Geometries, Electronic Structures, and Electron Detachment Energies of Small Boron Sulfide Anions: A Density Functional Theory Investigation[①]

GUO Qiao-Ling[a]   GUO Jin-Chang[b]   LI Si-Dian[b②]

[a] (*Department of Chemistry, Taiyuan Teachers' College, Taiyuan* 030001*, Shanxi*)

[b] (*Institute of Materials Science and Department of Chemistry,*
Xinzhou Teachers' University, Xinzhou 034000*, Shanxi*)

ABSTRACT   A density functional theory investigation on the geometries, electronic structures, and electron detachment energies of BS^-, BS_2^-, $B(BS)_2^-$ and $B(BS)_3^-$ has been performed in this work. The linear ground-state structures of BS^- ($C_{\infty v}$, $^1\sum^+$) and BS_2^- ($D_{\infty h}$, $^1\sum_g^+$) prove to be similar to the previously reported BO^- and BO_2^- with systematically lower electron detachment energies. Small boron sulfide clusters are found to favor the formation of -B=S groups which function basically as σ-radicals and dominate the ground-state structures of the systems. The perfect linear $B(BS)_2^-$ ($D_{\infty h}$, $^3\Sigma_g$) and beautiful equilateral triangle $B(BS)_3^-$ (D_{3h}, $^2A_1$") turn out to be analogous to the well-known C_{2v} BH_2 and D_{3h} BH_3, respectively. The electron affinities of BS, BS_2, $B(BS)_2$ and $B(BS)_3$ are predicted to be 2.3, 3.69, 3.00 and 3.45 eV, respectively. The electron detachment energies calculated for BS^-, BS_2^-, $B(BS)_2^-$, and $B(BS)_3^-$ may facilitate future photoelectron spectroscopy measurements to characterize the geometrical and electronic structures of these anions.

Keywords: boron sulfides, density functional theory, geometries, electronic structures, electron detachment energies, photoelectron spectroscopy

1 INTRODUCTION

In two recent papers[1, 2], Zhai, Li, and Wang performed a combined photoelectron spectroscopy (PES) and density functional theory (DFT) study on a series of small boron oxide anions including BO^-, BO_2^-, $B(BO)_2^-$, and $B(BO)_3^-$. DFT method proves to be a reliable approach in predicting the structures and one-electron detachment energies of small boron oxides. Considering the close similarity between S and O in valence electron configurations and the importance of B–S binary systems closely related with boron oxides, we extend the investigation to

small boron sulfide clusters in this work by applying DFT method to predict the geometries, electronic structures, and electron detachment energies of BS^-, BS_2^-, $B(BS)_2^-$, and $B(BS)_3^-$. Boron sulfides have received much limited attention in literatures. Mass spectroscopy studies performed about 30 years ago confirmed the existence of a wide range of boron sulfide cations in gas phases and suggested that BS_2^+, $B_2S_2^+$, and $B_2S_3^+$ be the most important parent ions of high molecular weight boron sulfide clusters[3~7]. Two previous *ab initio* calculations on BS[8, 9] presented very different excitation energies (3.83 eV[8] and 2.47 eV[9]) for the transition from the ground-

state BS $^2\Sigma^+$ to the first excited state BS $^2\Pi$, with both values significantly higher than the experimental term value of Te = 1.99 eV[10]. Linear BS_2 neutral was firstly observed with laser induced florescence technique[11, 12]. However, there have been neither geometries nor photoelectron spectroscopy measurements reported to date for boron sulfide anions in literatures. The B–S compounds are more volatile than their B–O analogues and thus investigations of their structures and thermodynamic properties were believed to be greatly facilitated[3]. More importantly, a detailed theoretical study on small B–S cluster anions may justify certain assumptions and conclusions in B–O systems[1~3]. Our DFT investigation indicates that BS^- and BS_2^- anions possess similar geometries and electronic structures with BO^- and BO_2^- and $B(BS)_2^-$ and $B(BS)_3^-$ anions and their neutrals turn out to be analogous to C_{2v} BH_2 and D_{3h} BH_3 in geometrical and electronic structures. Small boron-rich boron sulfides prove to favor the formation of -B=S groups which basically serve as σ-radicals and dominate the ground-state structures of the systems. The optimized $D_{\infty d}$ $B(BS)_2$ with a linear B–B–B chain and D_{3h} $B(BS)_3$ with a triangular BB_3 core present novel boron compound clusters containing direct B–B interactions absent in oxygen-rich boron oxides[13]. The adiabatic (ADEs) and vertical one-electron detachment energies (VDEs) predicted in this work may facilitate future PES characterizations of these small boron sulfides.

