

# Low-lying isomers of the $B_9^-$ boron cluster: The planar molecular wheel versus three-dimensional structures

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The  $B_9^-$  cluster was found previously to be an unprecedented molecular wheel containing an octacoordinate planar boron with  $D_{8h}$  symmetry in a combined photoelectron spectroscopy (PES) and theoretical study [H. J. Zhai *et al.*, *Angew. Chem., Int. Ed.* **42**, 6004 (2003)]. However, the PES spectra of  $B_9^-$  exhibit minor features that cannot be explained by the global minimum  $D_{8h}$  structure, suggesting possible contributions from low-lying isomers at finite temperatures. Here we present Car–Parrinello molecular dynamics with simulated annealing simulations to fully explore the potential energy surface of  $B_9^-$  and search for low-lying isomers that may account for the minor PES features. We performed density functional theory (DFT) calculations with different exchange-correlation functionals and *ab initio* calculations at various levels of theory with different basis sets. Two three-dimensional low-lying isomers were found, both of  $C_s$  symmetry, 6.29 ( $C_s-2$ ) and 10.23 ( $C_s-1$ ) kcal/mol higher in energy than the  $D_{8h}$  structure at the highest CCSD(T) level of theory. Calculated detachment transitions from the  $C_s-2$  isomer are in excellent agreement with the minor features observed in the PES spectra of  $B_9^-$ . The  $B_9^-$  cluster proves to be a challenge for most DFT methods and the calculated relative energies strongly depend on the exchange-correlation functionals, providing an excellent example for evaluating the accuracies of various DFT methods. © 2008 American Institute of Physics. [DOI: 10.1063/1.2948405]

## I. INTRODUCTION

While bulk elemental boron and many boron compounds possess three-dimensional (3D) structural motifs, early theoretical calculations suggest that small boron clusters may possess planar or quasiplanar structures.<sup>1–12</sup> Experimentally boron clusters were produced and studied shortly after the discovery of the fullerenes primarily using mass spectrometry-based methods.<sup>13–18</sup> However, structural characterizations of boron clusters have been possible fairly recently by combining photoelectron spectroscopy (PES) with high-level theoretical calculations.<sup>19–30</sup> Indeed, the combined experimental and theoretical investigations have shown that boron cluster anions are planar up to  $B_{20}^-$ , although for neutral clusters the global minimum of  $B_{20}$  remains 3D. A recent ion mobility and theoretical study showed that for cations low-lying 3D structures appeared already at  $B_{16}^+$ .<sup>31</sup>

Among the small boron clusters, the nine-atom cluster is very special. While earlier calculations suggested  $B_9$  and  $B_9^+$  to be low symmetry 3D structures with  $C_s$  symmetry,<sup>5–7</sup> the recent PES and theoretical study has shown that  $B_9^-$  and  $B_9$ , in fact, possess unprecedented molecular wheel structures with an octacoordinate planar boron atom.<sup>22</sup> The  $B_9^-$  anion has a perfect  $D_{8h}$  structure and is aromatic with six  $\pi$  electrons, analogous to benzene, whereas the  $B_9$  neutral cluster is

predicted to possess a slightly distorted  $D_{2h}$  ( ${}^2B_{1g}$ ) structure due to the Jahn–Teller effect. However, in the original PES spectra of  $B_9^-$  there were two weak spectral features around 3.1 and 4.4 eV, which could not be accounted for by the global minimum  $B_9^-$  molecular wheel. The 4.4 eV feature was quite prominent and was suggested to come from either a two-electron transition or a Jahn–Teller effect from the  $D_{8h}$  global minimum, but it was not definitively assigned. Another possibility was due to potential low-lying isomers, but this possibility was not raised because the closest isomer was found to be still more than 14 kcal/mol higher in energy than the  $D_{8h}$  global minimum and seemed unlikely to be viable experimentally.

Weak PES spectral features due to the presence of isomers in the cluster beam have been observed for a number of  $B_n^-$  clusters, specifically for  $B_7^-$ ,<sup>24</sup>  $B_{13}^-$ ,<sup>23</sup> and  $B_{20}^-$ .<sup>27</sup> In each case, low-lying structures have been found that are responsible for the weak PES features, contributing to a more complete understanding of their structures and chemical bonding. The unaccounted weak PES features for  $B_9^-$  raise some interesting questions. What is the nature of these features? Can they be due to unidentified low-lying isomers? In the current study, we performed Car–Parrinello molecular dynamics (CPMD) with simulated annealing simulations to fully explore the potential energy surface of  $B_9^-$  and search for alternative structures that may account for the minor PES features. Detailed investigations have been carried out for the  $B_9^-$  cluster using both density functional theory (DFT) and

