1. Introduction

Boron has a number of bulk allotropes consisting of three-dimensional (3D) cage-like structural units to compensate its electron deficiency. However, early theoretical studies suggested that small boron clusters with less than 14 atoms prefer planar or quasi-planar (2D) structures. During the past decade, the structures and bonding of size-selected boron clusters \( \text{B}_n \) have been systematically investigated using photoelectron spectroscopy (PES) and first-principles theory calculations. This body of work has established the 2D borophene concept of borophenes and the 3D fullerene-like \( \text{B}_{40} \) which marked the onset of borospherene chemistry. Here, we present a joint photoelectron spectroscopic and first-principles study of \( \text{B}_{37}^- \) and \( \text{B}_{38}^- \), which are in the transition size range between the 2D borophene-type clusters and the 3D borospherenes. These two clusters are found to possess highly stable 2D global-minimum structures consisting of a double-hexagonal vacancy. Detailed bonding analyses reveal that both \( \text{B}_{37}^- \) and \( \text{B}_{38}^- \) are all-boron analogues of coronene \((\text{C}_{24}\text{H}_{12})\) with a unique delocalized \( \pi \) system, featuring dual \( \pi \) aromaticity. These clusters with double hexagonal vacancies can be viewed as molecular motifs for the \( \chi_3 \)-borophene which is the most stable form of borophenes recently synthesized on an Ag(111) substrate.

Boron clusters have been found to exhibit a variety of interesting electronic, structural, and bonding properties. Of particular interest are the recent discoveries of the 2D hexagonal \( \text{B}_{36}^- \) which led to the concept of borophenes and the 3D fullerene-like \( \text{B}_{40} \) which marked the onset of borospherene chemistry. Here, we present a joint photoelectron spectroscopic and first-principles study of \( \text{B}_{37}^- \) and \( \text{B}_{38}^- \), which are in the transition size range between the 2D borophene-type clusters and the 3D borospherenes. These two clusters are found to possess highly stable 2D global-minimum structures consisting of a double-hexagonal vacancy. Detailed bonding analyses reveal that both \( \text{B}_{37}^- \) and \( \text{B}_{38}^- \) are all-boron analogues of coronene \((\text{C}_{24}\text{H}_{12})\) with a unique delocalized \( \pi \) system, featuring dual \( \pi \) aromaticity. These clusters with double hexagonal vacancies can be viewed as molecular motifs for the \( \chi_3 \)-borophene which is the most stable form of borophenes recently synthesized on an Ag(111) substrate.
the investigation of size-selected boron clusters. The global minimum of B$_{40}^-$ was found to be a 2D structure with a DHV, whereas the D$_{2d}$ B$_{40}^-$ borospherene was slightly higher in energy. However, for neutral B$_{40}$ the D$_{2d}$ borospherene cage consisting of twelve interwoven BDCs was overwhelmingly the global minimum. The B$_{39}^-$ cluster was subsequently found to consist of two nearly degenerate, axially chiral C$_1$ and C$_2$ borospherene isomers which are also dominated by interwoven BDCs.

An interesting question is what are the structures of B$_{37}^-$ and B$_{38}^-$? These two clusters are in the transition size range between the borophene-type 2D structures and the 3D borospherenes. A previous DFT calculation suggested that neutral B$_{38}$ possesses a borospherene cage global minimum with a low-lying 2D isomer consisting of a DHV. A subsequent comment at higher levels of theory showed that the 2D and 3D structures of B$_{38}$ are nearly degenerate with the 2D structure slightly lower in energy. However, there have been no studies on the B$_{38}^-$ anion or on B$_{37}^-$0. The two missing clusters are important to understand the structural transitions and there may be a competition between 2D and 3D isomers.

We have undertaken a joint PES and quantum chemical study on the B$_{37}^-$ and B$_{38}^-$ clusters in the current article. The PES spectra for both clusters display relatively well-resolved spectral features. Global minimum searches revealed that both B$_{37}^-$ and B$_{38}^-$ consist of 2D structures with a DHV. The 3D cage isomers are significantly higher in energy and were not present experimentally. Chemical bonding analyses show that the 2D B$_{38}^-$ and B$_{37}^-$ are all-boron analogues of coronene (C$_{24}$H$_{12}$), featuring unique dual $\pi$ aromaticity.