2   CALCULATION METHODS

To compare with our previous investigations on small boron oxide anions[1, 2], DFT structural optimizations, frequency analyses, and time-dependent DFT (TD-DFT) calculations[14] of small boron sulfide clusters were performed using the same hybrid B3LYP procedure[15] with Dunning's all-electron basis (aug-cc-pvtz) implemented in Gaussian 03 program[16]. Extensive searches have been performed on these small clusters to determine their ground-state structures. ADEs of the anions were calculated as the energy differences between the ground states of the anions and the corresponding neutrals and their VDEs were obtained with the TD-DFT method. Fig. 1 shows the optimized ground-state structures of BS^- and BS_2^- anions and their neutrals, and Fig. 2 describes the valence molecular orbitals (MOs) of the two anions. Fig. 3 compares the low-lying stable isomers of $B(BS)_2^-$ and $B(BS)_3^-$ with their neutrals and Fig. 4 shows the valence MO pictures of the two anions at their ground states. The calculated ADEs and the first three VDEs of the anions are listed in Table 1. The symmetrical vibrational frequencies of the anions and the corresponding neutrals are also listed to facilitate future high-resolution PES experiments. The lowest vibrational frequencies of the optimized structures have also been indicated in Figs. 1 and 3. The ADEs of the anions are equivalent to the electron affinities (EAs) of the corresponding neutrals in definitions.

3   RESULTS AND DISCUSSION

(a)

$C_{\infty v}$ BS^- ($^1\Sigma^+$) $C_{\infty v}$ BS ($^2\Sigma^+$)
V_{min} +988   +1180

(b)

$D_{\infty h}$ BS_2^- ($^1\Sigma_g^+$) $D_{\infty h}$ BS_2 ($^2\Pi_g$)
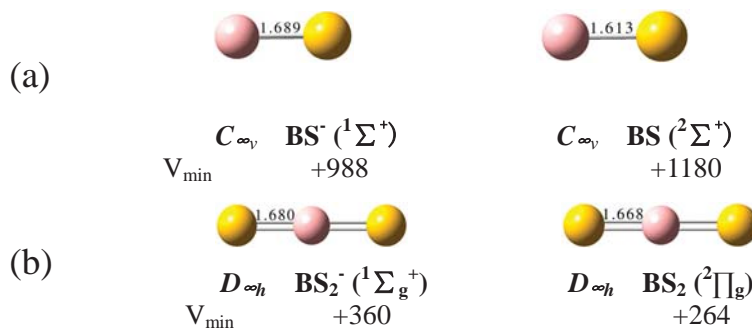V_{min} +360   +264

Fig. 1.   **Ground-state structures of BS^- (a) and $(BS)_2^-$ (b) anions and their neutrals with the necessary bond lengths (in Å) and the lowest vibrational frequencies V_{min} (in cm^{-1}) indicated**

Table 1.   Calculated First ADEs (eV) and the First Three VDEs (eV) of BS⁻, BS₂⁻, B(BS)₂⁻, and B(BS)₃⁻ at the B3LYP/aug-cc-pvtz Level, together with the Symmetrical Vibrational Frequencies (cm⁻¹) of These Anions and Their Neutrals

		Feature	Final state	TD-DFT		Vibrational frequency	
				ADE/eV	VDE /eV	Neutral	Anion
$C_{\infty v}$	BS⁻	X	$^2\sum^+$	2.33	2.43	$1180(\sigma)$	$988(\sigma)$
		A	$^2\prod$		4.50		
		B	$^2\sum^+$		7.59		
$D_{\infty h}$	BS₂⁻	X	$^2\prod_g$	3.69	3.69	$553(\sigma_g)$	$546(\sigma_g)$
		A	$^2\prod_u$		5.45		
		B	$^2\sum{_u^+}$		6.72		
$D_{\infty h}$	B(BS)₂⁻	X	$^2\prod_u$	3.00	3.08	$348(\sigma_g), 1354(\sigma_g)$	$352(\sigma_g), 1300(\sigma_g)$
		A	$^2\prod_g$		4.96		
		B	$^2\prod_u$		5.15		
D_{3h}	B(BS)₃⁻	X	$^1A_1'$	3.45	3.53	$315(a_1), 1325(a_1)$	$320(a_1'), 1281(a_1')$
		A	$^3E''$		5.46		
		B	$^3A_1''$		5.50		