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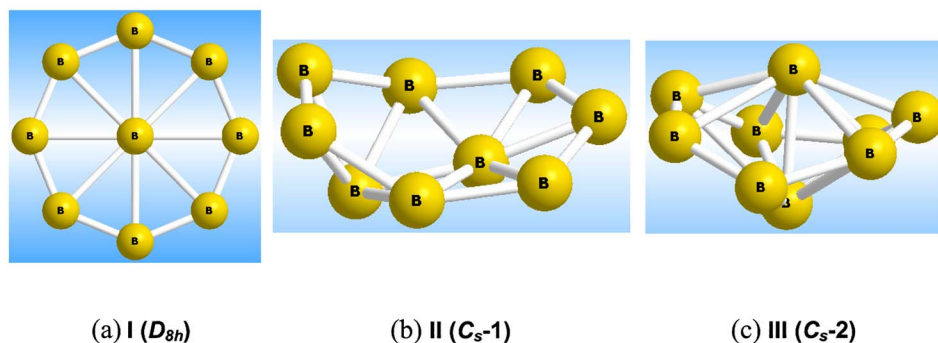


FIG. 1. (Color online) Optimized low-lying isomers of  $B_9^-$ : (a) The global minimum molecular wheel structure (I,  $D_{8h}$ ). (b) 3D convex structure (II,  $C_s-1$ ). (c) Distorted heptagonal bipyramidal structure (III,  $C_s-2$ ).

wave-function theory (WFT) *ab initio* methods. We have indeed found that a low-lying 3D structure with  $C_s$  symmetry, which yields calculated electron detachment energies in good agreement with the observed weak bands in the original PES experiment. This  $C_s$  isomer can be viewed as a distorted pseudo- $D_{7h}$  heptagonal bipyramid, which is much higher in energy in DFT calculations but is, in fact, much closer in energy to the  $D_{8h}$  global minimum from the most accurate WFT-based *ab initio* methods. We have shown that most DFT methods seriously overestimate the energy differences between the 3D and two-dimensional (2D) structures, likely due to the intrinsic self-interaction error of the presently available exchange-correlation functionals. Thus, the theoretical determination of the relative stabilities of the  $B_9^-$  isomers not only allows a complete understanding of the observed PES spectra but also provides a critical test for the accuracies of various DFT methods.

## II. THEORETICAL METHODS AND COMPUTATIONAL DETAILS

Our theoretical calculations were performed in three steps. First we carried out simulated annealing simulations based on CPMD to search for the global minimum and candidate low-lying isomers of  $B_9^-$ .<sup>32,33</sup> The CPMD simulated annealing calculations were performed at the level of local density approximation (LDA) using a simple cubic supercell with the dimension of  $20 \times 20 \times 20$  bohr<sup>3</sup> and a  $48 \times 48 \times 48$  grid for discretization along lattice vector directions, yielding a plane-wave energy cutoff of 28.424 hartree (773.47 eV). We used norm-conserving pseudopotentials of Hamman for the B atoms.<sup>34</sup> The clusters were first thermally equilibrated at 3500 K for 24.2 ps and then annealed for 26.6 ps with a time step of 5 a.u. The final annealing temperature was 245.3 K and the final simulated annealing structures were optimized through the CPMD energy minimization. These calculations were performed using the NWPW module of the plane-wave supercell DFT method implemented in NWCHEM 5.0.<sup>35</sup>

In the second step, we performed geometry optimizations using the analytic energy gradients implemented in the Gaussian-based molecular DFT modules of the NWCHEM (Ref. 35) and GAUSSIAN 03 programs.<sup>36</sup> The geometries obtained from the CPMD simulations were used as starting structures. The initial geometry optimizations were performed using the hybrid B3LYP method with the basis set 6-311+ $G(d)$ . The three lowest-energy structures obtained af-

ter optimization are depicted in Fig. 1. Because the energy differences of these three low-lying isomers are relatively small, we further investigated the effects of different exchange-correlation functionals, including the LDA (SVWN5), pure generalized gradient approximation (GGA: BLYP, BPW91, BPBE), hybrid GGA (B3LYP, BHLYP, B3PW91, PBE0, mPW1K), meta-GGA (M06-L), and hybrid meta-GGA (M06, M06-2X, M06-HF). The percentage of the Hartree-Fock exact exchange included in the functionals and the calculated results are listed in Table I. While isomer I is predicted to be the global minimum from all the DFT methods except LDA and the M06 sets of functionals, the relative energies calculated using different GGA and hybrid GGA methods vary significantly, indicating that the DFT methods are not adequate in sorting out the low-lying isomers for  $B_9^-$ . More accurate electron correlation methods are thus needed to assure the reliability of the calculated energies.

In the third step we performed further calculations using various WFT-based *ab initio* electron correlation methods. Both 6-311+ $G(d)$  and cc-pVnZ ( $n=D, T$ ) basis sets were employed to investigate the effects of the basis set incom-

TABLE I. The calculated DFT total electronic energies ( $E_e$  in hartree) and relative energies ( $\Delta E$  in kcal/mol) for the three low-lying structures of  $B_9^-$  at different levels of theory. The basis set used for all these methods are 6-311+ $G(d)$ .

