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A combined photoelectron spectroscopy and ab initio study of the quasi-planar B₂₄⁻ cluster

Ivan A. Popov,¹ Zachary A. Piazza,² Wei-Li Li,² Lai-Sheng Wang,^{2,a)} and Alexander I. Boldyrev^{1,b)}

¹Department of Chemistry and Biochemistry, Utah State University, Logan, Utah 84322, USA ²Department of Chemistry, Brown University, Providence, Rhode Island 02912, USA

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The structure and chemical bonding of the 24-atom boron cluster are investigated using photoelectron spectroscopy and *ab initio* calculations. The joint experimental and theoretical investigation shows that B_{24}^{-} possesses a quasi-planar structure containing fifteen outer and nine inner atoms with six of the inner atoms forming a filled pentagonal moiety. The central atom of the pentagonal moiety is puckered out of plane by 0.9 Å, reminiscent of the six-atom pentagonal caps of the wellknown B_{12} icosahedral unit. The next closest isomer at the ROCCSD(T) level of theory has a tubular double-ring structure. Comparison of the simulated spectra with the experimental data shows that the global minimum quasi-planar B_{24}^{-} isomer is the major contributor to the observed photoelectron spectrum, while the tubular isomer has no contribution to the experiment. Chemical bonding analyses reveal that the periphery of the quasi-planar B_{24} constitutes 15 classical 2c-2e B-B σ -bonds, whereas delocalized σ - and π -bonds are found in the interior of the cluster with one unique 6c-2e π -bond responsible for bonding in the B-centered pentagon. The current work suggests that the 24atom boron cluster continues to be quasi-2D, albeit the tendency to form filled pentagonal units, characteristic of 3D cage-like structures of bulk boron, is observed. © 2013 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4824156]

I. INTRODUCTION

The natural inclination of three-dimensional (3D) pure boron¹ and boron-rich^{2,3} solids to assemble in icosahedral units has spurred interests recently to consider them as potential candidates for semiconducting quasicrystals.⁴ Raman scattering experiments under high pressure were compared with ab initio lattice dynamics calculations for the icosahedral α -boron.⁵ However, for isolated clusters it was computationally shown^{6,7} that icosahedral cage structures of B_{12} and B_{13} were unstable, even though they were initially proposed as possible candidates for these two clusters.⁸ Instead, small boron clusters have been experimentally and theoretically shown to exhibit planar or quasi-planar structures in their ground states up to B_{23}^{-} for anionic, $^{9-20}$ B_{20} for neutral 15,21 (except for B₁₄, which is also 3D as shown in Ref. 22), and B_{16}^+ for cationic clusters.²³ Chemical bonding analyses of these clusters have established that the presence of strong peripheral 2c-2e B-B σ -bonds along with 2D electron delocalization plays a crucial role in their stability, which is associated with the concepts of aromaticity, multiple aromaticity, and antiaromaticity. The validity of applying these concepts in describing the electronic structure of planar and quasiplanar boron clusters is evident through the striking similarities of the π -systems of these clusters when compared to unsaturated cyclic hydrocarbons. In fact, the 2D boron clusters have been shown to be all-boron analogs of such hydrocarbons as benzene,^{13, 14, 24, 25} naphthalene,¹⁸ coronene,¹⁸ anthracene,¹⁶ and phenanthrene.¹⁶

In addition to their interesting electronic and bonding properties, the planar boron clusters also display peculiar structural features. For example, the B₁₉⁻ cluster possesses a perfectly planar geometry with a 13-atom outer ring and an internal B-centered pentagonal unit. Molecular dynamic calculations revealed that the central pentagon is capable of internal rotation against the 13-atom peripheral ring with a low energy barrier.²⁶ Such systems have been considered as molecular Wankel motors.²⁶ It has been further shown that the internal pentagon can rotate in a chosen direction by employing circularly polarized infrared (IR) radiation.²⁷ This is possible due to the delocalized bonding inside of the planar B_{19}^{-1} cluster, which allows the rotation to occur without breaking any of the strong two-center two-electron (2c-2e) peripheral B-B bonds.²⁸ A similar filled pentagonal moiety was revealed in the B_{21}^{-} cluster, along with a unique 2c-2e σ -bond within the inner boron network.¹⁹ It is noteworthy that the B-centered pentagon in B_{21}^{-} is puckered out of plane by 0.5 Å compared to the perfectly planar structure of B_{19}^{-} . The puckered pentagonal pyramidal structural feature is reminiscent of the icosahedral B₁₂ units in bulk boron. However, such structural units were not observed in the larger B_{22}^{-} and B_{23}^{-} clusters.²⁰ Hence, at what size boron clusters begin to become bulk-like remains to be an intriguing unanswered question.