As the S atom is larger than O in size, the B–X bond lengths in B_xX_y systems (X = O, S) increase from $r_{B=O}\approx1.2$ Å in boron oxides[1, 17, 18] to $r_{B=S}\approx1.6$ Å in boron sulfides. Similar to BO⁻ and BO[2], the σ-typed highest occupied molecular orbitals (HOMOs) of both BS⁻ and BS (Fig. 2(a)) are mainly composed of the contribution from B 2*s*. Fig. 1(a) and Table 1 show that the B–S bond length increases from 1.613 Å in BS ($^2\sum^+$) to 1.689 Å in BS⁻ ($^1\sum^+$), while the B–S stretching vibrational frequency decreases from 1180 cm⁻¹ in BS to 988 cm⁻¹ in BS⁻, indicating that the σ-HOMO of BS radical is basically anti-bonding in nature, similar to the situation observed in BO[2]. Our calculated bond length of BS agrees nicely with the calculated value of 1.609 Å at the GSTEPS level[9] and our DFT vibrational frequency of 1180 cm⁻¹ fits the measured value of 1180.17 cm⁻¹ perfectly[8, 10]. The first ADE and VDE of BS⁻ are predicted to be 2.33 and 2.43 eV, respectively. They are slightly lower (about 0.20 eV) than the corresponding measured values of BO⁻ [2, 17, 18]. This defines an EA value of 2.33 eV for BS neutral. The second VDE of BS⁻ (4.50 eV) lies ~0.97 eV lower than the corresponding value of BO⁻[2]. The transition from the ground-state BS $^2\sum^+$ to the first excited state BS $^2\prod$ is predicted to have the DFT excitation energy of 2.07 eV which is in nice agreement with the mea- sured term value of Te = 1.99 eV[11, 12]. Our DFT excitation energy of 5.16 eV from the ground-state BS $^2\sum^+$ to the second excited state BS $^2\sum^+$ also agrees reasonably well with the measured term value of Te = 4.83 eV[11, 12]. We believe that the calculated ADE and VDE values and the vibrational frequencies for BS neutral and anion presented in Table 1 well repre- sent the true PES pattern and vibrational progres- sions of BS⁻ anion in the future experiments. The fact that B=S has a much lower stretching frequency (at about 1000 cm⁻¹) than B=O (at about 2000 cm⁻¹) indicates that the B=S interaction is much weaker than the B=O bonding reported before[1, 2].

TD-DFT calculation indicates that the main one-electron detaching processes from specific MOs of BS⁻ anion contribute 85~86% to the concerned ex-citation roots. The one-electron excitation processes listed in Table 1 can be definitely assigned to one-electron detachments from specific MOs of BS⁻ (Fig. 2(a)), with the X-band originating from deta-ching one electron from the anti-bonding HOMO(σ), A-band from the degenerate bonding HOMO-1(π), and B-band from the nonbonding HOMO-2(σ).

| HOMO(σ) | HOMO-1 (π) | HOMO-2(σ) | HOMO-3(σ) |

(a)

(b)

HOMO (π_g)   HOMO-1 (π_u)