2. Methods

2.1. Experimental methods

The experiments were performed using a magnetic-bottle PES apparatus equipped with a laser vaporization cluster source, details of which can be found elsewhere. Briefly, boron clusters were produced by focusing a laser beam on a 10B-enriched disk target. The laser-induced plasma was cooled by a high pressure He carrier gas seeded with 5% Ar. The nascent clusters were entrained by the carrier gas and underwent a supersonic expansion to produce a cold cluster beam (about 200 K). Negatively charged clusters were extracted perpendicularly from the collimated cluster beam and analyzed using a time-of-flight mass spectrometer. The B$_{38}^-$ and B$_{37}^-$ clusters of current interest were mass-selected and decelerated before being intercepted by a detachment laser beam. Photodetachment experiments were performed using the 193 nm (6.424 eV) radiation from an ArF excimer laser. Photoelectrons were collected at nearly 100% efficiency using a magnetic-bottle and analyzed in a 3.5 m long electron flight tube. The photoelectron spectra were calibrated using the known spectrum of Au$^+$. The energy resolution of the instrument was $\Delta E_k/E_k \approx 2.5\%$, that is, $\sim$25 meV for 1 eV kinetic energy electrons.

2.2. Computational methods

Global-minimum searches were first performed for B$_{38}^-$ using both the minima-hopping algorithm and the TGmin code, in combination with manual structural constructions based on the known low-lying isomers of B$_{35}$, B$_{36}$, and B$_{40}^-$.

On the basis of the structural information of B$_{38}^-$, only the minima-hopping approach was utilized to search for the global minimum of B$_{37}^-$. The minima-hopping searches for B$_{38}^-$ and B$_{37}^-$ were done using the BIGDFT electronic structure code employing a systematic wavelet basis in combination with pseudopotentials and the standard local-density approximation (LDA) and the Perdew–Burke–Ernzerhof (PBE) exchange–correlation functional. For each cluster anion, six independent minima-hopping runs were performed, starting from six different low-lying structures. About 1700 and 2200 stationary points were probed for B$_{38}^-$ and B$_{37}^-$, respectively. TGmin searches were done for B$_{38}^-$ to check the minima-hopping results. The TGmin code was implemented in the CP2K program and employed the DFT formalism with the PBE exchange–correlation functional and the Goedecker–Teter–Hutter pseudopotential with the associated double-$\zeta$ valence plus polarization (DZVP) basis set. With more than 1000 stationary points probed, the TGmin searches yielded the same global minimum for B$_{38}^-$, as the minima-hopping runs.

The low-lying isomers of B$_{38}^-$ and B$_{37}^-$ were then fully re-optimized at the PBE0/6-311+G* level, which has proved to be a reliable method for boron clusters in this size regime. Vibrational frequencies were checked to ensure that the reported isomers are true minima. We calculated the vertical detachment energies (VDEs) of the B$_{38}^-$ and B$_{37}^-$ global minima using the time-dependent DFT method (TD-PBE0/6-311+G*). The global minimum of B$_{38}^-$ was found to be a doublet (C$_{2h}$, $^2A'^\prime$) with an unpaired electron. Electron detachment from the $^3A'$ state produced two almost degenerate neutral states: a triplet B$_{38}$(A') and an open-shell singlet B$_{38}$(1A'). Thus, the first two VDEs of B$_{38}^-$ were calculated as the energy differences between the anion ground-state ($^3A'$) and the neutral triplet $^3A'$ and the open-shell singlet 1A' states at the anion ground-state geometry, respectively. Higher VDEs were obtained by adding the singlet and triplet excitation energies of the neutral to the first two VDEs. One-electron detachment from the closed-shell B$_{37}^-$ generates doublet neutral states only, yielding fewer detachment channels.

All calculations were performed using the Gaussian 09 package. Canonical molecular orbitals (CMOs) and the adaptive natural density partitioning (AdNDP) method were employed to analyze the chemical bonding. Orbital visualization was done using Molekel.