In the present article, we report a joint photoelectron spectroscopy (PES) and computational study of B₂₄⁻. We find B₂₄⁻ possesses a quasi-planar structure containing 15 outer and 9 inner atoms. Six of the inner boron atoms in B_{24}^{-} form

a)Electronic mail: lai-sheng_wang@brown.edu

^{b)}Electronic mail: a.i.boldyrev@usu.edu

a puckered pentagonal moiety, similar to that found in B_{21}^{-} ,¹⁹ with a more explicit out-of-plane distortion of 0.9 Å. The tendency of these clusters to form puckered pentagonal units with increasing cluster size may hint at the onset of the formation of 3D cage-like icosahedral building blocks common in the bulk boron.

II. EXPERIMENTAL METHOD

The experiment was carried out using a magnetic-bottle PES apparatus equipped with a laser vaporization cluster source, details of which can be found elsewhere.²⁹ Briefly, negatively charged boron clusters were produced by laser vaporization of a hot-pressed isotopically enriched ¹⁰B (96%) disk target. The clusters were entrained by a He carrier gas containing 5% Ar and underwent a supersonic expansion to form a collimated and vibrationally cold cluster beam. The cluster size distribution and cooling were controlled by the time delay between the pulsed valves and the vaporization laser and the resident time of the clusters in the nozzle.^{30–32} The anionic clusters were extracted from the cluster beam and analyzed with a time-of-flight mass spectrometer. The B_{24}^{-} cluster was mass-selected and decelerated before being intercepted by a detachment laser beam. For the current study, two detachment energies, 266 nm (4.661 eV) from a Nd: YAG laser and 193 nm (6.424 eV) from an ArF excimer laser, were used. Photoelectrons were collected at nearly 100% efficiency by a magnetic bottle and analyzed in a 3.5 m long electron flight tube. The PES spectrum was calibrated using the known spectra of Bi⁻ and Au⁻ and the electron energy resolution of the apparatus was $\Delta E_k/E_k \sim 2.5\%$, i.e., ~ 25 meV for 1 eV electrons.

III. THEORETICAL METHODS

We utilized two independent methods to search for the global minimum structure of B₂₄⁻, namely, the Coalescence Kick (CK)¹⁸ and Cartesian Walking (CW)¹⁹ methods. The initial CK search was conducted using the hybrid density functional B3LYP^{33,34} level of theory and the 3-21G basis set³⁵ for energy and gradient calculations, while the initial CW searches used the PBE036,37 functional and the 3-21G basis set. Approximately 10 000 trial structures were generated using the CK method and 3000 using the CW method. Briefly, the CK method allowed random structures to be generated in a box and checked for connectivity. If fragmented groups of atoms were found, all atoms coalesced towards the center of mass until a connected cluster was formed. Following this, geometry optimization was applied to the structure. The CK method was described in detail in Ref. 18. The CW method imposed restraints on a random walking process that took place upon a grid of Cartesian coordinates to generate trial structures. The result was the generation of random trial structures with atomic positions that were neither unrealistically close nor unrealistically far from each other. Furthermore, added effectiveness could be achieved by tuning the grid for the system at hand. In the current article, grids biased towards the creation of planar and quasi-planar structures were employed. A more detailed description of the CW method was given in Ref. 19.

