Reactivity of neutral and charged B_{13} clusters with O_2: A theoretical study

William J. Slough,[1] Anil K. Kandalam,[2,a)] and Ravindra Pandey[1,a)]

[1]*Department of Physics, Michigan Technological University, Houghton, Michigan 49931, USA*
[2]*Department of Physics, McNeese State University, Lake Charles, Louisiana 70609, USA*

The chemical reactivity of neutral, cationic, and anionic species of the gas phase B_{13} cluster with molecular oxygen, O_2, was investigated using density functional theory. All three species of B_{13} interact with an oxygen molecule to generate a variety of stable isomers, with those representing a dissociative chemisorption process forming the most stable configurations. Our results also show site-specific bonding of oxygen to the $B_{13}^{(+/0/-)}$ cluster. The effect of sequential ionization on the formation of products is pronounced. In ionic B_{13} clusters, in addition to energetics, the spin of the reactants and products plays a vital role in determining the most favorable product channel. In addition, this study reveals a richness of phenomena requiring a unified consideration of energy, geometry, spin conversion, and details of the electronic structure not previously illustrated for the reactivity of boron clusters. © *2010 American Institute of Physics*. [doi:10.1063/1.3336404]

I. INTRODUCTION

Historically, interest in boron clusters flowed from two main currents. One current has its origins in applying the development of cluster science to problems involving the practical use of boron in energy dense fuels.[1] The other current is intertwined with the broad desire to understand the overall nature of cluster systems in general, especially as to the expected insight that such systems would reveal about the transition from molecular to macroscopic systems. Small boron clusters ($B_n, n < 15$) were seen as approachable systems for study because they would be tractable at a high level of *ab initio* theory given the computational resources available at the time. Today, questions first generated from these considerations are still open for further study. In addition, the interest generated in initial investigations of small boron clusters blossomed into studies of larger systems—nanosheets[2] and nanotubes[3] constructed solely from boron atoms. Also, the diverse chemistry of boron continues to provide a wealth of structures for use in varied applications: as materials for hydrogen storage,[4] as targets for boron neutron capture therapy,[5] and as novel ligands for nanostructured materials.[6]

Experiments on the reactivity of small boron clusters have been carried out for two decades.[7–13] The results found primary use in elucidating the nature of the bare boron clusters and in motivating computational electronic structure studies to find lowest energy species among the many possible stable isomers. One experimental approach that has been employed for studying the structure and properties of gas phase boron clusters is to allow them to react with a variety of gas molecules. By studying these reactions, various properties of boron clusters, such as relative stability as a function of size may be determined. The specific choice of reacting gas molecule acts as a probe revealing specific details of the chemistry of boron clusters.

Molecular oxygen, O_2, is one such probe. Experimental oxidation studies with various species of boron clusters produced key insights into their properties and the nature of such chemical reactions.[9,13] Reaction studies of boron clusters with O_2 yield insight into their stability. Experiments done by Anderson's group[9] on the interaction of cationic clusters with molecular oxygen yielded reaction pathways predominately characterized by etching (the removal of boron atoms from the target cluster, for instance, $B_n^+ + O_2 \rightarrow B_{n-2}^+ + 2BO$). Whereas, more recent experimental work done by Castleman's group[13] suggests that anions may prefer additive channels in reactions with O_2 (for instance, $B_n^- + O_2 \rightarrow B_n O_2^-$). Although much has been learned through the execution and analysis of these experiments, there are aspects still awaiting further explanation. Theoretical work undertaken so far to illustrate the reaction processes uncovered by experiments has not been forthcoming. The current investigation seeks to utilize available experimental results and the wealth of knowledge gained in recent years through several theoretical studies of boron clusters to begin to delve into their reaction chemistry.

A variety of approaches is currently available for the computational study of reaction dynamics. For example, a direct dynamics simulation can be employed, solving the time-independent Schrödinger equation at each integration step along a classical trajectory following a reaction path of interest.[14] This approach, however, is computationally intensive if a large number of possible initial trajectories exist for study. One way to select trajectories of interest is by first conducting computational electronic structure studies involving various geometries of the reactants—in this case B_{13} ionic species and an oxygen molecule, O_2. We employed the latter strategy in this work.