HOMO-2 (σ_u) HOMO-3 (σ_g) HOMO-4(σ_u) HOMO-5 (σ_g)
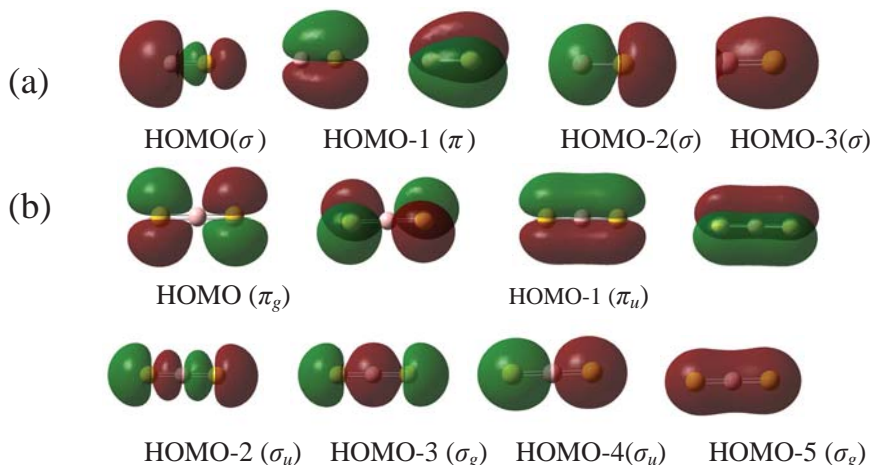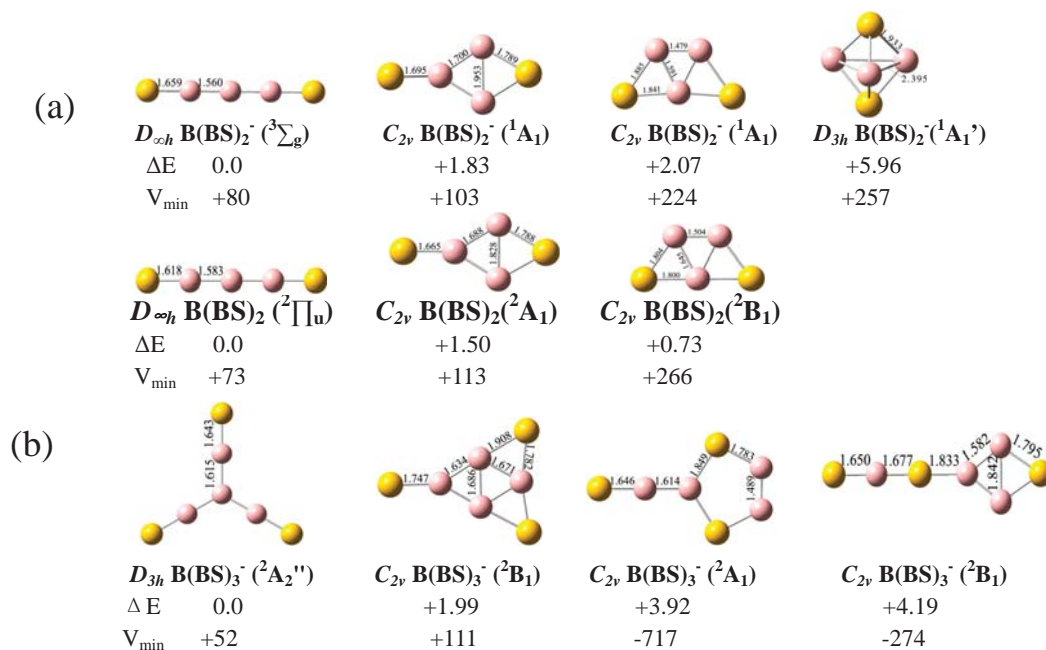
Fig. 2.   Valence MO pictures of BS⁻ (a) and BS$_2^-$ (b)

Similar to BO_2^- and BO_2 reported previously[2, 19, 20], both BS_2^- and BS_2 possess perfect linear ground-state structures (Fig. 1(b)) with the B–S bond lengths of 1.680 and 1.668 Å, respectively, in good agreement with DFT bond lengths reported before for BS_2 neutral[11, 12]. The first three calculated VDEs of BS_2^- at 3.69, 5.45 and 6.72 eV prove to be systematically lower than the correspondingly measured PES features of BO_2^- at 4.46, 6.72, and 7.50 eV[2]. The first ADE and VDE of BS_2^- have practically the same value (3.69 eV) for the reason that there exists only minor bond length difference (0.012 Å) between BS_2^- and BS_2. This defines an EA value of 3.69 eV for BS_2. There are no theoretical or experimental

values available to compare with our DFT results obtained for BS_2^- anion.

The first VDE (X-band) of BS_2^- at 3.69 eV, which originates from detaching one electron from the degenerate HOMO(π_g) (Fig. 2(b)), is expected to exhibit as a sharp PES feature. The first two excited states of the neutral ($^2\Pi_u$ and $^2\Sigma_u^+$) at 5.45 and 6.72 eV can be reached *via* detaching one electron from the degenerate HOMO-1(π_u) and HOMO-2(σ_u) of the anion, respectively. TD-DFT calculations show that these processes are almost pure one-electron detachment processes from specific MOs of the anion with the main electron-detaching channels contributing 85~100% to the concerned excitation roots.
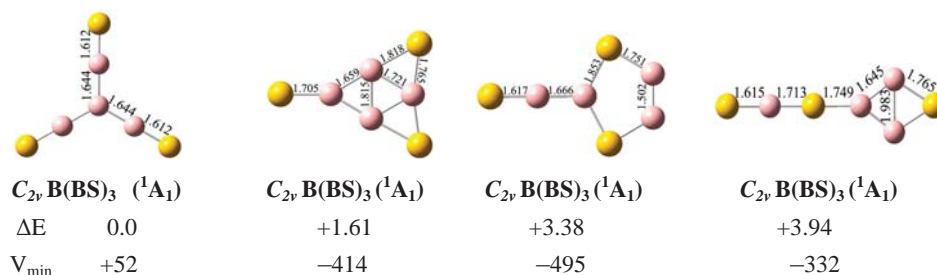

