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### ADVERTISEMENT



### A photoelectron spectroscopy and *ab initio* study of B<sub>21</sub><sup>-</sup>: Negatively charged boron clusters continue to be planar at 21

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The structures and chemical bonding of the  $B_{21}^{-}$  cluster have been investigated by a combined photoelectron spectroscopy and *ab initio* study. The photoelectron spectrum at 193 nm revealed a very high adiabatic electron binding energy of 4.38 eV for  $B_{21}^{-}$  and a congested spectral pattern. Extensive global minimum searches were conducted using two different methods, followed by high-level calculations of the low-lying isomers. The global minimum of  $B_{21}^{-}$  was found to be a quasiplanar structure with the next low-lying planar isomer only 1.9 kcal/mol higher in energy at the CCSD(T)/6-311-G\* level of theory. The calculated vertical detachment energies for the two isomers were found to be in good agreement with the experimental spectrum, suggesting that they were both present experimentally and contributed to the observed spectrum. Chemical bonding analyses showed that both isomers consist of a 14-atom periphery, which is bonded by classical two-center two-electron bonds, and seven interior atoms in the planar structures. A localized two-center two-electron bond is found in the interior of the two planar isomers, in addition to delocalized multi-center  $\sigma$  and  $\pi$  bonds. The structures and the delocalized bonding of the two lowest lying isomers of  $B_{21}^{-}$  were found to be similar to those in the two lowest energy isomers in  $B_{19}^{-}$ . © 2012 American Institute of Physics. [http://dx.doi.org/10.1063/1.3692967]

#### I. INTRODUCTION

Because of its electron deficiency, elemental boron forms unusual crystals dominated by cage-like structural units.<sup>1,2</sup> Early experimental studies focused on fragmentation and chemical reactivity of boron cation clusters,<sup>3–6</sup> while early computational studies suggested that three-dimensional icosahedral cage structures were not stable for  $B_{12}$  and  $B_{13}$ .<sup>7,8</sup> Instead, planar (2D) or quasiplanar structures were suggested to be more stable up to 14 atoms in both cationic and neutral boron clusters.<sup>9–19</sup> Reliable structural information for boron clusters came from combined photoelectron spectroscopy (PES) and ab initio calculations, with which we have systematically studied the structural evolution and chemical bonding of anionic boron clusters,  $B_n^-$ , up to n = 20.20-38 We have found that the global minima of all these clusters are planar or quasiplanar. It has been observed that the presence of two-dimensional electron delocalization is responsible for the stabilization of the planar or quasiplanar 2D structures of these clusters, giving rise to the concepts of multiple aromaticity/antiaromaticity and hydrocarbon analogues of boron clusters.<sup>24,25,27–29,38</sup> Aromaticity has been found in planar boron clusters in further computational analyses.<sup>39–44</sup> Interestingly, theoretical analyses have shown that the interior atoms in some planar boron clusters possess fluxional behaviour within the molecular plane with low activation barriers.45,46 Though the 2D to 3D transition was concluded to occur at  $B_{20}$  for the neutral clusters,<sup>28,47</sup> and  $B_{16}^+$  for the cationic species,<sup>48</sup> it remains to be resolved where this transition occurs for the anionic clusters. Thus, the continued systematic study of the size-dependent evolution of the geometric and electronic properties of anionic boron clusters are important to achieve a complete understanding of boron clusters and their chemical bonding.

However, the global minimum search for clusters of large sizes still presents a major challenge. In recent years, we have employed the gradient embedded genetic algorithm (GEGA),<sup>49–51</sup> Basin Hopping (BH) method,<sup>52–55</sup> and Coalescence-Kick (CK) method<sup>38,56,57</sup> for global minimum searches of relatively small clusters. Due to the projected exponential increase of minima on the potential energy surface and the computational expense of evaluating the energy of each visited region of the surface with increasing cluster size, new methods to deal with larger cluster systems that will reliably search relevant areas of the potential energy surface are of significant value.<sup>58</sup>

In this article, we report the structures and chemical bonding of the  $B_{21}^{-}$  cluster using PES and *ab initio* calculations. We developed a new global minimum search technique, the Cartesian Walking (CW) method, which was used in corroboration with the CK method to sample the potential energy surface for the global minimum and low lying isomers of the  $B_{21}^{-}$  cluster. We found that two planar structures of  $C_s$  symmetry, which are similar to the two lowest-lying isomers of  $B_{19}^{-}$ ,<sup>29</sup> compete for the global minimum of this cluster. A 3D double-ring structure, similar to that of  $B_{20}$ ,<sup>28</sup> was found to be 15 kcal/mol higher in energy than the two

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competing planar global minimum structures. Chemical bonding analyses revealed that, similar to smaller boron clusters, the two low-lying isomers of  $B_{21}^{-}$  have peripheral 2c-2e B-B  $\sigma$ -bonds. The  $\pi$ -bonding patterns of the two isomers are similar to those of the two lowest-lying structures of the  $B_{19}^{-}$  cluster. More interestingly, both isomers contain a 2c-2e B-B  $\sigma$ -bond within the cluster, making  $B_{21}^{-}$  the first known planar boron cluster featuring an internal localized  $\sigma$ -bond.

#### **II. EXPERIMENTAL METHOD**

The experiment was carried out using a magnetic-bottle PES apparatus equipped with a laser vaporization cluster source, details of which have been described previously.<sup>59</sup> Briefly, boron anionic clusters were produced by laser vaporization of either a hot pressed pure <sup>10</sup>B-enriched (96%) disk target or a cold pressed target containing  $\sim 15\%^{-10}$ B balanced by Au, which acted as a binder and at the same time provided the Au<sup>-</sup> atomic anion as a calibrant for the PES apparatus. The clusters, entrained by a He carrier gas containing 5% Ar, underwent a supersonic expansion to form a collimated and vibrationally cold cluster beam, and were subsequently analyzed using a time of flight mass spectrometer. Different source conditions were tested to ensure that a vibrationally cold cluster beam was produced. Our previous experience on  $Au_n^-$  clusters showed that the Ar-seeded He carrier gas produced the coldest clusters.<sup>60</sup> The B<sub>21</sub><sup>-</sup> cluster was mass-selected and decelerated before being photodetached by a probe laser. Due to its relatively high binding energy, only one photon energy was used in the photodetachment experiment, 6.424 eV (193 nm), from an ArF excimer laser. Photoelectrons were collected at nearly 100% efficiency by the magnetic bottle and analyzed in a 3.5 m long electron flight tube. The PES spectra were calibrated using the known spectra of Bi<sup>-</sup> and Au<sup>-</sup>, and the energy resolution of the apparatus was  $\Delta E_k/E_k \sim 2.5\%$ , that is,  $\sim 25$  meV for 1 eV electrons.