In our investigations we use several initial geometries, including various orientations in lowest energy optimization

---
a)Authors to whom correspondence should be addressed. Electronic addresses: akandalam@mcneese.edu and pandey@mtu.edu.
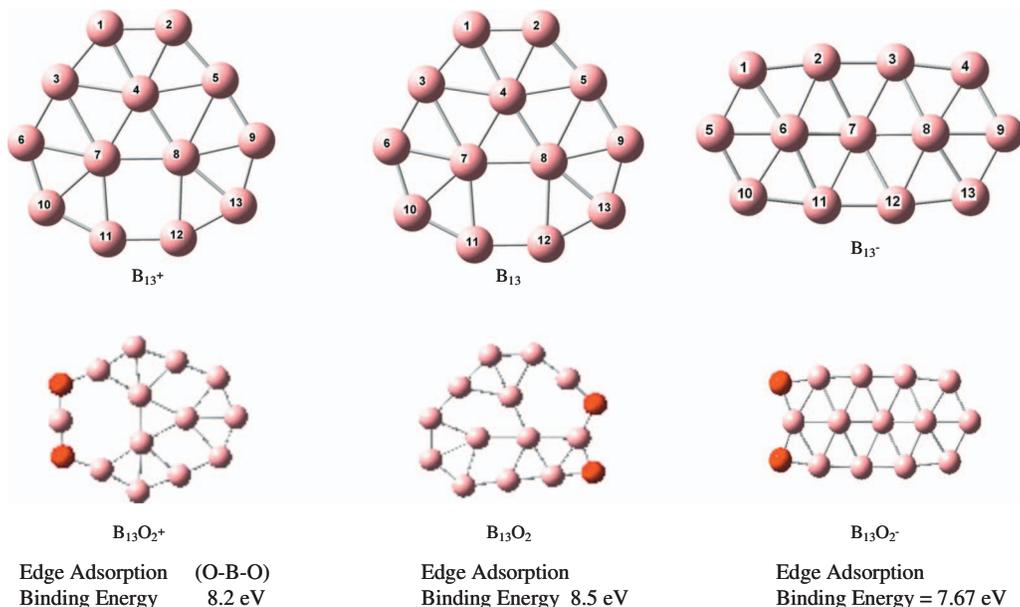
FIG. 1. The lowest energy structures for the $B_{13}^{(+/0/-)}$ and $B_{13}O_2^{(+/0/-)}$ clusters.

studies to simulate different approach paths for the reactants as would be experienced in reaction tube experiments. By using this approach we sought to discover what properties might be important in reactions involving small boron clusters with molecular oxygen. Although we use only B_{13} species in this investigation we believe this singular example will illustrate a number of points to consider when simulating the reaction of small boron clusters with molecular oxygen. At the outset we had good reason to investigate several features that we hypothesized to be important in this model reaction. For example, recent calculations on boron clusters[15] suggest that B_{13}^+ is moderately anisotropic in its electronic structure, with two-center-two-electron (2c-2e) bonding predominate for the ten atoms constituting the outer ring of the B_{13} species (see Fig. 1). The inner three atoms also participate in the 2c-2e bonding. These central atoms are then more loosely bonded to the outer atomic ring via different bonding structures involving molecular orbitals that are more diffuse in nature. We may expect that in some aspects of its behavior the B_{13}^+ cluster behaves as two independent units coupled together. As such, the interaction of O_2 molecules approaching the center three atoms of the B_{13}^+ cluster may be expected to lead to different structures—hence different reaction channels—than approaches to the outer boundary of the cluster. Thus geometric considerations can be expected to play a major role. This may then lead to site-specific reactions if the geometry favors bonding between localized orbitals—for example, with the boron atoms around the outer ring—instead of bonding that favors the interplay of a more diffuse orbital in the cluster.

Considerations of spin conservation may also help to illuminate aspects of $B_{13}^{(+/0/-)}+O_2$ reactions. For example, spin-forbidden reactions may proceed with rates at least 100 times slower than similar but spin-allowed reactions.[16] A recent theoretical study suggests that the dissociative adsorption of O_2 on silicon clusters is strongly affected by a local spin state conversion process.[17] For B_{13}^+ the change in reac-

tivity (cross section) and reaction products as a function of collision energy denoted by the work of Anderson's group identified a barrier to oxidative etching.[9] How much of this barrier is due to a requirement for spin conversion during the reaction is unknown. In addition, given the anisotropic nature of the electronic structure of the B_{13} ionic species, the reaction barrier may be expected to vary substantially depending on the reaction path into the interaction site of the cluster.

Finally, the evolution of reaction behavior from cationic to neutral to anionic cluster is expected to change in ways explainable by observed trends in the change in nature of the boron cluster species itself. Again, one motivation for this study is to decide how effective the judicious use of *first principles* calculations can be as a starting point in understanding the above aspects of a chemical reaction involving an ionic cluster. Specifically, we expect the reaction pathways for the cationic and anionic to depend strongly on spin conversion—with no such consideration required for reactivity of neutral species. Also, differences in the electronic structure between the cationic and anionic B_{13} clusters revealed by a theoretical study may account for the switch between etching and additive reactions as exhibited in the experimental studies.[9,13] The main focus of this work, however, is to explain and illustrate the reaction behavior of charged B_{13} clusters with O_2 as seen in previously conducted experiments.[9,13]