(a)

$D_{\infty h}$ B(BS)$_2^-$ ($^3\Sigma_g$)	C_{2v} B(BS)$_2^-$ ($^1A_1$)	C_{2v} B(BS)$_2^-$ ($^1A_1$)	D_{3h} B(BS)$_2^-$($^1A_1$')
ΔE 0.0	+1.83	+2.07	+5.96
V_{min} +80	+103	+224	+257

$D_{\infty h}$ B(BS)$_2$ ($^2\Pi_u$)	C_{2v} B(BS)$_2$($^2A_1$)	C_{2v} B(BS)$_2$($^2B_1$)
ΔE 0.0	+1.50	+0.73
V_{min} +73	+113	+266

(b)

D_{3h} B(BS)$_3^-$ ($^2A_2$'')	C_{2v} B(BS)$_3^-$ ($^2B_1$)	C_{2v} B(BS)$_3^-$ ($^2A_1$)	C_{2v} B(BS)$_3^-$ ($^2B_1$)
ΔE 0.0	+1.99	+3.92	+4.19
V_{min} +52	+111	-717	-274

C_{2v} B(BS)$_3$ ($^1A_1$) $\quad$ C_{2v} B(BS)$_3$ ($^1A_1$) $\quad$ C_{2v} B(BS)$_3$ ($^1A_1$) $\quad$ C_{2v} B(BS)$_3$ ($^1A_1$)

ΔE	0.0	+1.61	+3.38	+3.94
V_{min}	+52	−414	−495	−332

Fig. 3. Low-lying isomers of B(BS)$_2^-$ and B(BS)$_2$ (a) and B(BS)$_3^-$ and B(BS)$_3$
(b) with the necessary bond lengths (in Å), relative energies ΔE (in eV),
and the lowest vibrational frequencies V_{min} (in cm^{-1}) presented

The most striking finding obtained in this work is that small boron-rich B–S binary clusters $B_m(BO)_n$ prefer the formation of -BS groups which mainly serve as σ-radicals and dominate the ground-state structures of $B_m(BO)_n$ clusters, as clearly shown in Fig. 3. The -BS groups are found to directly coordinate with the central B atom in linear B(BS)$_2$ and triangular B(BS)$_3$, aping -H atoms in the well-known bent BH$_2$ (C_{2v})[21~23] and triangular BH$_3$ (D_{3h})[21, 23, 24]. Extensive searches indicate that all the other planar and stereo isomers are considerably less stable than the ground-state structures, as clearly shown in Fig. 3.

Both triplet B(BS)$_2^-$ ($^3\Sigma_g$) and doublet B(BS)$_2$($^2\Pi_u$) possess perfect linear ground-state structures ($D_{\infty h}$) with two -BS groups connected to the central B from opposite ends along the molecular axis, forming a linear B–B–B chain absent in the previously reported oxygen-rich boron oxides[13]. The degenerate delocalized π-interactions of HOMO-2 (π_u, Fig. 4(a)) involving in-phase overlaps between B p_z (or p_y) and the π orbitals of two -B=S groups help to stabilize the linear geometries of both the neutral and the anion. It should be stressed that the triplet linear ground state of B(BS)$_2^-$ ($^3\Sigma_g$) with two singly occupied HOMOs (π_u) turned out to be 0.61 eV more stable than its singlet linear isomer. Both bent B(BS)$_2^-$ and B(BS)$_2$ (C_{2v}) were found to be automatically converted to their linear ground-state geometries during structural optimization. This situation is obviously different

from C_{2v} BH$_2$ which has a H–B–H bond angle of 128°[23]. Coulomb repulsion between the two -B=S terminal groups in B(BS)$_2$ proves to be more effective than that between two H atoms in BH$_2$, making the bent B(BS)$_2$ linear.