#### **III. THEORETICAL METHODS**

We searched for the global minimum and low-lying isomers of  $B_{21}^{-}$  using both the CK (Refs. 38, 56, and 57) and CW methods. Both searches were initially done at the B3LYP level of theory<sup>61–63</sup> using the 3-21G basis set.<sup>64</sup> We generated roughly 4000 trial structures using the CK method and about 1500 trial structures with the CW method. The results of each search were not compared until they were completed. The CK method is described in detail in Ref. 38.

The most time consuming step of searching the potential energy surface of quantum mechanical systems is the local relaxation of trial structures usually achieved by calling an external density functional theory (DFT) package and running a gradient-based local optimization procedure. Thus, a searching algorithm that generates trial structures as close as possible to their geometrically relaxed states while not sacrificing the importance of randomness in structure generation is desirable. Methods which utilize force fields or molecular dynamics to pre-optimize trial structures have been developed for this reason, and have shown success for silicon clusters<sup>65</sup> and crystalline systems,<sup>66</sup> though these methods depend somewhat upon the aptness of the empirical potential employed for the system at hand. The CW method imposes restraints on a random walking process that takes place upon a grid of Cartesian coordinates to generate trial structures. The result is the generation of random trial structures with atomic positions that are neither unrealistically close nor unrealistically far from each other, and so they are relatively close to their corresponding relaxed geometries before quantum mechanical optimization is applied. Furthermore, added effectiveness can be achieved by tuning the grid for the system at hand. In the current work, three grids were constructed with a mesh of 0.4 Å (roughly 1/4 of the bond length of the B-B dimer). The dimensions of the four grids were  $20 \times 24 \times 0$ ,  $20 \times 24 \times 8$ , and  $20 \times 20 \times 20$ . The first two grids were tailored to search planar and quasiplanar geometries with a linear chain of boron atoms up to seven atoms. The third grid was designed to allow for three-dimensional geometries. The random walks were performed, allowing a maximum distance of five mesh points in each Cartesian direction per step. The minimum distance allowed between atoms was 1.3 Å. A more detailed description of the CW method is given in the Appendix.

All isomers below 1 eV relative to the global minimum found at 3-21G in the two searches were then re-optimized at the B3LYP/6-311+G\* (Refs 67–69) and PBE1PBE (Refs. 70–72)/6-311+G\* levels of theory. Vibrational frequencies were calculated to ensure that all the structures were true minima. The lowest five structures were also optimized at the MP2/6-311+G\* level. Subsequently, single point calculations at the CCSD(T) (Refs. 73–75)/6-311+G\* level of theory were carried out for the lowest five isomers using the optimized B3LYP/6-311+G\* geometries.

We calculated the vertical electron detachment energies (VDEs) of the lowest five isomers for  $B_{21}^{-}$  to compare with the experimental PES data. We employed three methods for this comparison, the restricted outer valence Green's function method,<sup>76–79</sup> ROVGF/6-311+G(2df), as well as two time-dependent DFT methods, 80,81 TD-B3LYP/6-311+G(2df), and TD-PBE1PBE/6-311+G(2df), all at the optimized B3LYP/6-311+G\* anion geometries. Core electrons were frozen in treating the electron correlation at the ROVGF level of theory. In the TD-DFT approaches, the first VDE of  $B_{21}^{-}$  was calculated at the B3LYP or PBE1PBE level as the lowest transition from the singlet state of the anion into the final lowest doublet state of the neutral. Then, the vertical excitation energies of the neutral species (at the TD-B3LYP or TD-PBE1PBE level) were added to the first VDE to approximate the second and higher VDEs.

The B3LYP, PBE1PBE, ROVGF, TD-B3LYP, TD-PBE1PBE, and MP2 calculations were performed using the GAUSSIAN 09 program.<sup>82</sup> The CCSD(T) calculations were performed using NWCHEM 6.0.<sup>83</sup> Molecular structure visualization was done using the MOLDEN 3.4 program.<sup>84</sup> Chemical bonding analyses were performed using the adaptive natural density partitioning (AdNDP) method<sup>85–87</sup> at the B3LYP/6-31G\*//B3LYP/6-311+G\* level. It has been shown previously that the AdNDP results are not sensitive to the level of theory or basis set used.<sup>88</sup> Molecular orbital (MO) visualization was performed using MOLEKEL 5.4.0.8.<sup>89</sup>



FIG. 1. Photoelectron spectrum of  $B_{21}^{-}$  at 193 nm (6.424 eV).

#### **IV. EXPERIMENTAL RESULTS**

The photoelectron spectrum for  $B_{21}^{-}$  is shown in Fig. 1 at 193 nm. The observed spectral bands are labeled with letters (X, A, B, ...). The measured VDEs are summarized in Table I, where they are compared with theoretical calculations.

The 193 nm spectrum of  $B_{21}^{-}$  shows a broad detachment band at around 4.6 eV, followed by an almost continuous spectral region spanning the binding energy range from 5 to beyond 6 eV with discernible fine features. The intense and broad 4.6 eV band seems to consist of more than one detachment channel. We assign the leading edge of the peak to the X band and a shoulder on the higher energy side to the A band. We measured a VDE of 4.58 eV for the X band. Since no vibrational structure was resolved for the X band, the ground state adiabatic detachment energy (ADE) was es-

timated 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 value so obtained for  $B_{21}^{-}$  is  $4.38 \pm 0.05$  eV, which represents the electron affinity of neutral  $B_{21}$ . For the A band, we estimated a VDE of 4.79 eV.

On the high binding energy side, we tentatively assign three more electronic bands (B, C, and D) with VDEs of 5.17, 5.43, and 5.72 eV, respectively. Finally, we note the presence of a weak tail on the low binding energy side below 4.3 eV. This tail was present in all of our experiments using different boron isotopes and targets. We conclude that this feature could be due to either hot band transitions and/or higher energy isomers in the cluster beam because its contribution diminishes when colder expansion conditions were used.<sup>90,91</sup>

#### **V. THEORETICAL RESULTS**

The isomers under 1 eV relative to the global minimum at B3LYP/3-21G from both the CK and CW searches were re-optimized at the B3LYP/6-311+G\* and PBE1PBE/ 6-311+G\* levels of theory. Vibrational frequencies were calculated to ensure that each isomer was a true minimum. We found that the CK and CW methods both identified the same set of ten low-lying isomers, as shown in Fig. 2. We also reoptimized the geometries and calculated the frequencies of the five lowest energy isomers at the MP2-6-311+G\* level and found that structure II distorts to a quasiplanar  $C_1$  structure at this level. The Cartesian coordinates of isomers I-V are given in the supplementary material along with their zeropoint energy (ZPE) values.<sup>92</sup> Also presented in Fig. 2 are results of the relative energies of the single-point energy calcu-

TABLE I. Comparison of the experimental VDEs with the calculated values from isomer I ( $C_s$ , <sup>1</sup>A') and isomer II ( $C_s$ , <sup>1</sup>A') of B<sub>21</sub><sup>-</sup>. All energies are in eV.