II. COMPUTATIONAL METHOD

The results presented in this work were computed by employing density-functional theory under the generalized gradient approximation using the B3LYP hybrid functional and 6-31G* basis set as implemented in the GAUSSIAN03 code.[18] All reported structures were optimized and checked for stability by calculating the vibrational frequencies. In order to test the accuracy of the 6-31G* basis set employed in

this study, we also considered several of the low lying planar isomers of B$_{13}$ cluster. The same structures were also modeled using a larger basis set, namely, 6−311G* and compared (results not reported here). Our calculations (using either basis sets) reproduced the lowest energy structure and the expected succession of isomers for each of the B$_{13}^{(+/0/−)}$ species reported in the earlier studies[6,15] where a larger basis set (6-311+G*) was employed. This agreement between our results and the previously reported studies establishes the reliability of our modeling elements.

To investigate the possible stable products resulting from a B$_{13}^{(+/0/−)}$+O$_2$ interaction, an O$_2$ molecule was placed near the B$_{13}^{(+/0/−)}$ species forming an initial "unreacted" configuration. Several initial configurations were considered for each B$_{13}^{(+/0/−)}$ species. The O$_2$ molecule was allowed to approach a variety of sites on the cluster with differing orientations with respect to B$_{13}$. Initial calculations on the B$_{13}^{(+/0/−)}$+O$_2$ system revealed that a substantial barrier to interaction exists. As such, the starting distance between the nearest oxygen and boron atoms for all initial configurations was set to roughly 1.55 Å to ensure a resulting "reaction" product. Configurations with a greater starting distance between the boron cluster and oxygen molecule often resulted in an unbound or weakly bonded (on the order of 0.1 eV) system.

Early on in this investigation, a clear trend relating the total energy of the B$_{13}$O$_2^{(+/0/−)}$ system and the O–O distance within the product cluster appeared. Seemingly a greater O–O distance resulted in a lower energy for the composite structure. This motivated additional calculations that adducted two oxygen atoms at differing sites of the boron cluster to develop structures for comparison. The oxygen atoms were placed at a B–B bridge site with a distance between the oxygen and each boron atom of 1.40 Å. These B$_{13}^{(+/0/−)}$+2O structures were used in an attempt provide a lowest energy bound toward which the B$_{13}^{(+/0/−)}$O$_2$ systems might approach.

III. RESULTS AND DISCUSSIONS

The product channels for the reaction of cationic boron clusters with molecular oxygen have been studied by Anderson's group.[9] We first discuss the reactivity of the cationic cluster, paying special attention to the role played by spin conversion considerations in determining product channels. The results from studying the neutral cluster provide a contrasting case showing a much simplified reaction path when spin conversion does not need to occur. The anionic cluster reaction with O$_2$ once again shows the need to consider spin conversion when determining product channels. Finally, the electronic structure of the [B$_{13}^{(+/0/−)}$O$_2$] complexes is examined illustrating site-specific bonding for each case—cationic, neutral, and anionic.

A. B$_{13}^+$+O$_2$ system

The experimental work done by Anderson's group on cationic boron clusters identified the B$_{13}^+$ species as relatively more stable and less reactive than other cationic boron clusters.[9–11] Motivated by these experimental results, a number of computational and theoretical studies[19–24] was undertaken to describe the geometrical structure and underlying

cause for the anomalous stability of B$_{13}^+$. The interesting behavior of the B$_{13}$ cation precipitated its selection by us for use in this study. Our calculations find the lowest energy geometry for B$_{13}^+$ to be planar, where three boron atoms form a near equilateral triangle roughly centered within a ten-member outer atomic ring (Fig. 1). This structure has C$_{2v}$ symmetry and prefers a singlet spin state. Earlier calculations reported by other groups also find this structure to be the ground state for the B$_{13}^+$ species.[6,15]

The B–B bond lengths for the outer atomic ring range from 1.54 to 1.59 Å, whereas the atomic distances interior to the structure range from 1.68 to 1.97 Å. Mulliken charge analysis shows that the cationic nature of B$_{13}$ results in a slightly positive charge residing on atoms 3–5 and 11–12 (Fig. 1), with the remaining atoms in the cluster nearly neutral. Vibrational frequency calculations reveal that the dominant modes corresponding to the greatest IR intensity involve in-plane oscillations of the three-atom interior triangle. The calculated gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied orbital (LUMO) for B$_{13}^+$ is 3.0 eV, indicating an unusual chemical stability. This is significantly higher than for B$_{12}^+$ at 1.7 eV. In addition, recent analysis of the electronic structure of B$_{13}^+$ suggests that its relatively high stability when compared with other small cationic boron clusters stems from a triply aromatic nature in both sigma- and pi-bonding analogous to that seen in certain organic molecules as well as the bonding interaction between the interior atoms with the outer ring.[15,24]

A simple scan of energy versus distance along varying approaches to the B$_{13}^+$ cluster with an O$_2$ molecule (with internal atomic distances held fixed) revealed a strong orientation and distance dependent energy surface (Fig. 2). This is an indication that a reaction with an O$_2$ molecule is site dependent.