TD-DFT calculation indicates that multireference configuration interactions (MRCI) play an increasing role in B(BS)$_2^-$, with the main electron-detaching processes contributing 56~74% to the concerned excitation roots. However, the calculated VDE values should be reliable because the involved shake-up states have been included in our TD-DFT calculation. The first VDE of 3.08 eV mainly originates from detaching one electron from the degenerate HOMO (π_u). It is only 0.08 eV higher than the ADE value of 3.00 eV for B(BS)$_2^-$, in consistent with the small structural relaxation from B(BS)$_2^-$ to B(BS)$_2$ (Fig. 3(a)). The A-band at 4.96 eV mainly comes from de- taching one electron from the degenerate HOMO- 1(π_g) which purely contains the out-phase interactions between the π orbitals of the two BS groups. The B-band at 5.15 eV, however, mainly originates from detaching one electron from the degenerate delocalized HOMO-2(π_u) mainly representing the inphase bonding overlaps between the π orbitals of the two BS groups. All the other σ-typed inner-shell MOs of B(BS)$_2^-$ in Fig. 4(a) require higher detachment energies.
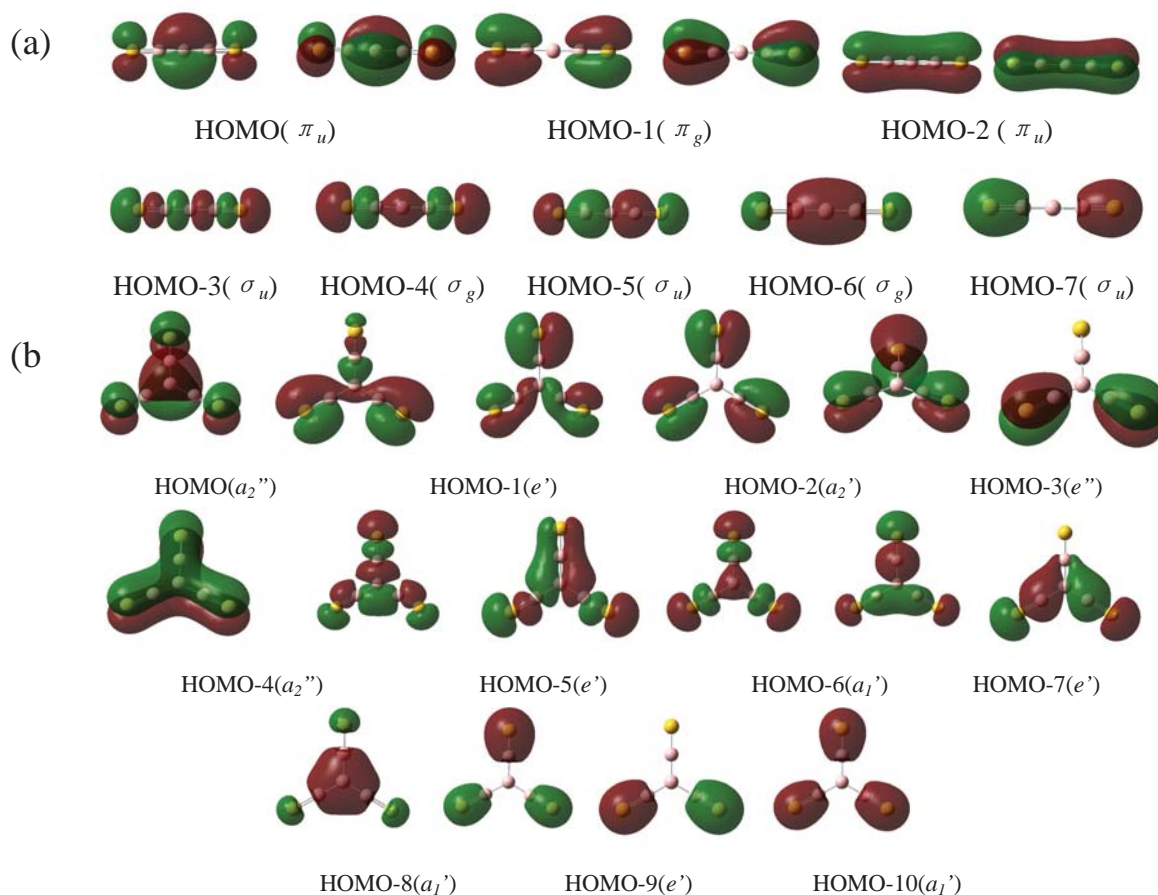
(a)

HOMO(π_u)   HOMO-1(π_g)   HOMO-2 (π_u)

HOMO-3(σ_u)   HOMO-4(σ_g)   HOMO-5(σ_u)   HOMO-6(σ_g)   HOMO-7(σ_u)

(b

HOMO(a_2'')   HOMO-1(e')   HOMO-2(a_2')   HOMO-3(e'')

HOMO-4(a_2'')   HOMO-5(e')   HOMO-6(a_1')   HOMO-7(e')