It has been recently shown that among different DFT methods tested, the PBE0,36,37 TPSS,38 and TPSSh39 functionals are able to reasonably reproduce relative energies among the low-lying isomers. In the current work, all the low-lying isomers obtained from both searches below 25 kcal/mol relative to the global minimum at 3-21G were re-optimized at the PBE0/6-311+G(d)⁴⁰⁻⁴² and TPSSh/6-311+G(d) levels of theory. For each isomer, vibrational frequencies were calculated and imaginary frequencies were followed to ensure that they correspond to a true minimum on the potential energy surface. In order to assess the relative energies more accurately, we performed single point calculations of all the structures at two DFT levels of theory: PBE0/6-311+G(2df)//PBE0/6-311+G(d) and TPSSh/6-311+G(2df)//TPSSh/6-311+G(d). Subsequently, the most accurate single point calculations were performed at the $ROCCSD^{43-45}/6-311+G(d)//PBE0/6-311+G(d)$ and ROCCSD(T)/6-311+G(d)//PBE0/6-311+G(d) levels of theory. The restricted open-shell formalism was used to give the proper $\langle S^2 \rangle$ value for the open-shell B_{24}^- system. The single-configurational nature of each wavefunction was checked through an open-shell T₁ diagnostic based on the formalism of Jayatilaka and Lee.46

Vertical detachment energies (VDEs) of the lowest energy isomers were calculated at two different levels of theory: PBE0/6-311+G(2df)//PBE0/6-311+G(d) and TPSSh/6-311+G(2df)//TPSSh/6-311+G(d) to compare with the experimental data. In each case, the first VDE was calculated as the difference in energy between the lowest anionic state and the lowest neutral state at the geometry of the anion. Then, vertical excitation energies of the neutral species calculated at the TD-PBE0 and TD-TPSSh levels were added to the first VDE to approximate the second and higher VDEs.

Chemical bonding analysis of the global minimum structure of B₂₄⁻ was performed using the adaptive natural density partitioning (AdNDP) method developed by Zubarev and Boldyrev.^{47–49} It has been successfully used to produce chemical bonding pictures of small boron clusters as well as of 2D materials of boron and carbon.⁵⁰⁻⁵⁴ The AdNDP method analyzes the first-order reduced density matrix in order to obtain its local block eigenfunctions with optimal convergence properties for an electron density description. The obtained local blocks correspond to the sets of *n*-atoms (*n* ranging from one to the total number of atoms in the molecule) that are tested for the presence of *n*-electron objects [*n*-center two electron (nc-2e) bonds], including core electrons and lone pairs as a special case of n = 1 associated with this particular set of natoms. AdNDP initially searches for core electron pairs and lone pairs (1c-2e), then 2c-2e, 3c-2e, ..., and finally up to nc-2e bonds. At every step, the density matrix is depleted of the density corresponding to the appropriate bonding elements. The user-directed form of the AdNDP analysis can be applied to specified molecular fragments and is analogous to the directed search option of the standard natural bond orbital (NBO) code.55,56 AdNDP accepts only those bonding elements whose occupation numbers (ONs) exceed specified threshold values which are usually chosen to be close to



FIG. 1. Photoelectron spectrum of B_{24}^{-} at 193 nm (6.424 eV).

2.00 lel. The AdNDP method recovers both Lewis bonding elements (1c-2e and 2c-2e objects, corresponding to the core electrons and lone pairs, and 2c-2e bonds) and delocalized bonding elements, which are associated with the concepts of aromaticity and antiaromaticity. From this point of view, AdNDP achieves a seamless description of systems featuring both localized and delocalized bonding without invoking the concept of resonance. We used the B3LYP/6-31G level of theory for the AdNDP calculations. AdNDP results have been shown to be insensitive to the level of theory or basis set used.⁵⁷

All the calculations (PBE0, TPSSh, TD-PBE0, TD-TPSSh, ROCCSD, and ROCSSD(T)) were performed using the GAUSSIAN 09 program.⁵⁸ Molecular structure visualization was done using the MOLDEN 3.4⁵⁹ and Chemcraft programs.⁶⁰ Molecular orbital (MO) visualization was performed using MOLEKEL 5.4.0.8.⁶¹

IV. EXPERIMENTAL RESULTS

The photoelectron spectrum of B_{24}^{-} is shown in Fig. 1 at 193 nm. The spectrum was also obtained at 266 nm, but not

shown, because no fine features were resolved. The detachment features are labeled with letters X, A, and B, The measured VDEs are compared with theoretical calculations at the TPSSh and PBE0 levels of theory in Table I and they serve as spectral signatures for the global minimum quasi-planar structure of B_{24}^{-} (*vide infra*).

