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Photoelectron spectroscopy and *ab initio* study of boron-carbon mixed clusters: CB_9^- and $C_2B_8^-$

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We performed a joint photoelectron spectroscopy and *ab initio* study of two carbon-doped boron clusters, CB_9^- and $C_2B_8^-$. Unbiased computational searches revealed similar global minimum structures for both clusters. The comparison of the experimentally observed and theoretically calculated vertical detachment energies revealed that only the global minimum structure is responsible for the experimental spectra of CB_9^- , whereas the two lowest-lying isomers of $C_2B_8^-$ contribute to the experimental spectra. The planar "distorted wheel" type structures with a single inner boron atom found for CB_9^- and $C_2B_8^-$ are different from the quasi-planar structure of B_{10}^- , which consists of two inner atoms and eight peripheral boron atoms. The adaptive natural density partitioning chemical bonding analysis revealed that CB_9^- and C_2B_8 clusters exhibit π aromaticity and σ antiaromaticity, which is consistent with their planar distorted structures. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4770231]

I. INTRODUCTION

Experimental and theoretical studies over the last decade showed that anionic boron clusters are planar or quasi-planar at least up to B_{23}^{-} .^{1–14} Neutral boron clusters have been reported to have planar structures up to B_{20} ,^{15–17} except for B_{14} , for which a three-dimensional global minimum structure was proposed.¹⁸ Boron cationic clusters are planar up to B_{16}^{+} .¹⁹ The exceptional stability of the icosahedral B_{12} cage found in bulk boron allotropes and boranes led to suggestions in early experimental studies that 3D cage structures might occur for small boron clusters.^{20–22} However, subsequent computational studies showed that icosahedral cage structures for B_{12} and B_{13} were unstable.^{23–30}

Chemical bonding analyses revealed that the concepts of aromaticity, multiple aromaticity/antiaromaticity, and conflicting aromaticity could nicely explain the geometries and stabilities of these quasi-planar boron clusters.^{1–13,31–34} The following chemical bonding model was developed for planar boron clusters: all peripheral boron atoms are bonded to their neighbors by two-center two-electron (2c–2e) σ bonds, while the central atoms are bonded via delocalized multi-center σ and π bonds with the peripheral atoms. If the number of delocalized σ or π electrons satisfies the 4n+2 Hückel rule, the cluster exhibits σ or π aromaticity. The planarity, stability, and high symmetry of some of the boron clusters suggested that they may serve as ligands or building blocks.¹³ A planar cyclic B₆ building block has recently been observed in a tertiary boride compound, Ti₇Rh₄Ir₂B₈, showing that planar boron clusters can indeed exist in solid compounds.³⁵

Doping boron clusters with other elements widens the range of potential ligands and building blocks. The CB_6^{2-} , CB7⁻, and CB8 clusters have been suggested theoretically to be hexa-, hepta-, and octacoordinated planar carbon species, respectively, though they are only local minima, not global minima.^{36–38} In joint experimental and theoretical investigations, we have shown that the wheel-type structures are indeed global minima for the CB_6^{2-} , CB_7^{-} , and CB_8 clusters, ^{39–41} but carbon avoids hypercoordination in these species and occupies a peripheral position instead. Theoretical investigations on planar tetra-, penta-, hexa-, hepta-, and octacoordinated structures of boron-carbon mixed clusters showed that boron-centered isomers are generally more stable than the ones with carbon in the center.⁴² Carbon being more electronegative than boron prefers localized bonding, which is only possible on the periphery of the cluster, and avoids the central position since the central atoms participate only in delocalized bonding. We have also studied a series of AlB_{x} clusters and found that the Al atom also avoids hypercoordination in the anionic clusters.^{43–45} A variety of elements have been tested computationally for the central position in high symmetry wheel-type structures.^{38,46–52} In recent joint experimental and theoretical works, we discovered a series of transition metal-centered boron wheels.^{53–56} In particular, we have shown⁵⁵ that Ta in Ta $(c)B_{10}^{-}$ and Nb in Nb $(c)B_{10}^{-}$ have the highest coordination number for an atom in two-dimensional environment.⁵⁷ All of these wheel-type clusters belong to a new class of aromatic borometallic compounds and may be viable for condensed phase synthesis.