	VDE (Expt.) <sup>a</sup>	Final state and electronic configuration	VDE (theory)		
Feature			TD-B3LYP <sup>b</sup>	TD-PBE1PBE <sup>c</sup>	OVGF <sup>d</sup>
		Isomer I ( $C_s$ , <sup>1</sup> A')			
X <sup>e</sup>	4.58 (4)	<sup>2</sup> A", 17a' <sup>2</sup> 18a' <sup>2</sup> 11a" <sup>2</sup> 12a" <sup>2</sup> 19a' <sup>2</sup> 13a" <sup>1</sup>	4.46	4.60	4.63 (0.88)
А	4.79 (6)	<sup>2</sup> A', 17a' <sup>2</sup> 18a' <sup>2</sup> 11a'' <sup>2</sup> 12a'' <sup>2</sup> 19a' <sup>1</sup> 13a'' <sup>2</sup>	4.50	4.68	4.71 (0.89)
		<sup>2</sup> A", 17a <sup>2</sup> 18a <sup>2</sup> 11a <sup>2</sup> 12a <sup>11</sup> 19a <sup>2</sup> 13a <sup>2</sup>	4.60	4.75	4.70 (0.88)
В	5.17 (4)	<sup>2</sup> A", 17a' <sup>2</sup> 18a' <sup>2</sup> 11a" <sup>1</sup> 12a" <sup>2</sup> 19a' <sup>2</sup> 13a" <sup>2</sup>	5.00	5.12	5.25 (0.86)
С	5.43 (5)	<sup>2</sup> A', 17a' <sup>2</sup> 18a' <sup>1</sup> 11a'' <sup>2</sup> 12a'' <sup>2</sup> 19a' <sup>2</sup> 13a'' <sup>2</sup>	5.24	5.40	5.39 (0.88)
D	5.72 (5)	${}^{2}A'$ , 17 $a'^{1}18a'^{2}11a''^{2}12a''^{2}19a'^{2}13a''^{2}$	5.53	5.73	5.54 (0.88)
		Isomer II $(C_s, {}^1A')$			
Х	4.58 (4)	<sup>2</sup> A", 23a' <sup>2</sup> 4a" <sup>2</sup> 24a' <sup>2</sup> 5a" <sup>2</sup> 25a' <sup>2</sup> 26a' <sup>2</sup> 6a" <sup>1</sup>	4.46	4.67	4.59 (0.88)
		<sup>2</sup> A', 23a' <sup>2</sup> 4a'' <sup>2</sup> 24a' <sup>2</sup> 5a'' <sup>2</sup> 25a' <sup>2</sup> 26a' <sup>1</sup> 6a'' <sup>2</sup>	4.52 <sup>f</sup>	4.57	4.61 (0.89)
А	4.79 (6)	<sup>2</sup> A', 23a' <sup>2</sup> 4a'' <sup>2</sup> 24a' <sup>2</sup> 5a'' <sup>2</sup> 25a' <sup>1</sup> 26a' <sup>2</sup> 6a'' <sup>2</sup>	4.66 <sup>f</sup>	4.77	4.81 (0.88)
В	5.17 (4)	<sup>2</sup> A", 23a' <sup>2</sup> 4a" <sup>2</sup> 24a' <sup>2</sup> 5a" <sup>1</sup> 25a' <sup>2</sup> 26a' <sup>2</sup> 6a" <sup>2</sup>	4.86	5.05	5.07 (0.89)
С	5.43 (5)	<sup>2</sup> A', 23a' <sup>2</sup> 4a'' <sup>2</sup> 24a' <sup>1</sup> 5a'' <sup>2</sup> 25a' <sup>2</sup> 26a' <sup>2</sup> 6a'' <sup>2</sup>	5.32	5.52	5.54 (0.87)
		<sup>2</sup> A", 23a' <sup>2</sup> 4a" <sup>1</sup> 24a' <sup>2</sup> 5a" <sup>2</sup> 25a' <sup>2</sup> 26a' <sup>2</sup> 6a" <sup>2</sup>	5.33	5.51	5.56 (0.88)
D	5.61 (5)	<sup>2</sup> A', 23a' <sup>1</sup> 4a'' <sup>2</sup> 24a' <sup>2</sup> 5a'' <sup>2</sup> 25a' <sup>2</sup> 26a' <sup>2</sup> 6a'' <sup>2</sup>	5.66	5.77	5.91 (0.87)

<sup>a</sup>Numbers in parentheses represent the uncertainty in the last digits

<sup>b</sup>Calculated at TD-B3LYP/6-311+G(2df)//B3LYP/6-311+G\* level.

<sup>c</sup>Calculated at TD-PBE1PBE/6-311+G(2df)//B3LYP/6-311+G\* level.

<sup>d</sup>Calculated at ROVGF/6-311+G(2df)//B3LYP/6-311+G\* level. Values in parentheses represent the pole strength, which characterizes the validity of the one-electron detachment picture.

<sup>e</sup>Adiabatic detachment energy of  $B_{21}^{-1}$  is 4.38 (5) eV.

<sup>f</sup>Multiconfigurational value.



FIG. 2. The low-lying isomers of  $B_{21}^-$ . Relative energies are given at the CCSD(T)/6-311+G\*//B3LYP/6-311+G\* level (**I-V**), at the B3LYP/6-311+G\* level (in parenthesis), at the PBE1PBE/6-311+G\* level (in curly brackets), and at MP2/6-311+G\* level (in square brackets for **I-V**). All values are corrected for zero-point vibrational energies. Note that lines are drawn for B-B distances of < 2.0 Å to help the visualization of the structures and they do not necessarily represent single B-B bonds.

lations for the five lowest energy isomers at the  $CCSD(T)/6-311+G^*$  level using optimized  $B3LYP/6-311+G^*$  geometries along with their relative energies at the MP2/6-311+G\* level, and the relative energies of the ten lowest lying isomers at the B3LYP/6-311+G\* and PBE1PBE/6-311+G\* levels.

