 5 B₇ hexagonal pyramids on the top waist, 5 6c-2e π bonds over 5 B_6 pentagonal pyramids on the top, 5 7c-2e π bonds over 5 B_7 hexagonal pyramids on the middle waist, 1 7c-2e σ bond on the B₇ hexagonal pyramid at the bottom, and 7 7c-2e π bonds on 2 pentagonal bipyramids on the top and bottom and 5 pentagonal bipyramids on the lower waist, in an overall symmetry of Cs. The remaining 13 12c-2e skeletal bonds on the icosahedral B12²⁻ core in the following four rows exhibit obvious superatomic characteristics, including 1 12c-2e S-type bond, 3 12c-2e P-type bonds, 5 12c-2e D-type bonds, and 4 12c-2e F-type bonds, well corresponding to the 13 12c-2e bonds of $I_h B_{12}H_{12}^{2-}$ in Fig. 3(a). $C_{5\nu} B_{111}^+$ (3) possesses a similar bonding pattern with $C_s B_{112}$ (5) (Fig. S7 in the ESM). It also contains a superatomic icosahedral B122- core with the electronic configuration of 1S²1P⁶1D¹⁰1F⁸. Such bonding patterns render spherical aromaticity to B_{111}^+ (3) and B_{112} (5), as evidenced by the negative calculated NICS values of NICS = -24.4 and -41.8 ppm at their geometrical centers, respectively. With the calculated NICS = -32.8, -31.8, and -25.2 ppm at the cage centers, respectively, the open-shell $B_{111}(4)$ and $B_{113}(6)$ and closed-shell B_{114} (7) also appear to be spherically aromatic in nature.

3.3 IR and Raman spectral simulations

The infrared (IR) and Raman spectra of $C_{5\nu} B_{111}^+$ (3) and $C_{s\nu}$ B_{112} (5) are computationally simulated at PBE0/6-31G(d) in Fig. 4 to facilitate their spectral characterizations. $C_{5\nu} B_{111}^+$ (3) exhibits six major IR peaks at 285 cm⁻¹ (e₁), 676 cm⁻¹ (a₁), 783 cm⁻¹ (e₁), 964 cm⁻¹ (a₁), 1,056 cm⁻¹ (e₁), and 1,235 cm⁻¹ (e₁), while $C_s B_{112}$ (5) possesses six strong IR peaks at 639 cm⁻¹ (a'), 730 cm⁻¹ (a"), 982 cm⁻¹ (a'), 1,102 cm⁻¹ (a'), 1,191 cm⁻¹ (a'), and 1,234 cm⁻¹ (a'), respectively. The major Raman active peaks of B_{111}^+ (3) occur at 391 cm⁻¹ (a₁), 632 cm⁻¹ (a₁), 1,038 cm⁻¹ (a_1) , 1,055 cm⁻¹ (a_1) , 1,124 cm⁻¹ (e_2) , and 1,253 cm⁻¹ (a_1) , with the weak peaks at 203 cm⁻¹ (a₁) and 320 cm⁻¹ (a₁) representing typical radial breathing modes (RBMs) of the core-shell system which can be used to characterize hollow boron nanostructures [40]. B₁₁₂ (5) displays six major Raman active peaks at 196 cm⁻¹ (a'), 350 cm⁻¹ (a'), 615 cm⁻¹ (a'), 932 cm⁻¹ (a'), 1,102 cm⁻¹ (a'), and 1,454 cm⁻¹ (a'), with two typical RBM vibrations at 213 cm⁻¹ (a') and 350 cm^{-1} (a'), respectively.

4 Conclusions

Extensive first-principles theory calculations performed in this work indicate that the icosahedral- B_{12} stuffed $C_s B_{111}$ (4), $C_s B_{112}$ (5), $C_s B_{113}$ (6), and $C_s B_{114}$ (7) based on the structural motif of D_{5h} C₇₀ and D_{5d} B₁₂₄, C_s B₁₂₅, and C₂ B₁₂₆ based on the structural motif of I_h C₈₀ are systematically more stable than the previously reported C_1/C_s B₁₀₁ and C_1/D_{3d} B₁₀₂ in the structural motif of I_h C₆₀ [23, 24], with C_s B₁₁₂ (5) being the most stable core-shell borospherene with a B12 icosahedron at the center in the size range between B_{68} - B_{130} . These spherically aromatic nanoclusters all contain a negatively charged spherically aromatic icosahedral B12²⁻ core exhibiting typical superatomic behaviors in the electronic configuration of 1S²1P⁶1D¹⁰1F⁸. Using B₁₁₁ (4), B₁₁₂ (5), B₁₁₃ (6), and B₁₁₄ (7) as "seeds", bigger core-shell borospherenes with bi- or multi-icoschedral-B₁₂ cores could be achieved which may serve as intermediate species to form bulk boron allotropes in bottom-up mechanisms.



Figure 4 Simulated IR and Raman spectra of (a) $C_{5\nu} B_{111}^+$ (3) and (b) $C_s B_{112}$ (5) at PBE0/6-31G(d) level.

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