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FIG. 1. Global minima structures of B₁₀⁻ (Ref. 14), CB₉⁻, and C₂B₈⁻.

A few systematic studies of the influence of elemental substitution in clusters on their geometries and electronic properties have been reported. For the $C_x B_{5-x}$ series, a planar-to-linear structural transition was observed:⁵⁸ the global minimum structures of the boron-rich clusters CB₄⁻ and $C_2B_3^-$, are planar, similar to B_5^- , and those of the carbon-rich clusters, $C_3B_2^-$ and C_4B^- , are linear, similar to C_5^{-} . A wheel-to-ring structural transition was reported⁵⁹ for the $C_x B_{8-x}^{-}$ series between x = 2 and 3. In the $B_n Al_{6-n}^{2-}$ and $\text{LiB}_n\text{Al}_{6-n}^-$ cluster series, 3D to 2D transitions in both series occur between n = 2 and $3.^{60}$ Computational studies of the $C_x H_x P_{6-x}$ $(x = 0-6)^{61}$ and $C_x H_x P_{4-x}$ $(x = 0-4)^{62}$ series showed that the global minima become planar at x = 4 and x= 3, respectively. A 3D to 2D transition in the $Si_{6-n}C_nH_6$ (*n* = 0-6) series occurs between n = 4 and 5.⁶³ Finally, a 3D to linear transition in the $Si_{6-n}C_n$ series was observed between n = 3 and 4 in a joint experimental and theoretical study.⁶⁴

In the current work, we report a joint photoelectron spectroscopic and *ab initio* study of the CB_9^- and $C_2B_8^-$ clusters. It was previously found that B_{10}^- has a quasi-planar structure (Figure 1), which could be described as an eight-membered outer ring enclosing two inner atoms.¹⁴ Substitution of one and two boron atoms in the B_{10}^- cluster by carbon results in planar global minima in CB_9^- and $C_2B_8^-$, as presented in Figure 1. The carbon atoms not only occupy peripheral positions, as expected, but they also induce significant structural changes to the boron networks: one of the inner boron atoms is pushed to a peripheral position, resulting in the "distorted wheel" structures.

II. EXPERIMENTAL AND COMPUTATIONAL METHODS

A. Experimental method

The experiment was performed using a magnetic-bottle PES apparatus equipped with a laser vaporization cluster source, details of which have been published in Ref. 65. Briefly, the CB₉⁻ and C₂B₈⁻ clusters were produced by laser vaporization of composite targets made with isotopically enriched ¹⁰B containing about 0.1% C. Clusters formed in the source were entrained by a helium carrier and underwent a supersonic expansion to produce a cold cluster beam. Negatively charged clusters were extracted from the cluster beam and analyzed using a time-of-flight mass spectrometer. The CB₉⁻ and C₂B₈⁻ clusters of interest were mass selected and decelerated before being intercepted by a 193 nm (6.424 eV)

laser beam from an ArF excimer laser or 355 nm (3.496 eV) and 266 nm (4.661 eV) from a Nd:YAG laser for photodetachment. Photoelectron time-of-flight spectra were measured and calibrated using the known spectra of Bi⁻ at 193, 266, and 355 nm and converted to the binding energy spectra by subtracting the kinetic energy spectra from the corresponding photon energies. The energy resolution of the magnetic-bottle PES spectrometer is $\Delta E/E \approx 2.5\%$, i.e., about 25 meV for 1 eV electrons.