Energy minimization calculations of various structural configurations, with different orientations of O$_2$ relative to the B$_{13}^+$ cluster, resulted in two distinct classes of structures: oxygen physisorbed structures and oxygen chemisorbed structures. A few geometries lead to structures in which the O$_2$ molecule is physically adsorbed onto the cation, with the O$_2$ molecule maintaining its separate structural identity. However, these systems are bound together with energies in the range of a few tenth of an eV. In the other class of structures, the O$_2$ molecule is chemisorbed, either molecularly or dissociatively. The lowest energy structure of [B$_{13}$O$_2$]$^+$ corresponds to binding of O$_2$ to the edge sites of the outer ring boron atoms in a dissociative fashion with the formation of an O–B–O subunit (see Fig. 1). A few other higher energy "edge adsorbed" structures were also found to be stable, in which a B–B bond is broken and two individual B–O bonds were formed. Two such isomers are found to be of particular interest in interpreting the oxidative etching results of Anderson's group (see Fig. 3).[9] The configurations in which the O$_2$ approaches the B$_{13}$ cluster from the above (face adsorption) were found to be very high in energy and thus are not discussed further. In addition to studies of B$_{13}^+$+O$_2$ systems, B$_{13}^+$+2O geometries were also examined to provide an additional "lowest boundary" to possible isomers. All isomers formed from adducting two separate oxygen atoms to
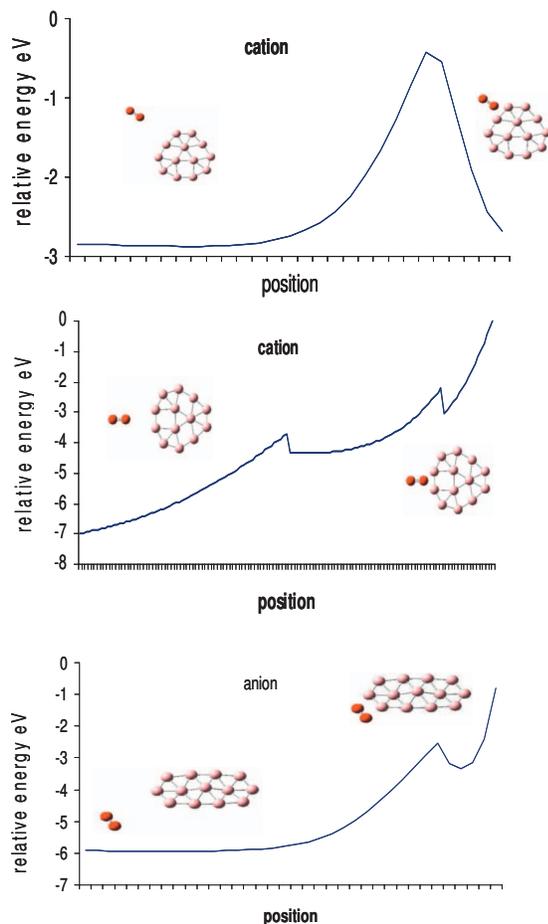
FIG. 2. Single point energy scans of B_{13} ions with O_2 along differing approach paths.

FIG. 4. Energy dependence as a function of spin and O–O distance of $B_{13}O_2$ (molecular oxygen interaction) and $B_{13}2O$ (atomic oxygen) species edge structures.

the cationic cluster were higher in energy for comparative O–O distances (Fig. 4). Several $B_{13}^+ + 2O$ geometries lead to lower energy isomers, but only for a very large O–O separation. In any case, the isomers found via the adduction of two oxygen atoms provide another useful avenue as a bound for the production of a lowest energy "edge adsorbed" structure.