The first detachment channel of B_{24}^{-} is defined by feature X with a VDE value of 3.75 eV. The adiabatic detachment energy (ADE) or the electron affinity of the corresponding neutral is measured by drawing a straight line along the leading edge of the band and then adding the experimental resolution to the intersection with the binding energy axis. The ADE so obtained is 3.55 ± 0.07 eV. The broad width of the X band and relatively large difference between the ADE and VDE suggests significant geometry changes from the anion ground state to that of the neutral upon electron detachment. Following an energy gap of $\sim 1 \text{ eV}$, a set of intense and congested features are observed. Features A, B, and C are observed with VDEs of 4.61, 4.79, and 5.12 eV, respectively. One more intense feature D is observed at 5.62 eV, followed by a weaker feature E at 5.96 eV. All these spectral bands are relatively broad, suggesting that they may contain more than one detachment channel.

V. THEORETICAL RESULTS

Using both the CK and CW searching procedures, about 13 000 trial structures were generated and underwent the processes of optimization and frequency calculations. The two searches provided us with a set of low-lying isomers, which were subsequently re-optimized at the higher levels of theory: PBE0/6-311+G(d) and TPSSh/6-311+G(d). All isomers were checked to be true minima with no imaginary frequencies. An abbreviated set of these low-lying isomers is presented in Fig. 2. It should be noted that the tubular structure II was not found by our searching methods, but instead built manually. It was examined based on similar structures reported to be present among the low-lying isomers of several

TABLE I. Comparison of the experimental VDEs with the calculated values for isomer I (C_1 , ²A) of B_{24}^{-} . All energies are in eV.

Feature	VDE (Expt.) ^a	Final state and electronic configuration	VDE (theory)	
			TD-TPSSh	TD-PBE1PBE
X	3.75(7)	$^{1}A(29a)^{2}(30a)^{2}(31a)^{2}(32a)^{2}(33a)^{2}(34a)^{2}(35a)^{2}(36a)^{2}(37a)^{0}$	3.70	3.79
А	4.61(8)	${}^{3}A(29a)^{2}(30a)^{2}(31a)^{2}(32a)^{2}(33a)^{2}(34a)^{2}(35a)^{2}(36a)^{1}(37a)^{1}$	4.29	4.46
В	4.79(8)	${}^{1}A(29a)^{2}(30a)^{2}(31a)^{2}(32a)^{2}(33a)^{2}(34a)^{2}(35a)^{2}(36a)^{1}(37a)^{1}$	4.48	4.65
		${}^{3}A(29a)^{2}(30a)^{2}(31a)^{2}(32a)^{2}(33a)^{2}(34a)^{2}(35a)^{1}(36a)^{2}(37a)^{1}$	4.51	4.65
		${}^{3}A(29a)^{2}(30a)^{2}(31a)^{2}(32a)^{2}(33a)^{2}(34a)^{1}(35a)^{2}(36a)^{2}(37a)^{1}$	4.64	4.75
С	5.12(8)	1 A(29a) ² (30a) ² (31a) ² (32a) ² (33a) ² (34a) ² (35a) ¹ (36a) ² (37a) ¹	4.73	4.93
		1 A(29a) ² (30a) ² (31a) ² (32a) ² (33a) ² (34a) ¹ (35a) ² (36a) ² (37a) ¹	4.89	5.05
D	5.62(6)	${}^{3}A(29a)^{2}(30a)^{2}(31a)^{2}(32a)^{2}(33a)^{1}(34a)^{2}(35a)^{2}(36a)^{2}(37a)^{1}$	5.19	5.40
		${}^{3}A(29a)^{2}(30a)^{2}(31a)^{2}(32a)^{1}(33a)^{2}(34a)^{2}(35a)^{2}(36a)^{2}(37a)^{1}$	5.34	5.59
		1 A(29a) ² (30a) ² (31a) ² (32a) ¹ (33a) ² (34a) ² (35a) ² (36a) ² (37a) ¹	5.44	5.72
		1 A(29a) ² (30a) ² (31a) ² (32a) ² (33a) ¹ (34a) ² (35a) ² (36a) ² (37a) ¹	5.36	5.65
		${}^{3}A(29a)^{2}(30a)^{2}(31a)^{1}(32a)^{2}(33a)^{2}(34a)^{2}(35a)^{2}(36a)^{2}(37a)^{1}$	5.42	5.67
Е	5.96(5)	1 A(29a) ² (30a) ² (31a) ¹ (32a) ² (33a) ² (34a) ² (35a) ² (36a) ² (37a) ¹	5.85	6.07
		${}^{3}\mathrm{A}\ldots(29a)^2(30a)^1(31a)^2(32a)^2(33a)^2(34a)^2(35a)^2(36a)^2(37a)^1$	6.02	6.24