Method	HF% <sup>a</sup>	I ( $D_{8h}, {}^1A_{1g}$ )	II ( $C_s, {}^1A_1'$ )	III ( $C_s, {}^1A_1'$ )
		$E_e$	$\Delta E_{II-I}$ <sup>b</sup>	$\Delta E_{III-I}$ <sup>b</sup>
LDA	0	-221.974 55	-1.87	-1.52
BLYP	0	-223.421 40	19.57	24.71
B3LYP	20	-223.535 75	18.95	21.67
BHLYP	50	-223.376 32	20.55	20.43
BPW91	0	-223.491 35	10.10	10.52
B3PW91	20	-223.424 73	11.26	10.08
BPBE	0	-223.388 92	9.50	9.62
PBE	0	-223.188 24	7.10	7.03
PBE0	25	-223.214 43	8.23	4.11
TPSS	0	-223.603 94	12.86	7.27
TPSSh	10	-223.574 21	12.76	5.92
mPW1K	42.8	-223.483 56	10.24	11.49
M06-L	0	-223.545 69	4.93	-6.82
M06	27	-223.379 04	4.71	-0.89
M06-2X	54	-223.448 31	1.78	-8.49
M06-HF	100	-223.475 68	4.25	-6.96

<sup>a</sup>The percentage of the H-F exchange used in the exchange-correlation functional.

<sup>b</sup>Energies relative to isomer I.

TABLE II. The calculated total electronic energies ( $E_e$  in hartree) and relative energies ( $\Delta E$  in kcal/mol) at various levels of *ab initio* methods for the three structures of  $B_9^-$ . The HF, MP2, and CCSD(T) energies were fully optimized at the levels of the methods and basis sets specified. Coupled cluster single-point energies (e.g., CCSD(T)/MP2) were also calculated at the optimized MP2 geometries. The electron correlation calculations were performed with the  $1s^2$  electrons frozen on B.

Method	I ( $D_{8h}, {}^1A_{1g}$ )	II ( $C_s, {}^1A_1'$ )	III ( $C_s, {}^1A_1'$ )
	$E_e$	$\Delta E_{II-I}^a$ 6-311+G(d)	$\Delta E_{III-I}^a$
HF	-221.918 93	28.47	24.82
MP2	-222.738 19	12.39	0.43
CCSD/MP2	-222.728 54	11.65	8.47
CCSD[T]/MP2	-222.802 71	8.94	6.87
CCSD-T/MP2	-222.800 36	9.59	6.70
CCSD(T)/MP2	-222.801 01	9.58	6.75
CCSD(T)	-222.801 12	9.21	6.50
		cc-pVDZ	
HF	-221.890 08	27.89	22.36
MP2	-222.663 65	14.02	1.32
CCSD/MP2	-222.659 34	12.19	8.32
CCSD[T]/MP2	-222.728 22	9.88	7.11
CCSD-T/MP2	-222.725 97	10.52	6.98
CCSD(T)/MP2	-222.726 57	10.51	7.02
CCSD(T)	-222.726 70	10.09	6.78
		cc-pVTZ	
HF	-221.936 45	28.07	24.53
MP2	-222.849 85	12.37	-0.80
CCSD/MP2	-222.831 48	12.24	8.08
CCSD[T]/MP2	-222.914 74	9.96	6.62
CCSD-T/MP2	-222.912 54	10.57	6.45
CCSD(T)/MP2	-222.913 11	10.59	6.51
CCSD(T)	-222.913 15	10.23	6.29

<sup>a</sup>Energies relative to isomer I.

pleteness errors on the final calculated energies. The calculated energies at the level of HF, second-order Møller–Plesset perturbation theory (MP2), and coupled cluster theory [CCSD, CCSD[T], CCSD-T, CCSD(T)] are summarized in Table II. These HF and post-self-consistent field (SCF) *ab initio* calculations were accomplished using MOLPRO 2006.1.<sup>37</sup>

As seen from Tables I and II, the PBE0 functional together with TPSS and TPSSh functionals yielded relative energies very close to the most accurate CCSD(T) values. Thus, further DFT calculations of the vibrational properties and thermodynamic properties (enthalpy, entropy, and free energies) were all based on the PBE0 method. PES spectra were simulated using a combined  $\Delta$ SCF-TDDFT approach as outlined previously,<sup>38</sup> using the calculated vertical detachment energies (VDEs) at the PBE0 level of theory.

### III. RESULTS AND DISCUSSION

#### A. Geometries and relative energies

As shown in Fig. 1 the optimized B3LYP structures of the three lowest-energy isomers of  $B_9^-$  include (a) the global minimum molecular wheel structure with  $D_{8h}$  symmetry, (b) a 3D convex structure with  $C_s$  symmetry, and (c) a second 3D structure also with  $C_s$  symmetry. These structures are

referred to as isomers I, II (or  $C_s-1$ ), and III (or  $C_s-2$ ), respectively, hereafter. These structures and their energy ordering are similar to those reported previously at the B3LYP level of theory.<sup>22</sup> The convex structure of isomer II can be viewed as removing one B atom from the edge of the  $B_{10}$  global minimum structure.<sup>23</sup> The reduced periphery pushes one of the central B atoms further out of plane. The 3D isomer III can be viewed as a distorted heptagonal bipyramid. Indeed, the previous study showed that the perfect  $D_{7h}$ , heptagonal bipyramid is a transition state with two imaginary frequencies<sup>22</sup> and our geometry optimizations along the imaginary coordinates led to the final  $C_s-2$  structure, which is, in fact, due to a second-order Jahn–Teller effect.