B. Computational methods

We first performed global minimum searches for CB9⁻ and C₂B₈⁻ using the Coalescence Kick (CK) program.^{10,66} Low energy structures within 50 kcal/mol of the global minimum structure at the PBE0/6-31G level⁶⁷⁻⁶⁹ were reoptimized with follow-up frequency calculations at the PBE0/6-311+G(d) level⁷⁰ of theory (see Figs. S1 and S2).⁷¹ Single point coupled cluster including single, double and non-iterative triple excitations (CCSD(T)),⁷²⁻⁷⁴ CCSD(T)/6-311+G(2df), calculations were performed for the 10 lowest energy isomers of both clusters. Vertical detachment energies (VDEs) were calculated at the time dependent density functional theory (TD-DFT), 75,76 TD-PBE0/6-311+G(d), outervalence Green's Function method (OVGF),⁷⁷⁻⁸⁰ OVGF/6-311+G(2df), and CCSD(T)/6-311+G(2df), all at the PBE0/6-311+G(d) geometries. At the TD-DFT, the first VDEs for CB_9^- and $C_2B_8^-$ were calculated as the lowest transitions from the anions into the final lowest state of the neutral species at the geometry optimized for the anions. Then, the vertical excitation energies of the neutral species calculated at the anion geometry were added to the first VDE to obtain the second and higher VDEs. The OVGF/6-311+G(2df) energies are presented only for CB₉⁻, since high spin contamination was observed for C₂B₈⁻. Chemical bonding analysis was performed using the adaptive natural density partitioning method (AdNDP)⁸¹ at PBE0/6-31G.

All calculations were performed using the GAUSSIAN09⁸² and MOLPRO⁸³ software packages, Molekel 5.4.0.8⁸⁴ and Chemcraft⁸⁵ programs were used for visualizations.

III. EXPERIMENTAL RESULTS

The photoelectron spectra of CB_9^- and $C_2B_8^-$ at different photon energies are shown in Figs. 1 and 2, respectively. The PES bands are labeled with letters (X, A, B, ...) and the measured VDEs are given in Tables I and II, where they are also compared with computational results. In each spectrum, the X band represents the transition from the anionic ground state to the neutral ground state. The A, B, ... bands denote transitions to the excited states of the neutrals.

A. Photoelectron spectra of CB₉⁻

The 266 nm spectrum of CB_9^- (Fig. 2(a)) shows a vibrationally resolved ground state band with a VDE of 3.61 eV. The inset of Fig. 2(a) displays more clearly the vibrational

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FIG. 2. Photoelectron spectra of CB_9^- at (a) 266 nm (4.661 eV) and (b) 193 nm (6.424 eV). The inset in (a) shows the resolved vibrational structures in band X.

progression with an average spacing of $340 \pm 50 \text{ cm}^{-1}$. The adiabatic detachment energy (ADE) or the electron affinity of the corresponding neutral CB₉ is defined by the 0-0 vibrational peak, which is 3.61 ± 0.03 eV, the same as the VDE. Following an energy gap of ~0.8 eV, a relatively broad band A is observed with a VDE of 4.49 eV. Two more bands are observed in the 193 nm spectrum with VDEs of 4.88 eV for band B and 5.74 eV for band C. There is discernible signal beyond 6 eV and a band D with a VDE of ~6.2 eV is tentatively identified.

The weak feature labeled as "*" in the low binding energy range comes from the B_{10}^- cluster, which has a first VDE of 3.06 eV.¹⁴ The mass of B_{10}^- is very close to that of CB₉⁻ and its intensity was very high in the mass spectrum, making it difficult to be completely eliminated when the CB₉⁻ mass peak was selected during the PES experiment. In fact, contributions from the B_{10}^- contamination can be identified in other parts of the CB₉⁻ spectra, namely, around 3.8 eV and between 5 and 5.6 eV by comparing with the previously reported PES spectra of $B_{10}^{-.14}$

B. Photoelectron spectra of C₂B₈⁻

The 355 nm spectrum (Fig. 3(a)) displays two relatively sharp and vibrationally resolved bands. The band labeled as X' has the same ADE and VDE of 2.39 ± 0.03 eV. The sharp onset of band X' suggests a minimal geometry change upon photodetachment. Two vibrational progressions are observed in band X' with frequencies of 390 ± 50 cm⁻¹ and $1330 \pm$ 50 cm⁻¹. The band labeled as X has an ADE and VDE of 2.67 ± 0.03 eV. There are also two vibrational progressions associated with band X with frequencies of 510 ± 50 cm⁻¹ and 1480 ± 50 cm⁻¹. As will be shown later, the X' and X bands come from two different isomers with close energies.