As an initial approach to understanding the reactivity of the $B_{13}^+ + O_2$ system we will consider in some detail two distinct product channels (Fig. 3). Fortunately, in addition to the

FIG. 3. Interaction process of a B_{13}^+ cluster with O_2.

computational results of this work, an excellent set of experimental data produced by Anderson's group[9] also exists. Experimentally, the most productive reaction channel for the $B_{13}^+ + O_2$ reaction has been shown to be $B_{13}^+ + O_2 \rightarrow B_{11}^+ + 2BO$. Our calculations show that the final products for this reaction are higher in energy than the reactants by 0.56 eV (Fig. 3). Anderson's experiment shows that this channel has a barrier of ~1 eV. One possible input to the makeup of this barrier is the consideration of spin conservation in the reaction. Since the cation is a closed-shell system, the need to move the system from a singlet $B_{13}^+ +$ triplet O_2 state ($^1B_{13}^+ + {}^3O_2$) to a state which we will approximate as $^3B_{13}^+ + {}^3O_2$ is necessary under this consideration. Calculating the energy difference for the spin conversion process $^1B_{13}^+ \rightarrow {}^3B_{13}^+$ between our $^1B_{13}^+$ structure and the optimized isomer structure for $^3B_{13}^+$ gives an adiabatic spin conversion excitation (ase) of 1.51 eV. The energy difference between our $^1B_{13}^+$ structure and the same structure at a triplet multiplicity gives a vertical spin excitation of 1.78 eV. It is probable that a local spin conversion process is required for the initiation of the cationic reaction and makes up at least part of the experimentally observed barrier.

As shown in Fig. 3, an isomer favorable to the formation of $B_{11}^+ + 2BO$ exists—denoted as $^3[B_{13}O_2]^+$, B–O isomer. This complex, however, has not completely dissociated the O_2 molecule, with O–O bond length elongated to 1.51 Å. This complex falls toward an accessible lower energy struc-

ture, the $^1[B_{13}O_2]^+$, B–O isomer. This process creates the required energy (roughly 5.2 eV for molecular O_2)[25] to completely dissociate the O_2 molecule. The complete dissociation of the O_2 molecule creates the necessary energy and spin environment for the liberation of the two boron oxide molecules and a singlet B_{11} cluster. In addition, an examination of the frontier orbitals for the $^3[B_{13}O_2]^+$ complex suggests bonding favorable to the formation of B_{11} and BO fragments [see Fig. 6(a)].

Anderson's results show several other product channels. Reaching these channels, however, required a much larger kinetic energy for the reactants, approaching 3 eV for some cases. Our results suggest that the channel $B_{13}^+ + O_2 \rightarrow B_{12}^+ + BO_2$ would be favorable from consideration of energetics. In fact, from the outset the products are immediately lower in energy than the reactants; however, B_{12} is an unusually stable cluster and this consideration is expected to play a role in the limited appearance of B_{12}^+ ions.[24,26] Although we did not investigate channels producing B_{10}^+ products in detail a few observations can be made. Stable isomers do exist for the chemisorption of molecular oxygen onto the three boron atoms making the inner triangle of the cation. However, considerations of spin and energetics do not appear to be immediately favorable for this channel. Given the coupling nature[24,26] of the inner three atom structure to the outer ring of ten atoms, and high kinetic energy requirements for experimental production, it is possible that this channel appears through collision induced dissociation—not purely through chemical reactivity—although both avenues for a future investigation should be considered. Finally, the complete absence in the experimental detection of $B_{13}O_2^+$ isomers (the lowest energy product in our calculations) stems from the fact that the formation of this product is highly exothermic ($\sim$8.2 eV). Compared to a binding energy per boron atom of $\sim$4.3 eV for the B_{13}^+ cluster, this structure will disintegrate into other products through any available channels.

B. B$_{13}$+O$_2$ system

The geometry of the neutral species is nearly identical to the cationic case. The global minimum structure is a doublet exhibiting C_{2v} symmetry (Fig. 1). Calculations by other researchers have also found this structure to be the ground state for the neutral B_{13} species.[26]

The distance between boron atoms around the outer ring of the neutral cluster is slightly shifted in length (smaller and larger) from that of the cationic cluster and range from 1.53 to 1.61 Å. Atom distances interior to the structure range from 1.66 to 1.91 Å. Mulliken charge analysis shows that the B_{13} species carries a slight positive charge on atoms 3–5 and 7–8, with a slight negative charge for atoms 1–2, 6, and 9 (see Fig. 1 for atom position number). Similar to the cationic case, vibration frequency calculations show that some of the dominant modes associated with greatest IR intensity involve in-plane oscillations of the three atom interior triangle; however, two other modes are comparable in intensity. One mode couples atoms 3–7 and 5–8 with a symmetric stretch. The other is an asymmetric stretching mode between the atoms around the outer ring of the cluster. The addition of an elec-

tron to the cationic cluster yields a neutral cluster with a positively charged triangular center, but the outer ring picks up an overall negative charge tying the structures together. The binding energy for the structure is 4.8 eV per atom and the calculated HOMO-LUMO gap is 1.6 eV.