As seen from Table I, at the popular B3LYP level of theory, isomers II and III are 18.98 and 21.67 kcal/mol higher in energy than the global minimum molecular wheel, respectively. These relative energies are identical to the previous investigations.<sup>22</sup> Unfortunately, we found that the relative energies are very sensitive to the exchange-correlation functionals, as shown in Table I. At the LDA level, the molecular wheel is less stable than either  $C_s$  structure, whereas all the meta-GGA methods predicted that isomer III is the global minimum.

As shown in Table II, all the WFT-based *ab initio* calculations predict that the  $D_{8h}$  molecular wheel is the global minimum. However, the relative stabilities of the two 3D isomers are observed to strongly depend on the levels of theory, whereas the basis sets seem to have much less effects. First of all, all the *ab initio* methods predict that isomer III is more stable than isomer II. Second, the relative stabilities of isomers II and III increase with increasing levels of theory. At the highest CCSD(T)/cc-pVTZ level of theory, isomer III is only 6.3 kcal/mol above the global minimum and isomer II is 10.2 kcal/mol higher than the global minimum.

In comparison with the benchmark results at the CCSD(T) level, LDA, meta-GGA (M06-L), and hybrid meta-GGA (M06, M06-2X, M06-HF) all significantly overestimate the relative stabilities of isomers II and III, while all the other DFT methods, except TPSS, TPSSh, and PBE0, severely underestimate the relative stabilities of these isomers. It was observed that the more the percentage of the HF exchange is included in the hybrid exchange-correlation functional the smaller the relative energies between the low-lying 3D isomers and the global minimum. This observation indicates that the failure of the DFT methods in predicting the relative energies of the  $B_9^-$  isomers is likely due to the self-interaction errors intrinsic to most of the exchange-correlation functionals in use today. In particular, the popular B3LYP functional is not reliable when evaluating the energy differences between the 3D structures and the planar global minimum structure of  $B_9^-$ : The relative energies of isomers II and III are calculated in error by 8.7 and 15.4 kcal/mol, respectively, in comparison to the best CCSD(T) results. Among the DFT methods tested, only the PBE0, TPSS, and TPSSh functionals are able to reasonably reproduce relative energies among the low-lying isomers relative to the CCSD(T) results.

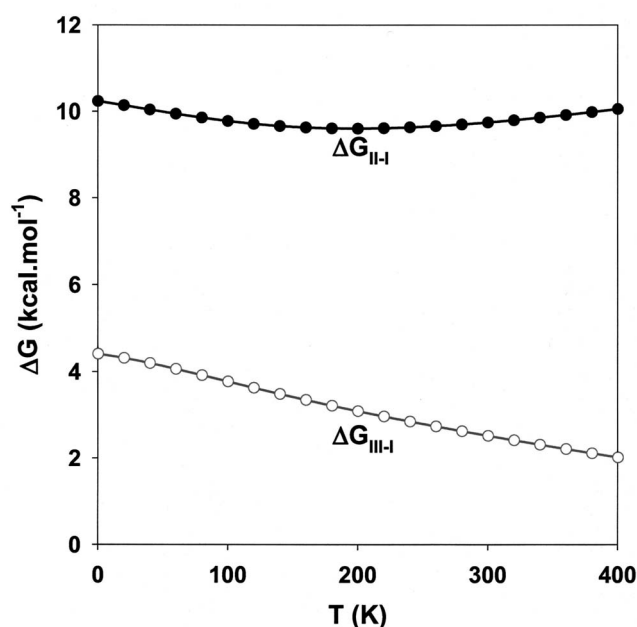


FIG. 2. Free energies (in kcal/mol) of isomers II and III relative to isomer I (upper:  $\Delta G_{II-I}$ , lower:  $\Delta G_{III-I}$ ) as a function of temperature.

### B. Entropy effects on the relative stabilities at finite temperatures

From Table II, we see that at the CCSD(T) level of theory isomer III is higher in energy than the global minimum structure by 6.8 kcal/mol with the cc-pVDZ basis set. This energy difference is only reduced by 0.5 kcal/mol with the cc-pVTZ basis set, indicating that latter value is close to the converged CCSD(T) value at the one-electron basis set limit. Thus, isomer III becomes the closest-lying isomer to the global minimum. However, even at the highest CCSD(T) level of theory this isomer is still 6.3 kcal/mol above the global minimum, and it seems still to be too high to be viable experimentally. However, this energy is calculated at 0 K. Since the experiment was conducted at room temperature, one must consider the free energies by taking into account the entropic effects at finite temperatures on the relative stabilities of the low-lying isomers.