The 266 nm spectrum (Fig. 3(b)) shows two sharp bands (A', A) at 4.05 eV and 4.14 eV and one broad band B at 4.52 eV. The 193 nm spectrum (Fig. 3(c)) has poor signal-to-noise ratio and three bands (C, D, and E) are tentatively identified with VDEs of 4.92 eV, 5.30 eV, and 5.58 eV, respectively. The weak peak labeled with "*" around 3.6 eV is likely due to contributions from CB_9^- , because these two clusters also have very close masses.

IV. THEORETICAL RESULTS

A. CB₉⁻

The lowest energy isomers ($\Delta E < 50$ kcal/mol) revealed by the unbiased global minimum search at PBE0/6-31G were reoptimized with frequency calculations at the PBE0/6-311+G(d) level of theory (Fig. S1).⁷¹ Single point CCSD(T)/6-311+G(2df) calculations were performed for the 10 lowest in energy isomers of CB_9^- , as shown in Fig. 4. All these structures are planar or quasi-planar and mostly are permutational isomers of either the global minimum structure or the structure analogous to the global minimum of B_{10}^{-14} . The lowest energy isomer I.1 is a distorted wheel-type structure with the carbon atom occupying a peripheral position. The isomers I.3, I.5, I.9, and I.10 are isostructural with the global minimum structure of B_{10}^{-} (Fig. 1), but are appreciably higher in energy. The structure I.9, which has a carbon atom in the central position, is 22.5 kcal/mol higher in energy than the global minimum. The preference for the peripheral

TABLE I. Observed VDEs of I.1 CB₉⁻ compared with the theoretically calculated values for the lowest isomer of CB₉⁻. All energies are in eV.

Observed features	VDE (exp) ^a	Final state and electronic configuration	VDE (theoretical)		
			TD-PBE0 ^b	ROVGF ^c	CCSD(T) ^d
$I.1 CB_9^- (C_{2v}, {}^1A_1)$					
X	3.61 (3)	${}^{2}A_{2} \dots 6a_{1}{}^{(2)} 1b_{1}{}^{(2)} 7a_{1}{}^{(2)} 2b_{1}{}^{(2)} 5b_{2}{}^{(2)} 8a_{1}{}^{(2)} 1a_{2}{}^{(1)}$	3.53	3.54 (0.88)	3.62
А	4.49 (3)	${}^{2}A_{1} \dots 6a_{1}{}^{(2)} 1b_{1}{}^{(2)} 7a_{1}{}^{(2)} 2b_{1}{}^{(2)} 5b_{2}{}^{(2)} 8a_{1}{}^{(1)} 1a_{2}{}^{(2)}$	4.64	4.49 (0.88)	4.57
В	4.88 (4)	${}^{2}B_{2} \dots 6a_{1}{}^{(2)} 1b_{1}{}^{(2)} 7a_{1}{}^{(2)} 2b_{1}{}^{(2)} 5b_{2}{}^{(1)} 8a_{1}{}^{(2)} 1a_{2}{}^{(2)}$	4.88	4.88 (0.88)	4.93
С	5.74 (4)	${}^{2}B_{1} \dots 6a_{1}{}^{(2)} 1b_{1}{}^{(2)} 7a_{1}{}^{(2)} 2b_{1}{}^{(1)} 5b_{2}{}^{(2)} 8a_{1}{}^{(2)} 1a_{2}{}^{(2)}$	5.67	5.73 (0.87)	5.74
D	6.2 (1)	${}^2A_1\ldots 6a_1{}^{(2)} 1b_1{}^{(2)} 7a_1{}^{(1)} 2b_1{}^{(2)} 5b_2{}^{(2)} 8a_1{}^{(2)} 1a_2{}^{(2)}$	5.96	6.05 (0.84)	

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

^bVDEs were calculated at TD-PBE0/6-311+G(2df)//PBE0/6-311+G(d).