^aNumbers in the parentheses represent uncertainties in the last digit.



FIG. 2. The global minimum and low-lying isomers of B_{24}^- . Relative energies are shown from single-point calculations at ROCCSD/6-311 + G(d)//PBE0/6-311 + G(d) (in curly brackets), as well those from PBE0/6-311 + G(2df)//PBE0/6-311 + G(d) (in parentheses) and TPSSh/6-311 + G(2df)//TPSSh/6-311 + G(d) (in square brackets). All energies have been corrected for zero-point energies at the corresponding levels of theory, aside from the CC methods, which have been corrected with the PBE0 zero-point energies. The relative energy of isomer III at ROCCSD(T)/6-311 + G(d)/PBE0/6-311 + G(d) could not be obtained. Kcal/mol denotes a unit to measure an amount of energy per mole of B_{24}^- molecules.

anionic boron clusters.^{17–20} The double ring structures have never been observed experimentally for any neutral or anionic boron clusters, even in cases where such isomers were found computationally to be rather low-lying.^{15,20}

The eight energetically lowest lying isomers at the DFT/6-311+G(d) level were further evaluated by single point calculations at their PBE0/6-311+G(d) geometries using the ROCCSD/6-311+G(d) and ROCCSD(T)/6-311+G(d) levels of theory, with the exception of isomer III, for which only the ROCCSD energy was obtained. The deviation in energy of these closely lying isomers at the corresponding ROCCSD and ROCCSD(T) levels was at most 1.5 kcal/mol. Some of the structures are very close in energy with each other and may be considered degenerate (i.e., isomers IV and V, as well as VI and VII). Both ROCCSD and ROCCSD(T) calculations show isomer I (C₁) as the global minimum, which is a quasi-planar cluster with a filled pentagonal unit. The Cartesian coordinates of the presented structures are given in Table S1 of the supplementary material.⁶²

In contrast to the quasi-planar structure of isomer I, the next low-lying isomer evaluated with the coupled cluster methods is the tubular double-ring structure II. This isomer has been suggested recently to be the most stable structure of B_{24}^{-} cluster by Nguyen and co-workers.⁶³ These authors showed that two 2D isomers, referred to in their work as B24-QP-1 and B24-QP-2, are less stable than the 3D double-ring structure at the TPSSh/6-311+G(d) level of theory. These two 2D isomers were also found among the

low-lying isomers via the CK and CW searches: isomer VIII and isomer IV, respectively (see Fig. 2). Nguyen's proposed relative energies are in agreement with both our DFT methods. However, the more accurate and reliable single-point ROCCSD and ROCCSD(T) calculations show that these quasi-planar structures, along with the double-ring structure, are all higher in energy than the quasi-planar isomer I, found via our global minimum searches.