We have calculated the free energies  $G(T)=U(T)+PV-TS$  of these  $B_9^-$  low-lying isomers using the PBE0 functional for the vibrational analyses ( $U$ ,  $S$ ,  $P$ ,  $V$ , and  $T$  stand for the internal energy, entropy, pressure, volume, and temperature, respectively). The relative free energies  $\Delta G$  at standard state in the range of  $T=0-400$  K for isomers II and III are plotted in Fig. 2, with the free energy of isomer I as reference. Clearly,  $\Delta G_{III-I}$  decreases when temperature increases, whereas  $\Delta G_{III-II}$  does not exhibit any significant temperature dependence. This observation is likely due to the fact that isomer III has a drastically different 3D structure while isomer II (being quasiplanar) and isomer I are more similar. Therefore, the free energy or thermodynamic stability of isomer III approaches that of isomer I with increasing temperature. At 300 K, the free energy of isomer III is reduced by  $\sim 2$  kcal/mol relative to isomer I at PBE0 level of theory and

TABLE III. Theoretical vertical detachment energies (VDE in eV) for the global minimum and isomer III of  $B_9^-$ .

Observed features	VDE (expt.) <sup>a</sup>	MO	Final state	VDE (calc.) <sup>b</sup>
		(I, $D_{8h}$ , $1A_{1g}$ )		
X	3.46(6)	HOMO( $1e_{1g}$ )	$2E_{1g}$	3.39,3.41
A	5.04(6)	HOMO-1( $3e_{1u}$ )	$2E_{1u}$	5.08,5.09
		HOMO-3( $1a_{2u}$ )	$2A_{2u}$	5.56
		HOMO-2( $1b_{2g}$ )	$2B_{2g}$	5.99
		(III, $C_s$ , $1A'$ )		
X'	$\sim 3.1$	HOMO( $15a'$ )	$2A'$	3.05
X''	4.40(6)	HOMO-1( $14a'$ )	$2A'$	4.42
		HOMO-2( $8a''$ )	$2A''$	4.44
		HOMO-3( $13a'$ )	$2A'$	5.00
		HOMO-4( $7a''$ )	$2A''$	5.03

<sup>a</sup>Experimental value from Ref. 22.

<sup>b</sup>VDEs were calculated at the PBE0/6-311+G(d) level of theory. The double values for the VDEs of the first and third detachment channels of isomer I are due to the Jahn–Teller effects.

may become viable experimentally. Thus, isomer III is the most likely candidate for the weak PES features observed for  $B_9^-$ .

### C. Comparison of simulated PES spectra of low-lying isomers to experiment

We calculated the VDEs of isomers I and III using the PBE0/6-311+G(d) method, as given in Table III and shown in Fig. 3(a) in comparison with the experimental values. The simulated PES spectra shown in Fig. 3(a) were obtained by

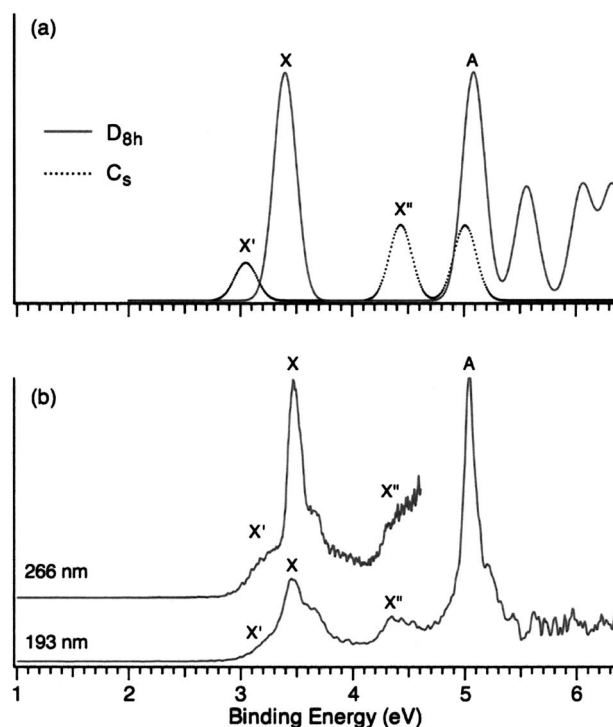


FIG. 3. (a) Simulated photoelectron spectra of the global minimum  $D_{8h}$  structure and the low-lying 3D structure ( $C_s-2$  in Fig. 1). The spectra were simulated by fitting the distributions of the calculated VDEs with unit-area Gaussian functions of 0.08 eV width. (b) Experimental photoelectron spectra of  $B_9^-$  (Ref. 22).