^cVDEs were calculated at ROVGF/6-311+G(2df)//PBE0/6-311+G(d). Values in parentheses represent the pole strength of the OVGF calculation.

^dVDEs were calculated at CCSD(T)/6-311+G(2df)//PBE0/6-311+G(d).

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TABLE II. Observed VDEs of C_2B_8 compared with the calculated values for the two lowest energy isomers of C_2B_8 . All energies
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	VDE (exp) ^a	Final state and electronic configuration	VDE (theoretical) ^b	
Observed features			TD-PBE0 ^c	CCSD(T) ^d
II.1 $C_2B_8^-$ (C_s , ² A'')				
Х	2.67 (3)	${}^{1}A' \dots 10a'^{(2)} 11a'^{(2)} 12a'^{(2)} 2a''^{(2)} 13a'^{(2)} 3a''^{(2)} 4a''^{(0)}$	2.78	2.66
А	4.14 (3)	${}^{3}A' \dots 10a'^{(2)} 11a'^{(2)} 12a'^{(2)} 2a''^{(2)} 13a'^{(2)} 3a''^{(1)} 4a''^{(1)}$	4.12	4.21
В	4.52 (3)	${}^{3}A'' \dots 10a'^{(2)} 11a'^{(2)} 12a'^{(2)} 2a''^{(2)} 13a'^{(1)} 3a''^{(2)} 4a''^{(1)}$	4.52	4.51
С	4.92 (5)	${}^{1}A'' \dots 10a'^{(2)} 11a'^{(2)} 12a'^{(2)} 2a''^{(2)} 13a'^{(1)} 3a''^{(2)} 4a''^{(1)}$	4.89	
D	5.30 (5)	${}^{1}A'' \dots 10a'^{(2)} 11a'^{(2)} 12a'^{(2)} 2a''^{(2)} 13a'^{(2)} 3a''^{(1)} 4a''^{(1)}$	5.11	
		${}^{3}A' \dots 10a'^{(2)} 11a'^{(2)} 12a'^{(2)} 2a''^{(1)} 13a'^{(2)} 3a''^{(2)} 4a''^{(1)}$	5.23	
Ε	5.58 (5)	${}^{3}A'' \dots 10a'^{(2)} 11a'^{(2)} 12a'^{(1)} 2a''^{(2)} 13a'^{(2)} 3a''^{(2)} 4a''^{(1)}$	5.58	
		${}^{3}A'' \dots 10a'^{(2)} 11a'^{(1)} 12a'^{(2)} 2a''^{(2)} 13a'^{(2)} 3a''^{(2)} 4a''^{(1)}$	5.83	
II.2 $C_2 B_8^- (C_s, {}^2 A'')$				
Χ′	2.39 (3)	${}^{1}A' \dots 10a'^{(2)} 11a'^{(2)} 2a''^{(2)} 12a'^{(2)} 13a'^{(2)} 3a''^{(2)} 4a''^{(0)}$	2.49	2.38
A′	4.05 (3)	${}^{3}A' \dots 10a'^{(2)} 11a'^{(2)} 2a''^{(2)} 12a'^{(2)} 13a'^{(2)} 3a''^{(1)} 4a''^{(1)}$	4.00	4.10
		${}^{3}A'' \dots 10a'^{(2)} 11a'^{(2)} 2a''^{(2)} 12a'^{(2)} 13a'^{(1)} 3a''^{(2)} 4a''^{(1)}$	4.61	4.57
		${}^{1}A' \dots 10a'^{(2)} 11a'^{(2)} 2a''^{(2)} 12a'^{(2)} 13a'^{(2)} 3a''^{(1)} 4a''^{(1)}$	4.90	
		${}^{1}A'' \dots 10a'^{(2)} 11a'^{(2)} 2a''^{(2)} 12a'^{(2)} 13a'^{(1)} 3a''^{(2)} 4a''^{(1)}$	4.96	
		${}^{3}A'' \dots 10a'^{(2)} 11a'^{(2)} 2a''^{(2)} 12a'^{(1)} 13a'^{(2)} 3a''^{(2)} 4a''^{(1)}$	5.29	
		${}^{1}A'' \dots 10a'^{(2)} 11a'^{(2)} 2a''^{(2)} 12a'^{(1)} 13a'^{(2)} 3a''^{(2)} 4a''^{(1)}$	5.54	
		${}^{3}A'' \dots 10a'^{(2)} 11a'^{(2)} 2a''^{(1)} 12a'^{(2)} 13a'^{(2)} 3a''^{(2)} 4a''^{(1)}$	5.63	
		${}^{3}A'' \dots 10a'^{(2)} 11a'^{(1)} 2a''^{(2)} 12a'^{(2)} 13a'^{(2)} 3a''^{(2)} 4a''^{(1)}$	6.08	