HOMO-8(a_1')   HOMO-9(e')   HOMO-10(a_1')

Fig. 4.   **Valence MO pictures of B(BS)$_2^-$ (a) and B(BS)$_3^-$ (b)**

The ground state of B(BS)$_3^-$ ($^2A_2''$) is a beautiful equilateral triangle (D_{3h}) with an sp^2-hybridized B atom at the center. Single occupation of the symmetrically delocalized π-typed HOMO (a_2'') (Fig. 4(b)) produces no structural distortion to B(BS)$_3^-$. But a perfect D_{3h} B(BS)$_3$ neutral has the problem of convergence at DFT: it is slightly distorted to a C_{2v} triangle with an apex angle of 120.08°. This C_{2v} structure is practically an equilateral triangle with the approximate symmetry of D_{3h} (Fig. 3(b)). Our triangular structures of B(BS)$_3$ and B(BS)$_3^-$ can be obtained from D_{3h} BH$_3$[21, 23, 24] by substituting three -H atoms with three -BS groups. B(BS)$_3$ neutral and B(BS)$_3^-$ anion form the first planar species in boron sulfides studied in this work and contain the first perfect equilateral triangle BB$_3$ with an sp^2 B at the center in boron sulfide clusters reported so far. These results provide strong evidence that the -BS groups mainly function as σ-radicals in boron-rich boron

sulfides, aping -H atoms in small boranes. The difference lies in that the -BS groups also form delocalized π interactions with the central B atom(s), as obviously evidenced by HOMO-2(π_u) of B(BS)$_2^-$ in Fig. 4(a) and HOMO-4(a_2'') of B(BS)$_3^-$ in Fig. 4(b).

TD-DFT calculations indicate that B(BS)$_3^-$ anion has the first ADE of 3.45 eV and VDE of 3.53 eV, corresponding to detaching one electron from the singly occupied π-HOMO(a_2'') of B(BS)$_3^-$. The second band (A) at 5.46 eV and third one (B) at 5.50 eV mainly originate from detaching one electron from the degenerate HOMO-1(e') and HOMO-2(a_2'), respectively. Excitation leading to other excited states proves to involve much more complicated MRCI contributions.

It should be pointed out that the calculated first VDE values (X bands) of B(BS)$_2^-$ (3.08 eV) and B(BS)$_3^-$ (3.53 eV) are well comparable with the corresponding values reported for B(BO)$_2^-$ (2.94 eV)

and $B(BO)_3^-$ (3.64 eV)[1]. However, their second (A bands)) and third (B bands) VDEs (Table 1) turned out to be much lower than that of the corresponding boron oxides (which is beyond 6.4 eV)[1]. These results indicate that the A and B bands of $B(BS)_2^-$ and $B(BS)_3^-$ should be observed in their 193 nm (6.424 eV) PES spectra to provide more detailed information for geometrical and electronic structure characterizations. In addition, the stretching symmetrical vibrational frequencies of B=S bonds at about $1180 \sim 1350$ cm^{-1} (Table 1) are also possible to be resolved in high resolution PES spectra of these anions.

The symmetrical stretching frequencies of B=S double bonds in $B(BS)_2^-$ (1300 cm^{-1}) and $B(BS)_3^-$ (1281 cm^{-1}) all turned out to be slightly lower than the corresponding vibrational frequencies of their neutrals (Table 1). Similar situation occurs in BS^- and BS_2^-. This phenomenon reflects anti-bonding nature of HOMOs in these anions, as shown in Figs. 2 and 4. Table 1 indicates that the B–S single bonds in $B(BS)_2$ and $B(BS)_3$ systems stretch at much lower frequencies in the range of $310 \sim 350$ cm^{-1}, while the B–S interactions in BS_2 neutral and anion show certain double bond character with the B–S stretching frequencies lying at about 550 cm^{-1} (Table 1 and Fig. 2). As shown in Fig. 3 and Table 1, when the coordination numbers of the central B increase, the B–B bond lengths increase and their stretching frequencies decrease.

4 SUMMARY

DFT investigations performed in this work show that linear BS^- and BS_2^- are similar to BO^- and BO_2^- in both geometrical and electronic structures, and linear $B(BS)_2^-$ and triangular $B(BS)_3^-$ together with their neutrals appear to be analogous to BH_2 and BH_3, respectively. The -BS groups prove to serve basically as σ-radicals to coordinate with the B center(s) in small boron sulfides, similar to -H, -CN[25] and -BO[1, 2] in coordination abilities. Direct B–B bonds, which are absent in oxygen-rich boron oxides reported before[13], are found to exist in small boron-rich boron sulfides. The predicted ADE and VDE values of BS^-, BS_2^-, $B(BS)_2^-$ and $B(BS)_3^-$ may well facilitate future PES experiments to confirm these species. The results obtained in this work may also provide useful reference to the investigations of boron oxides which still remain a huge challenge in both experimental and theoretical chemistry[1, 2, 13, 17, 18].