We found five isomers within 7 kcal/mol at B3LYP/6-311+G\* and PBE1PBE/6-311+G\*. The order of the isomers depends on the choice of the exchange-correlation potential. The lowest five structures at the DFT levels were found to be within 4 kcal/mol at our highest level of theory, CCSD(T)/6-311+G\*//B3LYP/6-311+G\*, which puts isomer II just 1.9 kcal/mol above the global minimum isomer I. It should be pointed out that the MP2/6-311+G\* results differ significantly from the most accurate CCSD(T)/6-311+G\*data, which are seen to agree much more closely with the DFT results, as also observed previously for smaller boron clusters.<sup>27,29,38</sup>

#### VI. COMPARISON BETWEEN THE EXPERIMENTAL AND THEORETICAL RESULTS

The calculated VDEs for isomers I and II at the TD-B3LYP/6-311+G(2df), TD-PBE1PBBE/6-311+G(2df), and ROVGF/6-311+G(2df) levels of theory are compared with the experimental VDEs in Table I. The pole strengths for the OVGF calculations are given in parentheses and they are all found to exceed 0.86, suggesting the single-electron description of the electron detachment processes for this system is a good approximation. Since the anion is a closed-shell system, electron detachment from each valence MO generates a final doublet electronic state within the one-electron picture. All three theoretical methods yield similar VDEs within 0.25 eV of each other for both isomers I and II

(Table I). Thus, the OVGF data will be used primarily in the following discussion.

#### A. Isomer I

The first calculated VDE of 4.63 eV from OVGF agrees well with the first experimental VDE of 4.58 eV. The calculated second and third VDEs are nearly identical to each other (4.7 eV) and are in good agreement with the experimental feature A at 4.79 eV. The X and A bands are not well resolved experimentally and clearly the first three detachment channels are responsible for the intense broad band near 4.6 eV in the PES spectrum (Fig. 1). The OVGF VDEs for the next three detachment channels, 5.25, 5.39, and 5.54 eV agree well with the observed band B at 5.17 eV, band C at 5.43 eV, and band D at 5.72 eV, respectively (Table I). The predicted spectral pattern for isomer I is fairly simple. The somewhat congested spectral pattern observed experimentally suggests that there must be contributions from other isomers.

#### B. Isomer II

At CCSD(T)/6-311+G\* level, isomer II is only 1.9 kcal/ mol higher in energy than isomer I and is expected to be significantly populated under our experimental conditions and contribute to the observed PES spectrum. The VDEs for the first three detachment channels for isomer II (Table I) are very similar to those from isomer I and they should contribute to the intense broad band at 4.6 eV in the experimental spectrum (Fig. 1). The VDEs for the next four detachment channels range from 5.07 to 5.91 eV (Table I); corresponding experimental features can be identified from the PES spectrum. We

	VDE (theory)			
Final state and electronic configuration	TD-B3LYP <sup>a</sup>	TD-PBE1PBE <sup>b</sup>	OVGF <sup>c</sup>	
	Isomer III $(C_1, {}^1A)$			
$^{2}$ A, 27a <sup>2</sup> 28a <sup>2</sup> 29a <sup>2</sup> 30a <sup>2</sup> 31a <sup>2</sup> 32a <sup>1</sup>	3.67	3.77	3.53 (0.89)	
$^{2}$ A, 27a <sup>2</sup> 28a <sup>2</sup> 29a <sup>2</sup> 30a <sup>2</sup> 31a <sup>1</sup> 32a <sup>2</sup>	4.27	4.4	4.35 (0.89)	
$^{2}$ A, $27a^{2}28a^{2}29a^{2}30a^{1}31a^{2}32a^{2}$	4.87 <sup>d</sup>	4.98	4.97 (0.89)	
$^{2}$ A, $27a^{2}28a^{2}29a^{1}30a^{2}31a^{2}32a^{2}$	4.97 <sup>d</sup>	5.07	5.20 (0.89)	
$^{2}$ A, $27a^{2}28a^{1}29a^{2}30a^{2}31a^{2}32a^{2}$	5.44	5.62 <sup>d</sup>	5.22 (0.88)	
$^{2}A, \dots 27a^{1}28a^{2}29a^{2}30a^{2}31a^{2}32a^{2}$	5.69 <sup>d</sup>	5.77 <sup>d</sup>	5.93 (0.85)	
	Isomer IV $(C_l, {}^1A)$			
$^{2}$ A, $27a^{2}28a^{2}29a^{2}30a^{2}31a^{2}32a^{1}$	4.23	4.27	4.42 (0.89)	
$^{2}$ A, $27a^{2}28a^{2}29a^{2}30a^{2}31a^{1}32a^{2}$	4.37	4.43	4.44 (0.89)	
$^{2}$ A, $27a^{2}28a^{2}29a^{2}30a^{1}31a^{2}32a^{2}$	4.58	4.7	4.66 (0.89)	
$^{2}$ A, 27a <sup>2</sup> 28a <sup>2</sup> 29a <sup>1</sup> 30a <sup>2</sup> 31a <sup>2</sup> 32a <sup>2</sup>	5.03	5.12	5.21 (0.86)	
$^{2}$ A, 27a <sup>2</sup> 28a <sup>1</sup> 29a <sup>2</sup> 30a <sup>2</sup> 31a <sup>2</sup> 32a <sup>2</sup>	5.34	5.45	5.36 (0.88)	
$^{2}$ A, 27a <sup>1</sup> 28a <sup>2</sup> 29a <sup>2</sup> 30a <sup>2</sup> 31a <sup>2</sup> 32a <sup>2</sup>	5.42	5.59	5.63 (0.88)	
	Isomer V ( $C_I$ , <sup>1</sup> A)			
$^{2}$ A, $27a^{2}28a^{2}29a^{2}30a^{2}31a^{2}32a^{1}$	4.15	4.23	4.28 (0.88)	
$^{2}$ A, $27a^{2}28a^{2}29a^{2}30a^{2}31a^{1}32a^{2}$	4.3	4.44	4.46 (0.88)	
$^{2}$ A, $27a^{2}28a^{2}29a^{2}30a^{1}31a^{2}32a^{2}$	4.65	4.75	4.81 (0.88)	
$^{2}$ A, $27a^{2}28a^{2}29a^{1}30a^{2}31a^{2}32a^{2}$	5.08	5.23	5.09 (0.87)	
$^{2}$ A, 27a <sup>2</sup> 28a <sup>1</sup> 29a <sup>2</sup> 30a <sup>2</sup> 31a <sup>2</sup> 32a <sup>2</sup>	5.33	5.51	5.48 (0.86)	
$^{2}$ A, 27a <sup>1</sup> 28a <sup>2</sup> 29a <sup>2</sup> 30a <sup>2</sup> 31a <sup>2</sup> 32a <sup>2</sup>	5.56	5.69	5.83 (0.86)	

TABLE II. The calculated VDEs for isomers III, IV, and V of B21<sup>-</sup>. All energies are in eV.