The global minimum structure I (C_1 , ²A) possesses a slightly puckered geometry featuring a filled pentagonal moiety with the central boron atom sticking out of the molecular plane by approximately 0.9 Å. For comparison, the same filled pentagonal moiety is found in B₂₁⁻ with an out of plane distortion of about 0.5 Å, whereas in B_{19}^{-} the filled pentagonal unit is found to be perfectly planar. Interestingly, the B-B bond lengths inside the pentagon vary from 1.61 to 1.68 Å, whereas the same bonds in the 3D α -boron icosahedral units are about 1.73 Å. Both the PBE0/6-311+G(2df)//PBE0/6-311+G(d) and TPSSh/6-311+G(2df)//TPSSh /6-311+G(d) levels of theory show the lowest energy as isomer II, but it turns out to be 4.46 and 4.54 kcal/mol higher in energy than structure I at the highest ROCCSD/6-311+G(d)//PBE0/6-311+G(d) and ROCCSD(T)/6-311+G(d)//PBE0/6-311+G(d) levels of theory, respectively. As will be discussed below, the comparison between the simulated PES spectra and the experiment supports our findings of the quasi-planar structure I as the global minimum of B_{24}^{-} .

The next two lowest energy isomers (III and IV) possess pentagon-shaped cavities much like the global minimum structure I, but do not contain a filled pentagonal moiety. Structures III and IV are 4.59 and 6.24 kcal/mol higher in energy, at ROCCSD/6-311+G(d)//PBE0/6-311+G(d) level, than isomer I, respectively. Isomer V has a triangular lattice, similar to the global minimum of $B_{22}{}^-$ reported recently.²⁰ Even though this structure is just 2.2 kcal/mol higher in energy than the double-ring isomer II at PBE0/6-311+G(2df)//PBE0/6-311+G(d), it is found to be a highenergy isomer at the highest levels of theory (ROCCSD and ROCCSD(T)). All other structures in Fig. 2 represent planar and quasi-planar high-energy isomers with relative energies >10 kcal/mol above the global minimum at the highest levels of theory. It is noteworthy that the robustness of planar geometry⁹⁻²³ is seen for many boron clusters. Conditions of the formation of 2D boron sheets have recently been reported elsewhere.64

In order to compare the stability of the global minimum structure I with one of the most stable 2D sheet of boron atoms, the so-called α -sheet,^{51,65–68} and 3D α -rhombohedral bulk boron,⁵ we have performed additional calculations at the PBE/6-31G(d, p) level of theory to find a cohesive energy E_c of the ground B_{24}^- isomer. It turned out that E_c of the B_{24}^- cluster is 5.62 eV per boron atom. The E_c values of the 2D α -sheet and 3D α -rhombohedral bulk boron were previously calculated^{65–68} to be 5.93 eV⁶⁵ (6.11 eV⁶⁶) and 6.33 eV,⁶⁷ respectively.

In order to assess the multi-reference character in the ROCCSD(T) method, we used an open-shell T₁ diagnostic, which can produce a qualitative picture of the significance of non-dynamical (or static) correlation: the larger the T₁ value, the less reliable the results of the single-reference coupled cluster wave function. In the current work, we obtained T₁ diagnostic values using the open-shell T₁ formalism of Jayatilaka and Lee,⁴⁶ who suggested that open-shell T₁ values may be larger than those of closed-shell systems, where T₁ values greater than 0.02 are typically suspicious.^{69,70} Table II shows the T₁ values at the ROCCSD(T)/6-311+G(d)//PBE0/ 6-311+G(d) level of theory for all the isomers of B₂₄⁻ except isomer III, which is not presented due to the missing energy value at ROCCSD(T).

As was suggested by Schaefer III and co-workers,⁷¹ the T_1 values above 0.044 are considered somewhat less reliable for open-shell systems. According to our results, all the values are below 0.027, which supports the reasonable assessment of

TABLE II. Open-shell T_1 diagnostic values at the ROCCSD(T)/6-311+G(d)//PBE0/6-311+G(d) level of theory.

Isomers	T ₁ values	
Ι	0.025	
II	0.027	
IV	0.025	
V	0.023	
VI	0.022	
VII	0.019	
VIII	0.025	

our wave-function as single-configurational for all the studied species.

VI. COMPARISON BETWEEN THE EXPERIMENTAL AND THEORETICAL RESULTS

The calculated VDEs at the TPSSh and PBE0 levels of theory for isomer I are summarized in Table I along with the experimental data. The calculated VDEs for other low-lying isomers are given in Table S2 of the supplementary material.⁶² Simulated spectra for isomer I using both functionals are compared with the experimental spectrum in Fig. 3. The overall patterns at both functionals are in excellent agreement with the experimental data. The PBE0 data will be used in the following discussion.