Since the neutral B_{13} cluster is an open shell doublet, spin conservation is readily satisfied in a reaction with triplet oxygen, and the study of this interaction leads to simpler energy considerations of the geometry dependence of bonding. Our calculations on the interaction of neutral B_{13} cluster with an O_2 molecule resulted in a variety of stable isomers. Our results suggest that an O_2 molecule may be physically adsorbed onto the cluster with a binding energy of several tenths of an eV ($<$0.5 eV). However, such a physisorbed product is found to be very high in energy. Unlike the cationic reactivity case, several isomers with a strong binding of the O_2 molecule as a single unit (O–O$<$1.5 Å) to the B_{13} cluster were found to be stable, with a binding energy of 3.4 eV. These structures suggest that oxygen may be molecularly chemisorbed onto a neutral B_{13} cluster. The initial approach of the O_2 molecule produces two general types of molecularly chemisorbed products. An approach near the center of the B_{13} cluster (perpendicular to the plane containing the cluster atoms) leads to a "face adsorption" based structures. On the other hand, approaches near the edge of the cluster lead to "edge adsorption" structures that have roughly twice the binding energy of face adsorbed structures. We also found several stable structures in which the O_2 molecule is bound atomically to neutral B_{13}, both face-adsorbed and edge-adsorbed, suggesting that a dissociative chemisorption process is also supported. In fact, we found that dissociative binding is more favorable than molecular binding of O_2 molecule with B_{13}. Among all the different geometries, the lowest energy product representing the $B_{13}+O_2$ system is found to be an edge-adsorbed structure shown in Fig. 1 (binding energy of 8.5 eV). As a check for structures even lower in energy, a variety of geometries built using a $B_{13}+2O$ approach to create edge adsorption structures was investigated. None of these geometries produced a structure lower in energy. The dependence of structure energy as a function of O–O distance for edge adsorption on a neutral cluster is shown in Fig. 4.

These results are suggestive for three reaction channels of interest. The first to consider is a purely additive channel: $B_{13}+O_2 \rightarrow B_{13}O_2$. This is the lowest energy structure formed during our simulations, but it produces 8.5 eV in energy (exothermic) and it is doubtful that it would not disintegrate through any other available channel (binding energy per boron atom for the cluster is 4.8 eV). One such channel is the production of $B_{12}+BO_2$. The products are 4.3 eV lower in energy than the initial reactants, and this channel is favorable to spin conversion considerations since the B_{12} cluster is a singlet and BO_2 a doublet. The B_{12} cluster, like the B_{13} cation is an unusually stable cluster.[24] The products will result in the release of 4.3 eV of energy. Although this is a bit high, the products should still resist further disintegration. One further channel for comment is the production of $B_{11}+2BO$. This channel is energetically favorable (exothermic by 0.33 eV). Although no experimental results on this cluster reac-

tion are known to us, based on our calculations we predict that the production of $B_{12}+BO_2$ is a favored channel in the reaction of O_2 with the neutral B_{13} cluster.

C. $B_{13}^-+O_2$ system

For anionic B_{13}, the predicted ground state is a singlet structure having its three central atoms along a single line with a 10 atom outer ring in the shape of an ellipse of high eccentricity (see Fig. 1). In addition, the three central atoms are slightly displaced from the plane of the outer ring: the central atom of the cluster (atom 7 in B_{13}^- of Fig. 1) is displaced in a direction completely opposite to the other two interior atoms. The overall structure then may be considered as quasi- or pseudoplanar with an overall C_{2v} symmetry. Others reported a structure with the central atom of the cluster slightly off line from the central row of atoms resulting in an overall symmetry of C_s with a very slight energy difference between structures.[26] Mulliken charge analysis assigns an almost neutral or a partial negative charge to each atom of the outer ring. The central atom is essentially neutral, with the atoms on each side of center slightly positive in charge. In essence the anionic cluster embeds two positively charge atoms on each side of center slightly out of plane into an elliptical ring of negative charge—with an additional boron atom at the center. The two dominant modes of vibration involve the three central atoms. One mode is the vibration of the central atom in a plane parallel to the outer ring, oscillating toward one edge of the cluster then the other (along a line connecting the narrow dimension of the cluster). The mode with highest intensity is the oscillation of the two atoms on either side of the central atom in concert. This mode is analogous in description to that of the central atom mode. The calculated HOMO-LUMO gap for the singlet B_{13}^- cluster is 2.3 eV.

Interactions of the anionic cluster with molecular oxygen produce a variety of stable isomers with differing bonding characteristics. The oxygen molecule may be physically adsorbed onto the anion or molecularly chemisorbed onto the "face" and "edge" of the cluster. The lowest energy structure results from the complete dissociation of the O_2 molecule into the edge of the anionic cluster (see Fig. 1). Since the ground state of B_{13}^- is a singlet, considerations of spin conversion must again be used in concert with energy to explore potential reaction channels. Calculations for the spin conversion of the anion yield $^1B_{13}^- \rightarrow {}^3B_{13}^-$ with an ase=0.66 eV and vse=1.16 eV. Thus, a slight barrier to the reaction of triplet oxygen with the anionic should exist based on considerations of spin conversion alone.