<sup>a</sup>Calculated at TD-B3LYP/6-311+G(2df)//B3LYP/6-311+G\* level.

<sup>b</sup>Calculated at TD-PBE1PBE/6-311+G(2df)//B3LYP/6-311+G\* level.

 $^{c}$ Calculated at ROVGF/6-311+G(2df)//B3LYP/6-311+G\* level. Values in parentheses represent the pole strength, which characterizes the validity of the one-electron detachment picture.

<sup>d</sup>Multiconfigurational value.

conclude that the calculated VDEs for isomers I and II are consistent with the experimental data and that it is the presence of the two nearly degenerate isomers that produced the somewhat congested PES spectrum observed experimentally.

#### C. Isomers III, IV, and V

The calculated VDEs for isomers III, IV, and V at the TD-B3LYP/6-311+G(2df), TD-PBE1PBE/6-311+G(2df), and ROVGF/6-311+G(2df) levels of theory are given in Table II. The calculated first VDEs for all these isomers are much smaller than the experimental value of 4.58 eV. However, these low VDEs are consistent with the weak low binding energy tail in the experimental spectrum (Fig. 1). This observation suggests that these isomers might be very weakly populated. Overall, the good agreement between the experimental and theoretical results lends considerable credence to the planar structures and the energetics of the global minimum and low-lying isomers of B<sub>21</sub><sup>-</sup>.

#### **VII. STRUCTURES AND CHEMICAL BONDING**

The two low-lying isomers of  $B_{21}^{-}$  are very similar to the two corresponding low-lying isomers of  $B_{19}^{-}$ .<sup>29</sup> The global minimum of  $B_{19}^{-}$  is a perfect planar and doubly  $\pi$  aromatic system with a central B atom surrounded by a five-membered ring and a 13-atom outer ring. The global minimum of  $B_{21}^{-}$  (Fig. 2) can be viewed as adding a B atom to one apex of the five-memebered ring in the interior and one B atom to the outer ring of the global minimum of  $B_{19}^{-}$ . The isomer II of  $B_{21}^{-}$  can be viewed similarly as adding one B atom to the interior and one B atom to the outer ring of the second lowest-lying planar structure of B<sub>19</sub><sup>-</sup>.<sup>29</sup> It should be emphasized that the global minimum searches of  $B_{21}^{-}$  using the CK and CW methods were performed more extensively and were done totally independently without any references to the structures of B<sub>19</sub><sup>-</sup>. It is also interesting to note that the second isomer of  $B_{19}^{-}$  was found to be 3.73 kcal/mol higher in energy than the global minimum at the  $CCSD(T)/6-311+G^*$ level and was much less populated in the cluster beam under similar experimental conditions. In the current work, we find that isomer II of  $B_{21}^{-}$  is only 1.9 kcal/mol higher in energy than the global minimum isomer I at the  $CCSD(T)/6-311+G^*$ level and is expected to be much more populated experimentally. The CCSD(T) energetics are consistent with the fact that the PES spectrum of  $B_{21}^{-}$  appears more congested (Fig. 1) in comparison with the spectrum of B<sub>19</sub><sup>-</sup>, which displayed more prominent spectral features.<sup>29</sup> These observations suggest the validity of the CCSD(T) energetics for these complicated clusters and lend further credence to the identified global minima and low-lying isomers for both clusters.

We performed chemical bonding analyses of the two low-lying isomers of  $B_{21}^{-}$  using the AdNDP method at the B3LYP/6-31G\*//B3LYP/6-311+G\* level of theory

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FIG. 3. AdNDP analysis for isomer I. ON stands for occupation number and is equal to 2.0 lel in an ideal case.

(Figs. 3 and 4). AdNDP is based on the concept that the electron pair is the main element of the chemical bonding model. Thus, it represents the electronic structure in terms of n-centered 2-electron bonds (nc-2e), which can be localized

(1c-2e or 2c-2e bond) or delocalized (*nc*-2e bond, where n > 2). Each bond has an occupation number (ON), which is equal to 2 electrons (2.0 lel) in the ideal case of a doubly occupied bond.



FIG. 4. AdNDP analysis for isomer II. ON stands for occupation number and is equal to 2.0 lel in an ideal case.

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#### A. Isomer I: The global minimum

Similar to all the previously studied planar or quasiplanar boron clusters,<sup>20–38</sup> all the peripheral boron atoms in isomer I of  $B_{21}^{-}$  are bonded by localized B-B  $\sigma$ -bonds. In this case, the peripheral ring is comprised of 14 B-B bonds, as shown in Fig. 3. Surprisingly, we found a 2c-2e B-B  $\sigma$ -bond within the interior of the planar cluster, making  $B_{21}^{-}$  the first boron cluster to feature an internal localized  $\sigma$ -bond. The presence of this 2c-2e  $\sigma$ -bond is likely due to the neighboring holes in the lattice framework of the interior boron atoms. The holes allow room for a more localized bond analogous to that found in the BC<sub>3</sub> honeycomb sheet.<sup>93</sup> The remaining electron density is delocalized, forming bonds of three centers or higher. Isomer I is quasiplanar, therefore, the delocalized bonds can be approximately differentiated as " $\sigma$ " or " $\pi$ ." There are nine 3c-2e  $\sigma$ -bonds, two 4c-2e  $\sigma$ -bonds, and six delocalized  $\pi$ bonds. The  $\pi$ -bonding pattern of isomer I is similar to that of the lowest energy structure of the  $B_{19}^{-}$  cluster,<sup>29</sup> where one  $\pi$ -bond is responsible for the bonding in the internally centered pentagon of boron atoms and the other five  $\pi$ -bonds contribute to bonding between the interior boron atoms and the peripheral boron ring.

#### B. Isomer II

The AdNDP analysis of the second lowest-lying structure of  $B_{21}^{-}$  at the CCSD(T) level reveals a bonding picture very similar to that of isomer I, as shown in Fig. 4. Once again, we see the presence of fourteen peripheral 2c-2e B-B  $\sigma$ -bonds and one internal 2c-2e B-B  $\sigma$ -bond. The delocalized  $\sigma$ -electrons form ten 3c-2e and one 4c-2e  $\sigma$ -bond in isomer II (Fig. 4) versus the nine 3c-2e and two 4c-2e  $\sigma$ -bonds of isomer I (Fig. 3). The delocalized  $\pi$ -bonds can be again split into two subsets: one 3c-2e  $\pi$ -bond delocalized across internal atoms and five  $\pi$ -bonds responsible for bonding between the interior atoms and the peripheral 14-atom boron ring. The  $\pi$ -bonding pattern of isomer II is reminiscent of that of the second lowest lying structure of  $B_{19}^{-}$ , too,<sup>29</sup> as expected from their structural similarity.