A. Isomer I

The first VDE of B_{24}^{-} corresponds to the electron detachment of the singly occupied HOMO (37a) resulting in the singlet neutral ground state ¹A (Table I). The VDE value at the PBE0 level of theory is 3.79 eV, which is in excellent agreement with the experimental value of 3.75 eV. Detachment



FIG. 3. Comparison of the experimental PES spectrum (a) with the simulated PES spectra for the global minimum isomer I of B_{24}^{-} at PBE0 (b) and TPSSh (c).

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from HOMO-1 (36a) produces the first triplet neutral state, with a calculated VDE of 4.46 eV, in good agreement with the experimental VDE of feature A at about 4.61 eV. The next three detachment channels are calculated at VDEs of 4.65, 4.65, and 4.75 eV, which contribute to the intense and broad feature B at 4.79 eV. Feature C at 5.12 eV is assigned to the singlet final states from electron detachment from HOMO-2 (4.93 eV) and HOMO-3 (5.05 eV). The next five detachments channels are assigned to contribute to the intense and broad feature D at 5.62 eV. Following a 0.4 eV gap in the theoretical values, two detachment channels calculated at 6.07 and 6.24 eV are assigned to feature E at 5.96 eV.

No detachment channels are calculated to be in the gap between features X and A, which was not resolved to the baseline in the photoelectron spectrum. This might be due to contributions of possible low-lying isomers in the cluster beam.

B. Isomer II

The calculated VDEs for the double-ring isomer II totally disagree with the experimental features (see Table S2 of the supplementary material⁶²). The first VDE calculated at PBE0 (2.88 eV) and TPSSh (2.74 eV) are much lower than the observed first VDE and they do not correspond to any observable features in the experimental spectrum. Thus, we can rule out the presence of this isomer in any appreciable amount in the cluster beam.

C. Other isomers

The calculated VDEs for the quasi-planar isomers III and IV (see Table S2 of the supplementary material⁶²) show quite similar simulated spectral pattern as the global minima and thus they cannot be excluded on this ground. However, taking into account that their relative energies are quite low with respect to the global minimum, we could not completely rule out that they might be present in small amounts in the cluster beam and might make non-negligible contributions to the overall width of the experimental spectrum. Isomer V has a detachment channel that could be responsible for the intensity in the gap between features X and A. Other isomers are too high in energy and can be safely ruled out.

Thus, we believe that the global minimum isomer I is the main species responsible for the experimental photoelectron spectrum. The excellent overall agreement between the simulated spectra of isomer I and the experiment lends considerable credence for the identified global minimum for B_{24}^{-} .

VII. STRUCTURE AND CHEMICAL BONDING

The global minimum of B_{24}^- (Fig. 2) contains a tetragonal and a pentagonal hole. Previous investigations show that such defects are essential to keep the cluster flat because of the unique chemical bonding in all 2D boron clusters, which exhibit strong peripheral B-B bonding and delocalized interior bonding.^{13–20} However, the global minimum of B_{24}^- is only quasi-planar owing to the out-of-plane distortion of the boron atom in the center of the filled pentagonal motif, similar to that observed in the global minimum of B_{21}^{-} . The appearance of such filled pentagonal units with ever increasing out-of-plane distortions for large boron clusters may hint at the onset to form icosahedral blocks found in bulk boron. The results of our chemical bonding analysis (Fig. 4) using the AdNDP method (B3LYP/6-31G//PBE0/6-311+G(d)) provides further insight into this structural feature by revealing a separate bonding element (6c-2e π -bond with ON = 1.8 lel) located over the filled pentagonal moiety.