The reaction of the anion with molecular oxygen presents two immediate pathways of reaction for consideration. Like the cation, one pathway to consider contains channels that lead to other anions (such as B_{12}^- and B_{11}^-) and neutral oxides of boron. The unusually high stability of the B_{12} cluster[24] also suggests that a promising second avenue would be channels that produce neutral boron clusters (B_{12} and B_{11}) and ionized oxides of boron (such as BO_2^- and BO^-). There-
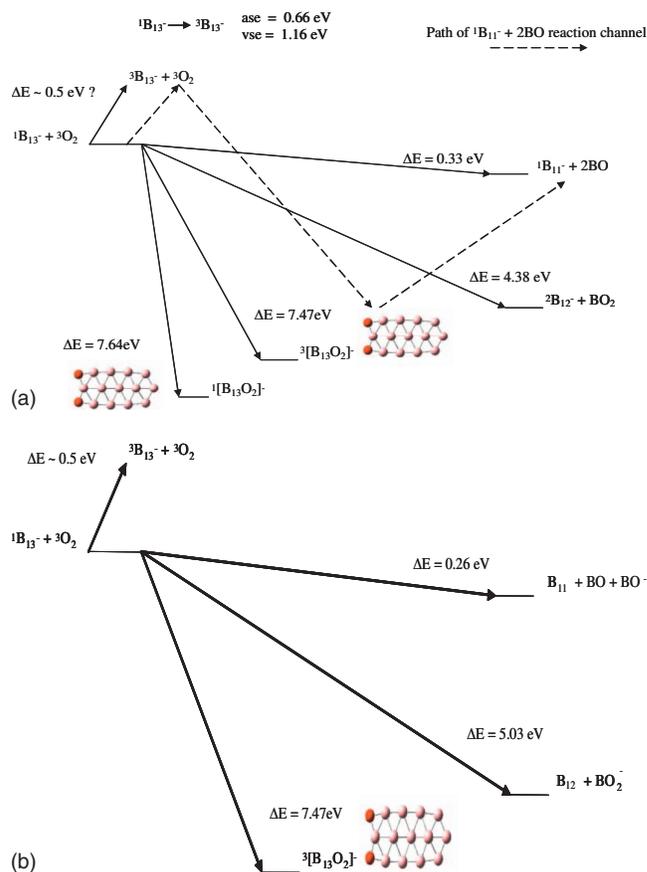
FIG. 5. (a) Interaction process of a B_{13}^- cluster with O_2: anion pathway. (b) Interaction process of a B_{13}^- cluster with O_2: neutral pathway.

fore, for the case of the $B_{13}^-+O_2$ system, two avenues for reaction is explored, one leads to anionic clusters of boron, the other to neutral clusters.

As shown in Fig. 5(a), analogous to the cation, one potential reaction channel would appear to be $B_{13}^-+O_2 \rightarrow B_{11}^- +2BO$. This channel dissipates most of the energy available in the exothermic formation of the $^3[B_{13}O_2]^-$ complex (ΔE =7.47 eV) and is favorable to considerations of spin assignment. Another possible reaction channel leads to the production of $B_{12}^-+BO_2$. Examination of the frontier orbitals of the $^1[B_{13}O_2]^-$ complex [Fig. 6(b)] is also favorable toward the formation of B_{12} and BO_2 fragments. Bergeron and Castleman[13] in their experimental study of anionic boron clusters reacting with O_2 reported results suggesting that an additive channel for anions was available for $B_n^-+O_2 \rightarrow B_nO_2^-$ for $n > 22$. The lowest energy structure found during this study for the interaction of $B_{13}^-+O_2$ is $^1[B_{13}O_2]^-$ shown in Figs. 1 and 5 (ΔE=7.64 eV). Compared to additive pathways for the cationic and neutral species, and with a binding energy of 5.0 eV per boron atom for the anion, addition versus etching becomes more of a possibility, although it may not be a prominent channel for clusters as small as the B_{13} anion. The favorability for the dominance of an additive pathway in boron anions (B_n^-) likely experiences a transition as n increases from 13 to 22 atoms. As in the examples shown for the cationic and neutral species reactions, the interaction of the anion with molecular oxygen shows evidence
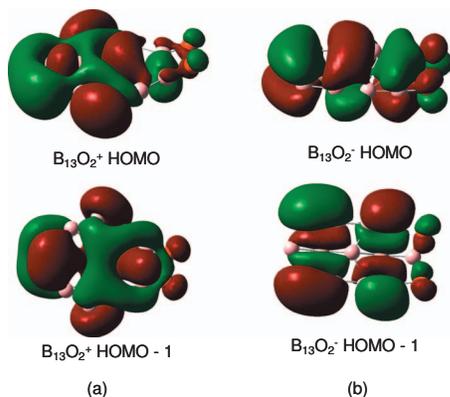
FIG. 6. Frontier molecular orbitals of (a) B$_{13}$O$_2^+$ and (b) B$_{13}$O$_2^-$.

for being site-specific, with the bonding between oxygen and boron atoms dependent upon the geometry of approach.