#### VIII. CONCLUSIONS

We report a combined photoelectron spectroscopy and *ab initio* study of the  $B_{21}^{-}$  cluster. The photoelectron spectrum at 193 nm revealed a very high electron affinity of 4.38 eV for neutral B<sub>21</sub> and congested spectral features. Extensive searches for the global minimum structure of B<sub>21</sub><sup>-</sup> were performed using the Coalescence Kick method and a newly developed Cartesian Walking method independently. The global searches revealed five planar or quasiplanar lowlying isomers. At our highest level of theory, two nearly isoenergetic isomers (I and II in Fig. 2) were found. The calculated vertical detachment energies of the two isomers were compared with the experimental data and good agreement was found, confirming that both isomers I and II were present in the experiment and contributed to the observed photoelectron spectrum of  $B_{21}^{-}$ . Thus, we can firmly conclude that anionic boron clusters  $(B_n^{-})$  continue to be planar at n = 21, despite indications that cationic and neutral boron clusters become 3D at smaller sizes.

The two lowest lying structures of  $B_{21}^{-}$  were found to be similar to the two lowest lying isomers for  $B_{19}^{-}$ . Chemical bonding analyses performed using the AdNDP method revealed that the overall chemical bonding picture of isomers I and II of the  $B_{21}^{-}$  cluster are also similar to those of  $B_{19}^{-}$ and other smaller planar or quasiplanar boron clusters: all the peripheral atoms are bonded to each other through localized 2c-2e  $\sigma$ -bonds, while the bonding in the interior of the planar cluster is delocalized and multi-centered with one localized 2c-2e  $\sigma$ -bond in each isomer. The latter is unique to the  $B_{21}^{-}$  cluster, which is the first instance of a localized 2c-2e  $\sigma$ -bond in the interior of a planar boron cluster. Various "defects" or "holes," such as four-membered or five-membered rings are found in the interior of the two lowest lying structures of B<sub>21</sub><sup>-</sup>. Hexagonal holes, similar to those in the proposed bulk 2D boron sheets,94-96 are observed in higher energy isomers (Fig. 2). It would be interesting to see if such hexagonal holes exist in the global minimum of larger boron clusters. Therefore, in addition to the 2D-to-3D transition, we expect that more interesting structures and bonding patterns may be discovered for larger boron clusters.

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#### **APPENDIX: THE CARTESIAN WALKING METHOD**

The local optimization of trial structures to their corresponding minimum on the potential energy surface is employed by many of the most successful global searching and global optimization methods used by computational chemists. This local optimization is by far the most time consuming portion of the search and thus the generation of trial structures

that are as near as possible to their corresponding minimum while maintaining the generality of randomness is desirable. Furthermore, trial structures, which do not reach SCF convergence, can be seen as a waste of computation time and should be avoided. The CW method was developed by one of the authors (Piazza) to deal with these issues. The CW method generates trial structures by performing constrained random walks on a user specified Cartesian grid; the trial structures are then optimized using an external quantum mechanical package. Both the overall volume of the grid and the grid mesh can be tailored to the system at hand. Keeping the volume of the grid small produces the effect of lowering the probability of finding elongated structures, while using a more rectangular grid may bias the search toward elongated structures. The choice of a fine grid mesh allows for trial structures that can result in highly coordinated atomic centers, while the choice of a more coarse mesh lowers the probability of trial structures, which will lead to high coordination. Once the appropriate grid is constructed, a constrained walk on the grid dictates the geometry of a trial structure. The walk takes place as follows:

- 1. Atom 1 is placed on the grid at random.
- 2. A random move of up to a set maximum distance from atom 1 is made. If the move lands within a set minimum distance to atom 1 the move is rejected and a new move is made. If not, it is accepted and atom 2 is placed.
- 3. A random move of a set maximum distance from atom 2 is made. If the move lands within a set minimum distance of atom 1 or atom 2, the move is rejected and a new move is made. If not, it is accepted and atom 3 is placed.
- 4. The procedure continues until all atoms are placed.
- 5. In rare cases, there may be no legal moves, i.e., the system may walks itself into a corner or an atom may become surrounded. Then, the walk starts over at step 1.

The effect of the appropriate maximum distance constraint is that the trial structures will never be fragmented, i.e., separate groups of one or a few atoms together. The effect of the appropriate minimum distance constraint is that no two atoms are positioned too close to one another. This leads to bond lengths that are close to their relaxed state, which alleviates SCF convergence issues and results in relatively quick local optimizations. With appropriately chosen constraints and the proper grid, or set of grids, the overall result is a set of trial structures, which are somewhat tailored to the system at hand while maintaining the generality of a random search.

- <sup>1</sup>N. Vast, S. Baroni, G. Zerah, J. M. Besson, A. Polian, M. Grimsditch, and J. C. Chervin, Phys. Rev. Lett. **78**, 693 (1997).
- <sup>2</sup>M. Fujimori, T. Nakata, T. Nakayama, E. Nishibori, K. Kimura, M. Takata, and M. Sakata, Phys. Rev. Lett. 82, 4452 (1999).
- <sup>3</sup>L. Hanley, J. L. Whitten, and S. L. Anderson, J. Phys. Chem. **92**, 5803 (1988).
- <sup>4</sup>P. A. Hintz, S. A. Ruatta, and S. L. Anderson, J. Chem. Phys. **92**, 292 (1990).
- <sup>5</sup>S. A. Ruatta, P. A. Hintz, and S. L. Anderson, J. Chem. Phys. **94**, 2833 (1991).
- <sup>6</sup>M. B. Sowa-Resat, J. Smolanoff, A. Lapiki, and S. L. Anderson, J. Chem. Phys. **106**, 9511 (1997).