fitting the calculated VDEs with unit-area Gaussian functions of 0.08 eV width (the relative intensity of isomer III was plotted at one-third of that for isomer I to guide the eyes). As assigned in the original work,<sup>22</sup> the X and A bands observed at 3.46 and 5.04 eV [also see Fig. 3(b)] are well reproduced by the calculated VDEs from the degenerate highest occupied molecular orbital (HOMO) ( $1e_{1g}$ ) and HOMO-1 ( $3e_{1u}$ ) at 3.39–3.41 and 5.08–5.09 eV (the doublet values are due to the Jahn–Teller effect), respectively, for the global minimum isomer I. The current PBE0 values are very close to the corresponding VDEs, 3.47 and 5.07 eV, calculated with the CCSD(T) method previously<sup>22</sup> for the first two detachment channels. The third detachment channel was calculated to be at 5.56 eV from the  $1a_{2u}$  HOMO-3, which is comparable to the previous value calculated at OVGF.<sup>22</sup> However, the PES spectrum above 5.5 eV did not reveal any distinct peaks, even though there were weak continuous signals [Fig. 3(b)], indicating either very large geometry changes upon detachment from the deeper molecular orbitals (MOs) or the breakdown of one-electron processes for such high energy excitations.

More importantly, the calculated VDEs for isomer III are in excellent agreement with the weak unexplained PES features for  $B_9^-$ . The first VDE calculated for isomer III is 3.05 eV, which agrees well with the low binding energy tail [ $X'$  in Fig. 3(b)] at  $\sim 3.1$  eV. The calculated VDEs for the second and third detachment channels are nearly degenerate, 4.42 and 4.44 eV, which are in excellent agreement with the weak  $X''$  band. The calculated VDEs for the fourth and fifth detachment channels are also very close to each other at 5.00 and 5.03 eV, which are likely buried under the strong A band from isomer I, as shown in Fig. 3(a). The excellent agreement of the calculated VDEs for isomer III with the weak PES features of  $B_9^-$  shows unequivocally that the 3D low-lying isomer is present in the original experiment, suggesting that higher levels of theory are needed, particularly for comparing relative energies for cluster isomers with very different structures, such as 2D versus 3D structures. A similar case was also observed previously for the  $B_{20}^-$  cluster, although in this case the B3LYP method appeared to underestimate the stability of the 2D structures.<sup>39</sup>

The relatively high stability of isomer III with respect to the global minimum  $D_{8h}$  molecular wheel of  $B_9^-$  is interesting. In the small planar boron clusters, there seems to be an optimal ring size to host a central atom in forming wheel-type structures. For example,  $B_5$  and  $B_6$  rings appear to be too small to fit a B atom in the center, as can be seen from the global minimum structures of  $B_6^-$  or  $B_7^-$ , which are not  $D_{5h}$  or  $D_{6h}$ .<sup>20,24,40–43</sup> The  $B_7$  ring seems to be the perfect size to host a central atom because the global minimum structures of both  $B_8$  and  $B_8^{2-}$  are perfect  $D_{7h}$  molecular wheels and  $B_8^-$  only exhibit a very slight in-plane distortion due to the Jahn–Teller effect.<sup>22</sup> The  $B_8$  ring is good enough to host a central atom to give the global minimum  $D_{8h}$   $B_9^-$  molecular wheel. However, the  $B_8$  ring is probably a little bit too large so that isomer III, which is a distorted heptagonal bipyramid, becomes energetically competitive and viable experimentally. It is interesting to note that the  $B_9$  ring is definitively too large to host a B atom for  $B_{10}^-$ .<sup>23</sup> Instead, its global

minimum features an elongated  $B_8$  ring with two central B atoms, which are pushed out of the plane because the  $B_8$  ring is clearly not large enough to fit two B atoms comfortably. However, a relatively large Al atom has been predicted to fit in the  $B_9$  ring to give an unprecedented noncoordinated Al in a planar  $D_{9h}$   $AlB_9$ .<sup>44</sup>

#### IV. CONCLUDING REMARKS

Through CPMD with simulated annealing and extensive geometry optimizations at various levels of DFT and *ab initio* theory, we carried out an extensive reinvestigation of the special  $B_9^-$  cluster and found three low-lying isomers. We confirmed the unprecedented  $D_{8h}$  molecular wheel as the global minimum for  $B_9^-$ . In addition, two low-lying isomers were identified, both with 3D structures and  $C_s$  symmetry: One can be viewed as a convex quasiplanar structure ( $C_s-1$ ) and the other one can be viewed as a distorted heptagonal bipyramid ( $C_s-2$ ). Both of these isomers were considered previously, but were shown to be much higher in energy at the hybrid density functional level of theory.<sup>22</sup> In the present study, we tested a series of representative DFT methods ranging from LDA to hybrid meta-GGA and observed that relative energies of the two 3D isomers strongly depend on the exchange-correlation functionals. We further performed extensive *ab initio* calculations and found that at the highest CCSD(T)/cc-pVTZ level of theory the  $C_s-2$  isomer is only 6.3 kcal/mol higher in energy than the  $D_{8h}$  global minimum. Free energy calculations further showed that at room temperature the  $C_s-2$  isomer is even closer in energy to the global minimum and became experimentally viable. Simulated photoelectron spectra of the  $C_s-2$  isomer are found to be in good agreement with the weak features in the experimental photoelectron spectra, which could not be accounted for by the  $D_{8h}$  global minimum. The current work presents a more complete understanding of the  $B_9^-$  cluster, which provides an interesting example for evaluating the accuracies of various DFT methods. The various DFT methods used in this paper can be found in Ref. 45.