3. Experimental results

The photoelectron spectra of B$_{38}^-$ and B$_{37}^-$ at 193 nm are shown in Fig. 1, along with the simulated spectra (vide infra). Spectral features are labeled with letters (X, A, B, etc.). All
experimental and theoretical VDEs and adiabatic detachment energies (ADEs) are summarized in Table S1 in the ESI.†

3.1. The photoelectron spectrum of B_{38}^−

The spectrum of B_{38}^− (Fig. 1a) reveals six well-spaced bands (X, A–E), as well as continuous signals above 6 eV, labeled as F for the sake of discussion. The first VDE was evaluated from the maximum of band X to be 4.02 eV. Since no vibrational structures were resolved for this band, the ADE was estimated by drawing a straight line along its leading edge and then adding the instrumental resolution to the intersection with the binding energy axis. The ADE of B_{38}^− so obtained is 3.91 ± 0.05 eV, which also represents the electron affinity of neutral B_{38}.

Band A, centered at ∼4.3 eV, is relatively broad and partially overlaps with band X. Bands B (4.62 eV) and C (5.04 eV) are sharper, followed by two intense and broader bands, D (5.39 eV) and E (5.74 eV). Neutral B_{38} has an even number of valence electrons. However, the intensity of band X is quite large relative to band A, and there exists only a small gap (∼0.3 eV) between them. The ADE of B_{38}^− is also unusually large, and breaks the even–odd alternation as a function of size. All these observations suggest that the ground-state of the neutral B_{38} final state upon electron detachment is probably not a closed-shell species.

3.2. The photoelectron spectrum of B_{37}^−

The spectrum of B_{37}^− was well resolved and nine spectral bands could be identified and labeled as X, A–H in Fig. 1c. The peak maximum of band X defines the ground-state VDE of 3.88 eV. The ADE or electron affinity of B_{37} was evaluated from the onset of band X to be 3.76 ± 0.05 eV. The VDEs for bands A–H could all be readily measured from their band maxima and are given in Table S1.†

4. Theoretical results

The global minimum structures of B_{38}^− (1, Cs, 2A″) and B_{37}^− (2, C_1, 1A) are shown in Fig. 2. Alternative low-lying isomers within 1.5 eV are given in Fig. S1 and S2,† for B_{38}^− and B_{37}^−, respectively. Their configurational energy spectra are given in Fig. 3 with selected structures indicated.

4.1. The global minimum and low-lying isomers of B_{38}^−

The cohesive energy trend for B_n (n = 7−40) presented in the previous study on the B_{40}− borospherene suggested a 2D to 3D cage structural transition for neutral B_n clusters at n ≈ 38.22 A subsequent DFT calculation showed that the B_{38} cluster has a D_{2h} cage global minimum with a low-lying 2D isomer consisting of a DHV.33 More accurate calculations found that the 2D structure was slightly lower in energy than the D_{2h} B_{38} cage structure.34 The current global minimum searches, in conjunction with full structural optimizations at PBE0/6-311+G*, found the same 2D isomer 1 (Cs, 2A″) as the overwhelming global minimum for B_{38}^−, as shown in Fig. 2 and 3a. The

![Fig. 2 The top and side views of the global minima of B_{38}^− and B_{37}^− at the PBE0/6-311+G* level.](image-url)
The anion is a result of the delocalization of the additional eV higher in energy. The stabilization of the 2D structure in B38 (Fig. 3a and S1†). In fact, the first nine isomers above the global minimum with the D
bracket2,23 Double- and triple-ring tubular-type isomers for B38 are complicated, because of the open-shell nature of B38, as hinted by the photoelectron spectrum (Fig. 1a).