- <sup>7</sup>R. Kawai and J. H. Weare, J. Chem. Phys. **95**, 1151 (1991).
- <sup>8</sup>R. Kawai and J. H. Weare, Chem. Phys. Lett. **191**, 311 (1992).
- <sup>9</sup>V. Bonacic-Koutecky, P. Fantucci, and J. Koutecky, Chem. Rev. **91**, 1035 (1991).
- <sup>10</sup>J. M. L. Martin, J. P. François, and R. Gijbels, Chem. Phys. Lett. **189**, 529 (1992).
- <sup>11</sup>H. Kato, K. Yamashita, and K. Morokuma, Chem. Phys. Lett. **190**, 361 (1992).
- <sup>12</sup>I. Boustani, Int. J. Quantum Chem. **52**, 1081 (1994).
- <sup>13</sup>I. Boustani, Chem. Phys. Lett. **233**, 273 (1995).
- <sup>14</sup>I. Boustani, Chem. Phys. Lett. **240**, 135 (1995).
- <sup>15</sup>A. Ricca and C. W. Bauschlicher, Jr., Chem. Phys. 208, 233 (1996).
- <sup>16</sup>I. Boustani, Surf. Sci. **370**, 355 (1997).
- <sup>17</sup>I. Boustani, Phys. Rev. B **55**, 16426 (1997).
- <sup>18</sup>J. Niu, B. K. Rao, and P. Jena, J. Chem. Phys. **107**, 132 (1997).
- <sup>19</sup>F. L. Gu, X. Yang, A. C. Tang, H. Jiao, and P. v. R. Schleyer, J. Comput. Chem. **19**, 203 (1998).
- <sup>20</sup>A. N. Alexandrova, A. I. Boldyrev, H. J. Zhai, and L. S. Wang, Coord. Chem. Rev. **250**, 2811 (2006).
- <sup>21</sup>H. J. Zhai, L. S. Wang, A. N. Alexandrova, and A. I. Boldyrev, J. Chem. Phys. **117**, 7917 (2002).
- <sup>22</sup>A. N. Alexandrova, A. I. Boldyrev, H. J. Zhai, L. S. Wang, E. Steiner, and P. W. Fowler, J. Phys. Chem. A **107**, 1359 (2003).
- <sup>23</sup>H. J. Zhai, L. S. Wang, A. N. Alexandrova, A. I. Boldyrev, and V. G. Zakrzewski, J. Phys. Chem. A **107**, 9319 (2003).
- <sup>24</sup>H. J. Zhai, A. N. Alexandrova, K. A. Birch, A. I. Boldyrev, and L. S. Wang, Angew. Chem. Int. Ed. **42**, 6004 (2003).
- <sup>25</sup>H. J. Zhai, B. Kiran, J. Li, and L. S. Wang, Nature Mat. 2, 827 (2003).
- <sup>26</sup>A. N. Alexandrova, A. I. Boldyrev, H. J. Zhai, and L. S. Wang, J. Phys. Chem. A **108**, 3509 (2004).
- <sup>27</sup>A. P. Sergeeva, D. Yu. Zubarev, H. J. Zhai, A. I. Boldyrev, and L. S. Wang, J. Am. Chem. Soc. **130**, 7244 (2008).
- <sup>28</sup>B. Kiran, S. Bulusu, H. J. Zhai, S. Yoo, X. C. Zeng, and L. S. Wang, Proc. Natl. Acad. Sci. U.S.A. **102**, 961 (2005).
- <sup>29</sup>W. Huang, A. P. Sergeeva, H. J. Zhai, B. B. Averkiev, L. S. Wang, and A. I. Boldyrev, Nat. Chem. 2, 202 (2010).
- <sup>30</sup>A. N. Alexandrova, H. J. Zhai, L. S. Wang, and A. I. Boldyrev, Inorg. Chem. 43, 3552 (2004).
- <sup>31</sup>A. N. Alexandrova, A. I. Boldyrev, H. J. Zhai, and L. S. Wang, J. Chem. Phys. **122**, 054313 (2005).
- <sup>32</sup>H. J. Zhai, L. S. Wang, D. Yu. Zubarev, and A. I. Boldyrev, J. Phys. Chem. A **110**, 1689 (2006).
- <sup>33</sup>L. M. Wang, W. Huang, B. B. Averkiev, A. I. Boldyrev, and L. S. Wang, Angew. Chem. Int. Ed. 46, 4550 (2007)
- <sup>34</sup>B. B. Averkiev, D. Yu. Zubarev, L. M. Wang, W. Huang, L. S. Wang, and A. I. Boldyrev, J. Am. Chem. Soc. **130**, 9248 (2008).
- <sup>35</sup>B. B. Averkiev, L. M. Wang, W. Huang, L. S. Wang, and A. I. Boldyrev, Phys. Chem. Chem. Phys. **11**, 9840 (2009).
- <sup>36</sup>L. L. Pan, J. Li, and L. S. Wang, J. Chem. Phys. **129**, 024302 (2008).
- <sup>37</sup>H. J. Zhai, C. Q. Miao, S. D. Li, and L. S. Wang, J. Phys. Chem. A 114, 12155 (2010).
- <sup>38</sup>A. P. Sergeeva, B. B. Averkiev, H.-J. Zhai, A. I. Boldyrev, and L. S. Wang, J. Chem. Phys. **134**, 224304 (2011).
- <sup>39</sup>J. E. Fowler and J. M. Ugalde, J. Phys. Chem. A **104**, 397 (2000).
- <sup>40</sup>J.-i. Aihara, J. Phys. Chem. A **105**, 5486 (2001).
- <sup>41</sup>J.-i. Aihara, H. Kanno, and T. Ishida, J. Am. Chem. Soc. **127**, 13324 (2005).
- <sup>42</sup>P. W. Fowler and B. R. Gray, Inorg. Chem. **46**, 2892 (2007).
- <sup>43</sup>D. Yu. Zubarev and A. I. Boldyrev, J. Comput. Chem. 28, 251 (2007).
- <sup>44</sup>D. Yu. Zubarev, A. P. Sergeeva, and A. I. Boldyrev, in *Chemical Reactivity Theory. A Density Functional View*, edited by P. K. Chattaraj (CRC, New York, 2009), pp. 439–452.
- <sup>45</sup>J. O. C. Jiménez-Halla, R. Islas, T. Heine, and G. Merino, Angew. Chem. Int. Ed. 49, 5668 (2010).
- <sup>46</sup>G. Martínez-Guajardo, A. P. Sergeeva, A. I. Boldyrev, T. Heine, J. M. Ugalde, and G. Merino, Chem. Commun. 47, 6242 (2011).
- <sup>47</sup>W. An, S. Bulusu, Y. Gao, and X. C. Zeng, J. Chem. Phys. **124**, 154310 (2006).
- <sup>48</sup>E. Oger, N. R. M. Crawford, R. Kelting, P. Weis, M. M. Kappes, and R. Ahlrichs, Angew. Chem. Int. Ed. **46**, 8503 (2007).
- <sup>49</sup>A. N. Alexandrova, A. I. Boldyrev, Y.-J. Fu, X. Yang, X.-B. Wang, and L. S. Wang, J. Chem. Phys. **121**, 5709 (2004).
- <sup>50</sup>A. N. Alexandrova and A. I. Boldyrev, J. Chem. Theory Comput. 1, 566 (2005).
- <sup>51</sup>A. N. Alexandrova, J. Phys. Chem. A **114**, 12591 (2010).