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

^bOVGF/6-311+G(2df) energies are not reported for $C_2B_8^-$ due to high spin contamination observed in the calculation.

^cVDEs were calculated at TD-PBE0/6-311+G(2*df*)//PBE0/6-311+G(*d*).

^dVDEs were calculated at CCSD(T)/6-311+G(2df)//PBE0/6-311+G(d).



FIG. 3. Photoelectron spectra of $C_2B_9^-$ at (a) 355 nm (3.496 eV), (b) 266 nm, and (c) 193 nm. The vertical lines in (a) show the resolved vibrational structures.

position of the carbon atom is consistent with the previous findings for the CB_6^{2-} , CB_7^{-} , and CB_8 clusters.^{39–41}

B. C₂B₈⁻

The global minimum structure search for $C_2B_8^-$ at PBE0/6-31G(*d*) revealed 35 isomers within $\Delta E < 50$ kcal/mol. The isomers were reoptimized with frequency calculations at the PBE0/6-311+G(*d*) level of theory



FIG. 4. Lowest energy isomers of the CB_9^- cluster, their point group symmetries, spectroscopic states, and ZPE corrected relative energies at CCSD(T)/6-311+G(2df)//PBE0/6-311+G(d). All energies are in kcal/mol.

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FIG. 5. Lowest energy isomers of the $C_2B_8^-$ cluster, their point group symmetries, spectroscopic states, and ZPE corrected relative energies at CCSD(T)/6-311+G(2*df*)//PBE0/6-311+G(*d*). All energies are in kcal/mol.

(Fig. S2).⁷¹ Single point CCSD(T)/6-311+G(2*df*) calculations were performed for the 10 lowest in energy isomers, as shown in Fig. 5. The global minimum structure **II.1** of $C_2B_8^-$ is very similar to the global minimum structure **I.1** of CB_9^- . The next 4 isomers (**II.2-II.5**), as well as the isomers **II.7-II.9**, are simply permutational isomers of the global minimum structure with the two carbon atoms occupying different peripheral positions. Interestingly, all structures with two neighboring carbon atoms are appreciably higher in energy (Fig. S2).⁷¹