The spin-polarized orbital energy order of 1 is shown in Fig. S3.† The unpaired CMO is the α-26a (shaded in pink), whereas the highest occupied α and β spins both belong to the 32a′ CMO, with little spin-polarization (within 0.001 eV). Consequently, upon detaching an electron from the highest α and β spins, we can reach both a triplet and a singlet final state, which are expected to be nearly degenerate competing for the ground electronic state of neutral B38. At the PBE0 level, the first detachment channel is from β-32a′ with a calculated VDE of 4.125 eV for the triplet neutral final state (3A″), whereas the detachment of α-32a′ gives a computed VDE of 4.126 eV for an open-shell singlet final state (1A′). Both values are close to each other and are in good agreement with band X (experimental VDE: 4.02 eV). The calculated ADE between 1 (C
bracket3, 3A′) and C
bracket3, 2A′) is 4.06 eV, consistent with the experimental ADE of 3.91 eV. Band A at ∼4.3 eV corresponds to detachments from β-31a′ and α-26a′ which lead to a triplet (1A′) and a singlet (1A″) final state, respectively. The calculated VDEs (4.27 and 4.34 eV, respectively) are also close to each other and are in good agreement with band A. The calculated VDEs for higher binding energy detachment channels are also in good agreement with the experimental bands (B, C, D, and E), as can be seen in Fig. 1b and Table S1.† Overall, the agreement between the simulated spectral pattern and the experimental spectrum is quite gratifying, considering the open-shell nature of both B38− and its neutral.

Fig. 3 The configurational energy spectra of (a) B38− and (b) B37− at the PBE0/6-311+G* level. Black, red, violet, and blue horizontal lines represent quasi-planar, cage-like, double- and triple-ring tubular structures, respectively. Relative energies are given in eV.

4.2. The global minimum and low-lying isomers of B37−

The spectral pattern of B37− was somewhat similar to that of B36− (Fig. 1) and both have relatively high ADEs, suggesting that they might have similar structures. Hence, we built the initial structures of B37− by removing one B atom from the shorter edge of C
bracket3, 3B38− (1) or adding two B atoms to the thinner edge of B35−. Full structural optimization at PBE0 led to the 2D isomer of C
bracket4, 3B37− [2, 3A] as shown in Fig. 2. Because there were only two B atoms in the top row, significant local distortions were found upon optimization. The C
bracket4, 3B37− isomer was subsequently located as the global minimum for B37− (Fig. 3) and S2† from minima-hopping searches.

As shown in Fig. 3b and S2† the second lowest-lying isomer is also 2D (C
bracket5, 3A′) at 0.23 eV above the global minimum. This isomer contains a hexagonal vacancy and can be viewed as adding a B atom to the edge of the hexagonal B36− cluster20 with some major local rearrangement. The third isomer C
bracket6, 3B37− (1A′) at 0.30 eV is cage-like, similar to the metalloborospherene Ca@B37−.49 The higher energy isomers of B37− display both 2D and 3D structures, which are generally similar to those of B38− (Fig. 3).

5. Comparison between experiment and theory

5.1. B38−

Since the global minimum 2D structure with a DHV for B38− (1, C
bracket7, 3A′) is overwhelmingly favored from our global search, no higher energy isomers need to be considered in comparison with the experimental spectrum. The calculated VDEs of 1 at TD-PBE0 are compared with the experimental data in Table S1† and the simulated spectrum is compared with the experiment in Fig. 1b. The electronic structures of B38− and B38 are complicated, because of the open-shell nature of B38, as hinted by the photoelectron spectrum (Fig. 1a).
5.2. B\textsubscript{37}⁻

Since B\textsubscript{37}⁻ has a closed-shell configuration, electron detachment from each CMO produces a doublet final state, giving rise to much fewer detachment channels relative to the open-shell B\textsubscript{38}⁻. The simulated spectrum and the calculated VDEs from the B\textsubscript{37}⁻ global minimum are compared with the experiment in Fig. 1d and Table S1, respectively. The theoretical first VDE from the HOMO (56a) is 3.75 eV, which is in good agreement with band X (VDE: 3.88 eV). The calculated ADE (3.67 eV) is also in good agreement with the experimental value of 3.76 eV. There is an excellent correspondence between all the higher detachment channels and the observed PES bands (Fig. 1c and d). The level of agreement between the theory and experiment is remarkable, confirming the 2D structure with a DHV (2) as the global minimum of B\textsubscript{37}⁻.