- <sup>52</sup>D. J. Wales and J. P. K. Doye, J. Phys. Chem. A **101**, 5111 (1997).
- <sup>53</sup>D. J. Wales and H. A. Scheraga, Science 285, 1368 (1999).
- <sup>54</sup>S. Yoo and X. C. Zeng, J. Chem. Phys. **119**, 1442 (2003).
- <sup>55</sup>S. Yoo and X. C. Zeng, Angew. Chem. Int. Ed. 44, 1491 (2005).
- <sup>56</sup>M. Saunders, J. Comput. Chem. 25, 621 (2004).
- <sup>57</sup>P. P. Bera, K. W. Sattelmeyer, M. Saunders, H. F. Schaefer, and P. v. R. Schleyer, J. Phys. Chem. A 110, 4287 (2006).
- <sup>58</sup>S. E. Schönbom, S. Goedecker, S. Roy, and A. R. Oganov, J. Chem. Phys. 130, 144108 (2009).
- <sup>59</sup>L. S. Wang, H. S. Cheng, and J. Fan, J. Chem. Phys. 102, 9480 (1995).
- <sup>60</sup>W. Huang and L. S. Wang, Phys. Rev. Lett. **102**, 153401 (2009).
- <sup>61</sup>A. D. Becke, J. Chem. Phys. **98**, 5648 (1993).
- <sup>62</sup>S. H. Vosko, L. Wilk, and M. Nusair, Can. J. Phys. 58, 1200 (1980).
- <sup>63</sup>C. Lee, W. Yang, and R. G. Parr, Phys. Rev. B 37, 785 (1988).
- <sup>64</sup>J. S. Binkley, J. A. Pople, and W. J. Hehre, J. Am. Chem. Soc. 102, 939 (1980).
- <sup>65</sup>S. Goedecker, W. Hellmann, and T. Lenosky, Phys. Rev. Lett. 95, 055501 (2005).
- <sup>66</sup>J. C. Schön, K. Doll, and M. Jansen, Phys. Status Solidi B 247, 23 (2010).
- <sup>67</sup>M. S. Gordon, J. S. Binkley, J. A. Pople, W. J. Pietro, and W. J. Hehre, J. Am. Chem. Soc. 104, 2797 (1982).
- <sup>68</sup>W. J. Pietro, M. M. Francl, W. J. Hehre, D. J. Defrees, J. A. Pople, and J. S. Binkley, J. Am. Chem. Soc. 104, 5039 (1982).
- <sup>69</sup>T. Clark, J. Chandrasekhar, G. W. Spitznagel, and P. v. R. Schleyer, J. Comput. Chem. 4, 294 (1983).
- <sup>70</sup>J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).
- <sup>71</sup>J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **78**, 1396 (1997).
- <sup>72</sup>C. Adamo and V. Barone, J. Chem. Phys. **110**, 6158 (1999).
- <sup>73</sup>J. Cizek, Adv. Chem. Phys. 14, 35 (1969).
- <sup>74</sup>G. D. Purvis and R. J. Bartlett, J. Chem. Phys. 76, 1910 (1982).
- <sup>75</sup>K. Raghavachari, G. W. Trucks, J. A. Pople, and M. Head-Gordon, Chem. Phys. Lett. 157, 479 (1989).
- <sup>76</sup>L. S. Cederbaum, J. Phys. B 8, 290 (1975).
- <sup>77</sup>J. V. Ortiz, Int. J. Quantum Chem., Quantum Chem. Symp. 23, 321 (1989).

J. Chem. Phys. 136, 104310 (2012)

- <sup>78</sup>J. S. Lin and J. V. Ortiz, Chem. Phys. Lett. **171**, 197 (1990).
- <sup>79</sup>V. G. Zakrzewski, J. V. Ortiz, J. A. Nichols, D. Heryadi, D. L. Yeager, and J. T. Golab, Int. J. Quantum Chem. 60, 29 (1996). <sup>80</sup>R. Bauernschmitt and R. Ahlrichs, Chem. Phys. Lett. 256, 454 (1996).
- <sup>81</sup>M. E. Casida, C. Jamorski, K. C. Casida, and D. R. Salahub, J. Chem. Phys. 108, 4439 (1998).
- <sup>82</sup>M. J. Frisch, G. W. Trucks, H. B. Schlegel et al., GAUSSIAN 09, Revision D.01, Gaussian, Inc., Wallingford, CT, 2004.
- <sup>83</sup>M. Valiev, E. J. Bylaska, N. Govind, K. Kawalski, T. P. Stroatsma, H. J. J. Van Dam, D. Wang, J. Nieplocha, E. Apra, T. L. Windus, and W. de Jong, Comput. Phys. Commun. 181, 1477 (2010).
- <sup>84</sup>G. Schaftenaar, MOLDEN 3.4, CAOS/CAMM Center, The Netherlands, 1998.
- <sup>85</sup>D. Yu. Zubarev and A. I. Boldyrev, Phys. Chem. Chem. Phys. 10, 5207 (2008).
- <sup>86</sup>D. Yu. Zubarev and A. I. Boldyrev, J. Org. Chem. **73**, 9251 (2008).
- <sup>87</sup>D. Yu. Zubarev and A. I. Boldyrev, J. Phys. Chem. A 113, 866 (2009).
- <sup>88</sup>A. P. Sergeeva and A. I. Boldyrev, Comments Inorg. Chem. 31, 2 (2010).
- <sup>89</sup>U. Varetto, MOLEKEL 5.4.0.8, Swiss National Supercomputing Centre: Manno, Switzerland, 2009.
- <sup>90</sup>L. S. Wang and X. Li, Temperature Effects in Anion Photoelectron Spectroscopy of Metal Clusters, in Proceedings of the International Symposium on Clusters and Nanostructure Interfaces, Richmond, VA, 25-28 October 1999, edited by P. Jena, S. N. Khanna, and B. K. Rao (World Scientific, NJ, 2000), pp. 293-300.
- <sup>91</sup>J. Akola, M. Manninen, H. Hakkinen, U. Landman, X. Li, and L. S. Wang, Phys. Rev. B 60, R11297 (1999).
- <sup>92</sup>See supplementary material at http://dx.doi.org/10.1063/1.3692967 for the Cartesian coordinated of the lowest lying five isomers.
- <sup>93</sup>I. A. Popov and A. I. Boldyrev, J. Phys. Chem. C 116, 3147 (2012).
- <sup>94</sup>H. Tang and S. Ismail-Beigi, Phys. Rev. Lett. **99**, 115501 (2007).
- <sup>95</sup>H. Tang and S. Ismail-Beigi, Phys. Rev. B 80, 134113 (2009).
- <sup>96</sup>X. Yang, Y. Ding, and J. Ni, Phys. Rev. B 77, 041402 (2008).