V. INTERPRETATION OF THE PHOTOELECTRON SPECTRA

A. CB₉⁻

According to the theoretical calculations, only the lowest in energy isomer **I.1** of CB_9^- is expected to contribute to the experimental photoelectron spectra because the second lowest energy isomer is significantly higher in energy (by 9.9 kcal/mol). The calculated VDEs, at TD-PBE0, OVGF, and CCSD(T) levels, all with the 6-311+G(2df) basis set and at the PBE0/6-311+G(d) geometry, are compared with the experimental features in Table I. The first peak X in the experimental spectrum of CB_9^- (Fig. 2) comes from electron detachment from the HOMO (1a2) of the global minimum structure **I.1**, leading to the final doublet state ${}^{2}A_{2}$ (see Fig. S3 for the valence molecular orbital plots).⁷¹ The three theoretical values for the first VDE, 3.53 eV (TD-PBE0), 3.54 eV (ROVGF), and 3.62 eV (CCSD(T)) are all in good agreement with the experimental value of 3.61 \pm 0.03 eV. The observed vibrational frequency of 340 cm^{-1} agrees well with the totally symmetric mode ω_1 of the neutral ground state with a calculated frequency of 346 $\rm cm^{-1}$ (Table S1).⁷¹ The band A corresponds to electron detachment from HOMO-1 (8a₁) with the final doublet state ${}^{2}A_{1}$. Again, all three theoretical VDEs, 4.64, 4.49, and 4.57 eV at TD- PBE0, ROVGF, and CCSD(T), respectively, are in excellent agreement with each other and the experimental value of 4.49 \pm 0.03 eV. Similarly, the bands B, C, and D can be assigned to electron detachments from HOMO-2 (5b₂), HOMO-3 (2b₁), and HOMO-4 (7a₁), respectively, resulting in the final ²B₂, ²B₁, and ²A₁ states. The corresponding theoretical VDEs also agree well with the experimental values (Table I). The overall excellent agreement between the experimentally observed and the theoretically calculated VDEs confirms unequivocally the predicted global minimum structure **I.1** for CB₉⁻.

B. C₂B₈⁻

According to our calculations, the second lowest energy isomer of $C_2B_8^-$ (II.2) is only 1.6 kcal/mol higher than the global minimum structure **II.1**, and thus is anticipated to contribute to the experimental spectra. The VDEs calculated for both isomers are compared with the experimental data in Table II. The valence canonical molecular orbitals for the global minimum of $C_2B_8^-$ are shown in Fig. S3.⁷¹ The first VDE of $C_2B_8^-$ II.1 corresponds to the detachment from the singly occupied HOMO (4a'') to produce the ground state neutral C_2B_8 (¹A'). The VDE is calculated to be 2.78 eV (TD-PBE0) and 2.66 eV (CCSD(T)), which agree well with band X at 2.67 \pm 0.03 eV. The observed vibrational structures with frequencies of 510 and 1480 cm⁻¹ can be assigned to the ω_4 mode (553 cm⁻¹) and the ω_{14} mode (1465 cm⁻¹) and/or the ω_{15} mode (1483 cm⁻¹), respectively, as given in Table S2.⁷¹ The next detachment channel from the doubly occupied HOMO-1 (3a") yields a ³A' final state with a VDE of 4.12 eV (TD-PBE0) and 4.21 eV (CCSD(T)), in good agreement with band A at 4.14 \pm 0.03 eV in the spectra. Thus, neutral C_2B_8 is closed with a large HOMO-LUMO gap (1.47 eV), as defined by the X-A bands. The corresponding singlet final state $({}^{1}A'')$ from the HOMO-1 (3a'') state has a VDE of 5.11 eV at TD-PBE0, falling in the congested region D. The detachment from the HOMO-2 (13a') gives rise to triplet (3A'') and singlet (1A'') final states with calculated VDEs of 4.52 and 4.89 eV at TD-PBE0, in excellent agreement with the observed bands B and C (Table II).