The current version of our AdNDP program allows performing analyses for only closed-shell systems. Therefore, in order to assess chemical bonding in the open-shell B_{24}^{-} anion cluster, we performed the AdNDP analyses of both the closed-shell neutral B_{24} (Fig. 4(a)) and closed-shell dianion B_{24}^{2-} (Figs. 4(a) and 4(b)), both at the geometry of B_{24}^{-} . It should be stressed that isomer I is not planar, and therefore, σ - and π -bonding could only be approximately assigned. The bonding elements obtained for B_{24} and B_{24}^{2-} are the same, except for the additional 5c-2e π -bond pertaining to B_{24}^{2-} , shown in Fig. 4(b) (ON = 1.8 lel). The addition of one electron to B_{24}^{-} can be seen as doubling ON value of the 5c π bond in B_{24}^{2-} . In other words, one can view the 5c-2e π -bond of B_{24}^{2-} as a 5c-1e π -bond with an ON of 0.9 lel in the B_{24}^{-}

Similar to all the boron clusters studied previously,^{9–18,20} only classical localized 2c-2e B-B σ -bonds are found between the 15 peripheral boron atoms in B₂₄⁻ (Fig. 4). The peripheral B-B bond distances are in the range of 1.52–1.63 Å, and their ON values are close to the ideal case of 2.0 lel. All other σ -bonds associated with the 9 inner atoms are found to be delocalized: eleven 3c-2e and three 4c-2e σ -bonds are found inside the filled pentagon; four 3c-2e and two 4c-2e σ -bonds are found inside the filled pentagon; four 3c-2e and two 4c-2e σ -bonds are found inside the filled pentagon; four 3c-2e and two 4c-2e σ -bonds are found in bord to be responsible for the bonding between the filled pentagonal unit and its surrounding atoms. This delocalized σ bonding patter is exactly the same as those observed in the B₂₁⁻.¹⁹

In addition to delocalized σ bonds, the 9 interior boron atoms in B_{24} are also bonded by seven delocalized π -bonds: six 4c-2e π -bonds and one 6c-2e π -bond. The B₂₄⁻ dianion contains an eighth delocalized 5c-2e π -bond, shown in Fig. 4(b). The four 4c-2e π -bonds found at the vertices of the filled pentagon in B_{24}^{-} look exactly the same as the corresponding ones in B_{21}^{-} . Furthermore, the unique 6c-2e π bond delocalized over the six inner B atoms comprising the B-centered pentagon is also similar to that in B₂₁⁻. An increase in the out-of-plane distortion of the filled pentagon fragment upon increasing the cluster size suggests the tendency to form icosahedral bulk-like structural features. The out-of-plane distortion in the filled pentagonal motif reduces the geometrical stress imposed by the periphery and may explain the energetic advantage of the global minimum of B_{24}^{-} . It is also interesting to note that isomers I, III, and IV all contain a pentagonal cavity, which also helps release of geometrical stresses. All the other higher lying 2D structures (V, VI, VII, and VIII), however, possess more regular triangular lattices (Fig. 2). These structures are higher in energy than isomers I, III, and IV, likely due to the geometric strain imposed by the uninterrupted triangular lattice motifs.



FIG. 4. AdNDP analyses of the closed-shell neutral B_{24} (a) and the dianion B_{24}^{2-} [(a) and (b)] at the geometry of B_{24}^{-} . ON stands for occupation number and is equal to 2.0 lel in an ideal case.

VIII. CONCLUSIONS

We report a joint theoretical and experimental study of the B_{24}^{-} cluster, the largest boron cluster to be characterized experimentally thus far. We found that the global minimum structure of this large boron cluster is quasi-planar, containing a filled pentagonal unit with the central boron atom distorted out of plane significantly. A double-ring 3D isomer was found to be higher in energy at the ROCCSD and ROCCSD(T) levels of theory, while it is the global minimum according to two DFT methods: PBE0 and TPSSh. Comparison of the simulated photoelectron spectra with the experimental data confirms unequivocally the quasi-planar global minimum identified for B_{24}^{-} at the higher levels of theory. Chemical bonding analysis revealed that the periphery of B_{24}^{-} is bonded only by classical 2c-2e B-B σ -bonds, whereas both delocalized σ and π -bonds are found in the interior of the cluster with one unique 6c-2e π -bond responsible for the bonding in the Bcentered pentagon. The current results seem to suggest a tendency to form filled pentagon-like units upon increasing the cluster size, an important structural feature in the icosahedral blocks of bulk boron.

versity of Russia, Moscow, Russia), on the occasion of his 65th birthday and wish him a long and happy life, full of happiness and accomplishments.

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