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<sup>1</sup>V. Bonacic-Koutecky, P. Fantucci, and J. Koutecky, *Chem. Rev. (Washington, D.C.)* **91**, 1035 (1991).

<sup>2</sup>J. M. L. Martin, J. P. François, and R. Gijbels, *Chem. Phys. Lett.* **189**, 529 (1992).

<sup>3</sup>H. Kato, K. Yamashita, and K. Morokuma, *Chem. Phys. Lett.* **190**, 361

- (1992).
- <sup>4</sup>I. Boustani, *Int. J. Quantum Chem.* **52**, 1081 (1994).
- <sup>5</sup>I. Boustani, *Chem. Phys. Lett.* **240**, 135 (1995).
- <sup>6</sup>A. Ricca and C. W. Bauschlicher, Jr., *Chem. Phys.* **208**, 233 (1996).
- <sup>7</sup>I. Boustani, *Phys. Rev. B* **53**, 016426 (1997).
- <sup>8</sup>J. Nie, B. K. Rao, and P. Jena, *J. Chem. Phys.* **107**, 132 (1997).
- <sup>9</sup>F. L. Gu, X. Yang, A. C. Tang, H. Jiao, and P. v. R. Schleyer, *J. Comput. Chem.* **19**, 203 (1998).
- <sup>10</sup>J. E. Fowler and J. M. Ugalde, *J. Phys. Chem. A* **104**, 397 (2000).
- <sup>11</sup>J. Aihara, *J. Phys. Chem. A* **105**, 5486 (2001).
- <sup>12</sup>P. L. Cao, W. Zhao, B. X. Li, B. Song, and X. Y. Zhou, *J. Phys.: Condens. Matter* **13**, 5065 (2001).
- <sup>13</sup>L. Hanley and S. L. Anderson, *J. Phys. Chem.* **91**, 5161 (1987).
- <sup>14</sup>L. Hanley, J. L. Whitten, and S. L. Anderson, *J. Chem. Phys.* **92**, 5803 (1988).
- <sup>15</sup>P. A. Hintz, S. A. Ruatta, and S. L. Anderson, *J. Chem. Phys.* **92**, 292 (1990).
- <sup>16</sup>S. A. Ruatta, P. A. Hintz, and S. L. Anderson, *J. Chem. Phys.* **94**, 2833 (1991).
- <sup>17</sup>M. B. Sowa-Resat, J. Smolanoff, A. Lapiki, and S. L. Anderson, *J. Chem. Phys.* **106**, 9511 (1997).
- <sup>18</sup>S. J. La Placa, P. A. Roland, and J. J. Wynne, *Chem. Phys. Lett.* **190**, 163 (1992).
- <sup>19</sup>H. J. Zhai, L. S. Wang, A. N. Alexandrova, and A. I. Boldyrev, *J. Chem. Phys.* **117**, 7917 (2002).
- <sup>20</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>21</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>22</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>23</sup>H. J. Zhai, B. Kiran, J. Li, and L. S. Wang, *Nat. Mater.* **2**, 827 (2003).
- <sup>24</sup>A. N. Alexandrova, A. I. Boldyrev, H. J. Zhai, and L. S. Wang, *J. Phys. Chem. A* **108**, 3509 (2004).
- <sup>25</sup>A. N. Alexandrova, H. J. Zhai, L. S. Wang, and A. I. Boldyrev, *Inorg. Chem.* **43**, 3552 (2004).
- <sup>26</sup>A. N. Alexandrova, A. I. Boldyrev, H. J. Zhai, and L. S. Wang, *J. Chem. Phys.* **122**, 054313 (2005).
- <sup>27</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>28</sup>H. J. Zhai, L. S. Wang, D. Yu. Zubarev, and A. I. Boldyrev, *J. Phys. Chem. A* **110**, 1689 (2006).
- <sup>29</sup>A. N. Alexandrova, A. I. Boldyrev, H. J. Zhai, and L. S. Wang, *Coord. Chem. Rev.* **250**, 2811 (2006).
- <sup>30</sup>A. P. Sergeeva, D. Y. Zubarev, H. J. Zhai, A. I. Boldyrev, and L. S. Wang, *J. Am. Chem. Soc.* **130**, 7244 (2008).
- <sup>31</sup>E. Oger, R. M. Crawford, R. Kelting, P. Weis, M. M. Kappes, and R. Ahlrichs, *Angew. Chem., Int. Ed.* **46**, 8503 (2007).
- <sup>32</sup>R. Car and M. Parrinello, *Phys. Rev. Lett.* **55**, 2471 (1985).
- <sup>33</sup>S. Kirkpatrick, C. D. Gelatt, Jr., and M. P. Vecchi, *Science* **220**, 671 (1983).