6. Structures and chemical bonding

6.1. Quasi-planar boron clusters with a double-hexagonal vacancy

The global minimum of B\textsubscript{38}⁻ (1) containing a DHV is directly related to the observed B\textsubscript{35}⁻ (ref. 21) by adding a three-atom row on the top of B\textsubscript{35}⁻ (Fig. 2), yielding the elongated and bowl-shaped 2D structure (length: 9.9 Å; width: 9.55 Å) with six apexes. The B\textsubscript{38}⁻ cluster can also be described as consisting of three cyclic rings of B atoms: the inner B\textsubscript{6} ring, a middle B\textsubscript{13} ring, and an external B\textsubscript{19} ring. The peripheral B–B bond lengths in B\textsubscript{38}⁻ range from 1.58 to 1.66 Å, whereas the interior B–B bond lengths range from 1.64 to 1.84 Å. The shortest peripheral B–B bonds are associated with the six apex atoms. The shorter peripheral B–B bonds relative to the interior B–B bonds cause the bowl-shape of B\textsubscript{38}⁻ with an out-of-plane distortion of 1.45 Å (1, Fig. 2).

The global minimum of B\textsubscript{37}⁻ (2) can be obtained by either adding two B atoms to the top of B\textsubscript{35}⁻ or removing a B atom from the top row of B\textsubscript{38}⁻ with a significant local distortion. Thus, B\textsubscript{37}⁻ differs from B\textsubscript{38}⁻ by one less peripheral B–B bond. The out-of-plane distortion of B\textsubscript{37}⁻ is increased to 2.31 Å.

Starting from B\textsubscript{35}⁻, the DHV seems to become a prevalent structural feature in 2D boron clusters. Even though the B\textsubscript{40} borospherene cage is overwhelmingly the global minimum in the neutral,\textsuperscript{22} the global minimum of B\textsubscript{40}⁻ is in fact a 2D structure, which can be viewed as adding two B atoms to the top of B\textsubscript{35}⁻ or removing a B atom from the top row of B\textsubscript{38}⁻ with a significant local distortion. It is remarkable that for both B\textsubscript{38}⁻ and B\textsubscript{37}⁻ the global minima with the DHV are significantly favored without competing low-lying isomers. It should be pointed out that, for smaller boron clusters in the size range from B\textsubscript{24}⁻ to B\textsubscript{29}⁻, competing low-lying isomers were observed in each case.\textsuperscript{18,23} It seems that the hexagonal vacancy, in particular the DHV, plays a major role in stabilizing the 2D structures for larger boron clusters.

6.2. Chemical bonding in B\textsubscript{38}⁻ and B\textsubscript{37}⁻: boron analogues of coronene

The chemical bonding in B\textsubscript{38}⁻ and B\textsubscript{37}⁻ has been analyzed using the AdNDP method (Fig. 4). For B\textsubscript{38}⁻, we used its closed-shell dianion B\textsubscript{38}²⁻ with 116 valence electrons (58 electron pairs) for the purpose of bonding analyses. We found that bonding in B\textsubscript{38}²⁻ is similar to that in B\textsubscript{35}⁻. The external B\textsubscript{19} ring and the inner B\textsubscript{2} bridge between the two hexagonal holes are described by 20 2c–2e σ bonds (Fig. 4a). The bonding between the DHV and the surrounding boron atoms is via 10 3c–2e σ bonds, whereas the bonding between the external B\textsubscript{19} ring and the middle B\textsubscript{13} ring is via 16 4c–2e σ bonds.
There are three types of π bonds in B$_{38}^{2−}$. We found six multi-center (four 4c−2e and two 5c−2e) π bonds around the six apex sites mainly involving bonding between the external B15 ring and the middle B13 ring. The inner B6 ring involves in six apex sites mainly involving bonding between the external zigzag BDCs, suggesting the importance of BDCs in stabilizing both 2D borophenes and 0D borospherenes.22,32