The first VDE of the $C_2B_8^-$ low-lying isomer **II.2** is calculated to be 2.49 eV (TD-PBE0) and 2.38 eV (CCSD(T)), in excellent agreement with band X' at 2.39 \pm 0.03 eV; it corresponds to electron detachment from the singly occupied HOMO (4a'') to the lowest singlet state ${}^{1}A'$ of neutral **II.2**. The observed vibrational structures with frequencies of 390 and 1330 cm⁻¹ can be assigned to the ω_2 mode (355 cm⁻¹) and the ω_{13} mode (1304 cm⁻¹), respectively, as given in Table S3.⁷¹ The next detachment channel from HOMO-1 (3a") of **II.2** is calculated to be 4.00 eV (TD-PBE0) and 4.10 eV (CCSD(T)), corresponding to band A' at 4.05 eV. This detachment channel leads to the lowest triplet state $({}^{3}A')$ of **II.2**. Thus, the X' and A' bands define a large HOMO-LUMO gap (1.66 eV) for the neutral of II.2. The higher detachment channels of isomer II.2 and those of the global minimum start to overlap, leading to the congested spectral features in the higher binding energy range. The relatively lower intensities of bands X' and A' compared to the X and A bands, respectively, are consistent with the higher energy of isomer



FIG. 6. Adaptive natural density partitioning chemical bonding analysis for (a) CB9⁻ and (b) C2B8 at the geometry optimized for C2B8⁻.

II.2. The good agreement between experimental and theoretical VDEs for both isomers **II.1** and **II.2** confirms firmly their structures and their energetic ordering.

VI. CHEMICAL BONDING

A single carbon substitution induces a major structural change to the B_{10}^- structure, giving rise to a rather peculiar global minimum for CB_9^- . Clearly, carbon prefers the lowest possible coordination site by bonding only to two boron atoms in a CB_2 triangle. The second carbon in $C_2B_8^-$ also prefers the low coordination peripheral sites, yielding two close-lying structures **II.1** and **II.2**. Neutral C_2B_8 is isoelectronic with CB_9^- and both isomers possess large HOMO-LUMO gaps, suggesting that the neutral C_2B_8 structures are both highly stable closed-shell electronic systems.

We performed chemical bonding analysis for the two clusters using the AdNDP. AdNDP analysis was performed for CB_9^- and for neutral C_2B_8 at the geometry of the lowest energy structure of $C_2B_8^-$. The chemical bonding in the $CB_9^$ cluster (Fig. 6(a)) can be described as a combination of seven $2c-2e B-B \sigma$ bonds and two $2c-2e C-B \sigma$ bonds (shown superimposed on a single molecular framework) responsible for the peripheral bonding in the cluster, four $3c-2e \sigma$ bonds responsible for the bonding between the central and peripheral atoms, and one 3c–2e and two 4c–2e π bonds also responsible for bonding between the central atom and the peripheral atoms. The AdNDP analysis for C_2B_8 (Fig. 6(b)) is nearly identical to that of CB₉⁻. The presence of the eight delocalized σ electrons in both clusters makes them σ antiaromatic,⁸⁶ consistent with their in-plane distortions. Both clusters have six π electrons, rendering them π aromatic. Overall, the two clusters can be characterized as systems with conflicting aromaticity.

VII. SUMMARY

We performed a joint photoelectron spectroscopy and ab initio study of two carbon-boron mixed clusters, CB9- and C₂B₈⁻. Computational global minimum searches revealed that both clusters have similar global minimum structures, which can be described as distorted wheel structures. Carbon atoms are found to occupy the peripheral positions in both cases, in agreement with previous findings for the CB_6^{2-} , CB₇⁻, and CB₈ clusters.³⁹⁻⁴¹ The comparison of the experimental and theoretical VDEs for both clusters revealed that only the global minimum structure is responsible for the experimental spectra of CB₉⁻, while two low-lying structures contribute to the experimental spectra for $C_2B_8^-$. The structural transition from B_{10}^{-} with two inner atoms to distorted wheel-like structures with a single inner atom in CB9⁻ and $C_2B_8^-$ occurs in part because of the preference of carbon to form localized bonds. The AdNDP chemical bonding analyses revealed that CB_9^- and C_2B_8 are both π aromatic, but σ antiaromatic, consistent with their planar distorted structures.

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