REFERENCES

(1)   Zhai, H. J.; Li, S. D.; Wang, L. S. *J. Am. Chem. Soc.* **2007**, 129, 9254–9255.

(2)   Zhai, H. J.; Wang, L. M.; Li, S. D.; Wang, L. S. *J. Phys. Chem. A* **2007**, 111, 1030–1035.

(3)   Sommer, A.; Walsh, P. N.; White, D. *J. Chem. Phys.* **1960**, 33, 296–297.

(4)   Gilles, P. W.; Greene, F. *J. Am. Chem. Soc.* **1962**, 84, 3598–3599.

(5)   Greene, F.; Gilles, P. W. *J. Am. Chem. Soc.* **1964**, 86, 3964–3969.

(6)   Chen, H. Y.; Gilles, P. W. *J. Am. Chem. Soc.* **1970**, 92, 2309–2312.

(7)   Chen, H. Y.; Gilles, P. W. *J. Phys. Chem.* **1972**, 76, 2035–2038.

(8)   Sennesal, J. M.; Robbe, J. M.; Schamps, J. *Chem. Phys.* **1981**, 55, 49–56.

(9)   Bruna, P. J.; Grein, F. *J. Phys. Chem. A* **2001**, 105, 3328–3339.

(10) Huber, K. P.; Herzberg, G. *Molecular Spectra and Molecular Structure, IV. Constants of Diatomic Molecules.* Van Nostrand: New York **1979**.

(11) He, S. G.; Evans, C. J.; Clouthier, D. J. *J. Chem. Phys.* **2003**, 119, 2047–2056.

(12) He, S. G.; Clouthier, D. J. *J. Chem. Phys.* **2004**, 120, 4258–4262.

(13) Doyle, R. J. Jr. *J. Am. Chem. Soc.* **1988**,110, 4120–4126.

(14) a) Casida, M. E.; Jamorski, C.; Casida, K. C.; Salahub, D. R. *J. Chem. Phys.* **1998**, 108, 4439–4449; b) Stratmann, R. E.; Scuseria, G. E.; Frisch, M. J. *J. Chem. Phys.* **1998**, 109, 8218–8224; c) Bauernschmitt, R.; Ahlrichs, R. *Chem. Phys. Lett.* **1996**, 256, 454–464.

(15) a) Becke, A. D. *J. Chem. Phys.* **1993**, 98, 5648–5652; b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, 37, 785–789.

GUO Q. L. *et al.*: Geometries, Electronic Structures, and Electron Detachment Energies
of Small Boron Sulfide Anions: A Density Functional Theory Investigation

658   No. 6

(16) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A. Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B. W.; Chen, M.; Wong, W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, Revision A.1; Gaussian, Inc.: Pittsburgh, PA **2003**.

(17) Wenthold, P. G.; Kim, J. B.; Jonas, K. L.; Lineberger, W. C. *J. Phys. Chem. A* **1997**, 101, 4472–4474.

(18) Rienstra, J. C.; Schaefer Ⅲ, H. F. *J. Chem. Phys.* **1997**, 106, 8278–8279.

(19) Ruscic, B. M.; Curtiss, L. A.; Berkowitz, J. *J. Chem. Phys.* **1984**, 80, 3962–3968.

(20) Nemukhin, A. V.; Weinhold, F. *J. Chem. Phys.* **1993**, 98, 1329–1335.

(21) Dill, J. D.; Schleyer, P. V. R.; Pople, J. A. *J. Am. Chem. Soc.* **1975**, 97, 3402–3409.

(22) Brommer, M.; Rosmus, P.; Carter, S.; Handy, N. *Mol. Phys.* **1992**, 77, 549.

(23) Feller, D.; Dixon, D. A.; Peterson, K. A. *J. Phys. Chem.* **1998**, 102, 7053–7059.

(24) Tian, S. X. *J. Phys. Chem. A* **2005**, 109, 5471–5480.

(25) Bradforth, S. E.; Kim, E. H.; Arnold, D. W.; Neumark, D. M. *J. Chem. Phys.* **1993**, 98, 800–810.