- <sup>34</sup>D. R. Hamann, *Phys. Rev. B* **40**, 2980 (1989).
- <sup>35</sup>E. J. Bylaska, W. A. de Jong, N. Govind, K. Kowalski, T. P. Straatsma, M. Valiev, D. Wang, E. Apra, T. L. Windus, J. Hammond, P. Nichols, S. Hirata, M. T. Hackler, Y. Zhao, P.-D. Fan, R. J. Harrison, M. Dupuis, D. M. A. Smith, J. Nieplocha, V. Tipparaju, M. Krishnan, Q. Wu, T. Van Voorhis, A. A. Auer, M. Nooijen, E. Brown, G. Cisneros, G. I. Fann, H. Fruchtl, J. Garza, K. Hirao, R. Kendall, J. A. Nichols, K. Tsemekhman, K. Wolinski, J. Anchell, D. Bernholdt, P. Borowski, T. Clark, D. Clerc, H. Dachsel, M. Deegan, K. Dyall, D. Elwood, E. Glendening, M. Gutowski, A. Hess, J. Jaffe, B. Johnson, J. Ju, R. Kobayashi, R. Kutteh, Z. Lin, R. Littlefield, X. Long, B. Meng, T. Nakajima, S. Niu, L. Pollack, M. Rosing, G. Sandrone, M. Stave, H. Taylor, G. Taylor, G. Thomas, J. van Lenthe, A. Wong, and Z. Zhang, NWChem, A Computational Chemistry Package for Parallel Computers, Version 5.0 2006, Pacific Northwest National Laboratory, Richland, Washington 99352-0999, USA.
- <sup>36</sup>M. J. Frisch, G. W. Trucks, H. B. Schlegel *et al.*, GAUSSIAN 03, Gaussian, Inc., Wallingford, CT, 2004.
- <sup>37</sup>H.-J. Werner, P. J. Knowles, R. Lindh *et al.*, MOLPRO, version 2006.1, a package of *ab initio* programs, see: <http://www.molpro.net>
- <sup>38</sup>J. Li, X. Li, H. J. Zhai, and L. S. Wang, *Science* **299**, 864 (2003).
- <sup>39</sup>W. An, S. Bulusu, Y. Gao, and X. C. Zeng, *J. Chem. Phys.* **124**, 154310 (2006).
- <sup>40</sup>Q.-S. Li, Q. Jin, Q. Luo, A.-C. Tang, J.-K. Yu, and H.-X. Zhang, *Int. J. Quantum Chem.* **94**, 269 (2003).
- <sup>41</sup>J. Ma, Z.-H. Li, K.-N. Fan, and M. F. Zhou, *Chem. Phys. Lett.* **372**, 708 (2003).
- <sup>42</sup>Q.-S. Li, L.-F. Gong, and Z.-M. Gao, *Chem. Phys. Lett.* **390**, 220 (2004).
- <sup>43</sup>D. Yu. Zubarev and A. I. Boldyrev, *J. Comput. Chem.* **28**, 251 (2007).
- <sup>44</sup>B. B. Averkiev and A. I. Boldyrev, *Russ. J. General Chem.* **78**, 769 (2008).
- <sup>45</sup>J. C. Slater and K. H. Johnson, *Phys. Rev. B* **5**, 844 (1972); S. H. Vosko, L. Wilk, and M. Nusair, *Can. J. Phys.* **58**, 1200 (1980); A. D. Becke, *Phys. Rev. A* **38**, 3098 (1988); C. Lee, W. Yang, and R. G. Parr, *Phys. Rev. B* **37**, 785 (1988); P. J. Stephens, F. J. Devlin, C. F. Chabalowski, and M. J. Frisch, *J. Phys. Chem.* **98**, 11623 (1994); A. D. Becke, *J. Chem. Phys.* **98**, 1372 (1993); J. P. Perdew and Y. Wang, *Phys. Rev. B* **45**, 13244 (1992); A. D. Becke, *J. Chem. Phys.* **98**, 5648 (1993); J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996); C. Adamo and V. Barone, *J. Chem. Phys.* **110**, 6158 (1999); B. J. Lynch, P. L. Fast, M. Harris, and D. G. Truhlar, *J. Phys. Chem. A* **104**, 4811 (2000); B. J. Lynch, Y. Zhao, and D. G. Truhlar, *J. Phys. Chem. A* **107**, 1384 (2003); Y. Zhao and D. G. Truhlar, *J. Chem. Phys.* **125**, 194101 (2006); Y. Zhao, N. E. Schultz, and D. G. Truhlar, *J. Chem. Theory Comput.* **2**, 364 (2006); Y. Zhao and D. G. Truhlar, *Acc. Chem. Res.* **41**, 157 (2008); J. Tao, J. Perdew, V. Staroverov, and G. Scuseria, *Phys. Rev. Lett.* **91**, 146401 (2003).