The bonding in B$_{37}^{−}$ is very similar to that in B$_{38}^{2−}$. Except the fact that B$_{37}^{−}$ has four fewer electrons than B$_{38}^{2−}$, all in the σ framework, the π bonding in the two systems is nearly identical according to the AdNDP analyses (Fig. 4b). Hence, B$_{37}^{−}$ can also be considered to possess dual π aromaticity. More interestingly, we found that the π bonding patterns in both B$_{37}^{−}$ and B$_{38}^{2−}$ are very similar to that in the polycyclic aromatic coronene ($C_{24}H_{12}$) (Fig. 4c). Comparisons of their π CMOs are presented in Fig. S4† which provide further evidence to support this analogy. Thus, B$_{37}^{−}$ and B$_{38}^{−}$ can be considered as all-boron analogues of coronene $C_{24}H_{12}$, continuing the hydrocarbon analogy of all 2D boron clusters studied thus far.11,17,23,24

6.3. B$_{38}^{−}$ and B$_{37}^{−}$ as motifs for borophenes

Since the first successful characterization of graphene, there has been intense interest in finding new 2D materials. Even though boron does not have a layered allotrope, single-walled boron nanotubes were suggested, using boron sheets made of a triangular lattice.50,51 The triangular lattice can be viewed by filling a boron atom to the hexagons of a graphene-like structure. However, such a triangular lattice is too electron-rich and undergoes distortion to a rippled boron layer.52−55 DFT calculations suggested that a triangular lattice with periodic hexagonal vacancies would be planar and would be more stable than a close-packed triangular lattice, more suitable for the construction of boron nanotubes.56,57 Further DFT studies predicted many different monolayer borons with different hole patterns and suggested that they could be formed on inert substrates, such as silver.29,30 The discovery of the C$_{60}$, B$_{16}$ cluster with a hexagonal vacancy provided the first indirect experimental evidence of the viability of atomically-thin borons and inspired the proposal of “borophene” to designate the potentially new class of 2D materials.20 Subsequently, the B$_{35}$− cluster with a DHV was found to be an even more flexible motif for borophenes with different hole patterns and densities.21 Recently, two groups have independently prepared borophenes on silver substrates.27,28 Even though the atomic resolution was not achieved in the STM characterization, the most stable structure seemed to be the so-called χ3-borophene, in which two columns of adjacent hexagonal vacancies are connected by zigzag BDCs, suggesting the importance of BDCs in stabilizing both 2D borophenes and 0D borospherenes.32,33

The DHV in B$_{38}^{−}$ and B$_{37}^{−}$ is reminiscent of the most stable χ3-borophene and can be viewed as its motifs. Fig. 5 illustrates the relationship between B$_{38}^{−}$ and the χ3-borophene. One can fuse four adjacent B$_{38}^{−}$ units to form a hexagonal vacancy between them by connecting two B$_{38}^{−}$ units head-to-tail in the vertical direction, sharing a B$_{7}$ double-chain and a B$_{4}$ rhombus between the two neighboring B$_{38}^{−}$ units in the horizontal direction. On the basis of this 2D pattern, one can further extend the molecular sheet to χ3-borophene by removing some hexacoordinate capping B atoms in the vertical direction to form the continuous zigzag BDCs, as shown by the rows of the adjacent hexagonal vacancies in the background. The present discussion is a simple model illustrating the connection of the 2D boron clusters with a DHV to borophenes. It is conceivable that with increasing size 2D boron clusters with more than two adjacent hexagonal vacancies may be possible. Hence, borophenes may be viewed as extended 2D cluster species. Such clusters have been considered computationally.60,64 It would be interesting to test if such clusters would exist experimentally in larger boron clusters. The existence of such large 2D boron clusters may provide information about the feasibility of free-standing borophenes.

7. Conclusions

The B$_{38}^{−}$ and B$_{37}^{−}$ clusters have been produced in the gas phase and characterized using anion photoelectron spectroscopy and theoretical calculations. The PE spectra were sufficiently well resolved and indicated that a single dominant isomer was the spectral carrier in each case. The most stable structures of B$_{38}^{−}$ and B$_{37}^{−}$ are established by comparisons of the experimental and computational data. Both clusters are found to adopt quasi-planar structures with a double-hexagonal vacancy, which seems to impart special stability to the large 2D boron clusters. Bonding analyses reveal that they are all-boron analogues of coronene, featuring unique dual π aromaticity. Such boron clusters with adjacent hexagonal vacancies may be used as structural motifs for χ3-borophenes, featuring rows of adjacent hexagonal vacancies connected by zigzag BDCs.
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