The unusually high stability of the B$_{12}$ cluster[24] (explainable from electron counting rules that are analogous to a "triple aromaticity" for this cluster) also suggests that the channels B$_{13}^-$+O$_2$→B$_{12}$+BO$_2^-$ and B$_{13}^-$+O$_2$→B$_{11}$+BO+BO$^-$ may play a roll in species production. Figure 5(b) shows the relevant energetics for these channels. As in the production channel for the B$_{12}^-$ cluster, the channel B$_{13}^-$+O$_2$→B$_{12}$+BO$_2^-$ is energetically favorable with a large amount of energy ($\Delta E = 5.0$ eV) to be carried away by the products. The channel B$_{13}^-$+O$_2$→B$_{11}$+BO+BO$^-$ is also similar in energy considerations to the production of B$_{11}^-$ ($\Delta E = 0.26$ eV) dissipating almost all available energy in the formation of the products of the reaction.

IV. SUMMARY

Using electronic structure calculations based on density functional theory to examine the reactivity of neutral and ionic B$_{13}$ clusters with O$_2$ and equilibrium structures of the reaction products obtained from different starting geometries reveal several important features. Stable isomers not detected in experiments to date are possible channels for this reaction, most notably weakly bound chemisorption isomers resulting in B$_{13}$O$_2$ structures. The reaction is strongly geometry dependent with the path of approach leading to cases of site-specific bonding. In ionic B$_{13}$ clusters, considerations of spin conversion are important for ultimately determining which energetically accessible channels are the most favorable for production. In this regard, the reactivity of boron clusters with a triplet oxygen molecule is spin influenced similar to the earlier reactivity studies on the clusters of silicon[17] and aluminum.[27,28] Most notably, the sequential ionization of boron cluster has a noticeable effect on the reaction. The sequential addition of an electron to boron cluster produces a more uniform nature between the central atoms and those on the outer ring of the cluster, changing the nature of the product [B$_{13}$O$_2$]$^{(+/0/-)}$ isomer species, and ultimately the favorable reaction channels.

[1] J. Smolanoff, M. Sowa-Resat, A. Lapicki, L. Hanley, S. Ruatta, P. Hintz, and S. L. Anderson, Combust. Flame **105**, 68 (1996).
[2] H. Tang and S. Ismail-Geigi, Phys. Rev. Lett. **99**, 115501 (2007).
[3] M. H. Evans, J. D. Joannopoulos, and S. T. Pantelides, Phys. Rev. B **72**, 045434 (2005).
[4] E. Fakioglu, Y. Yurum, and T. N. Veziroglu, Int. J. Hydrogen Energy **29**, 1371 (2004).
[5] Z. J. Leśnikowski, E. Paradowska, A. B. Olejniczak, M. Studzinska, P. Seekamp, U. Schußler, D. Gabel, R. F. Schinazi, and J. Plesek, Bioorg. Med. Chem. **13**, 4168 (2005).
[6] A. N. Alexandrova, A. I. Boldyrev, H.-J. Zhai, and L. S. Wang, Coord. Chem. Rev. **250**, 2811 (2006).
[7] L. Hanley and S. L. Anderson, J. Phys. Chem. **91**, 5161 (1987).
[8] L. Hanley, J. L. Whitten, and S. L. Anderson, J. Phys. Chem. **92**, 5803 (1988).
[9] L. Hanley and S. L. Anderson, J. Chem. Phys. **89**, 2848 (1988).
[10] P. A. Hintz, S. A. Ruatta, and S. L. Anderson, J. Chem. Phys. **92**, 292 (1990).
[11] S. A. Ruatta, P. A. Hintz, and S. L. Anderson, J. Chem. Phys. **94**, 2833 (1991).
[12] P. A. Hintz, M. B. Sowa, S. A. Ruatta, and S. L. Anderson, J. Chem. Phys. **94**, 6446 (1991).
[13] D. E. Bergeron and A. W. Castleman, Jr., Int. J. Mass Spectrom. **230**, 71 (2003).
[14] W. L. Hase, K. Song, and M. S. Gordon, Comput. Sci. Eng. **5**, 36 (2003).
[15] D. Y. Zubarev and A. I. Boldyrev, J. Comput. Chem. **28**, 251 (2007).
[16] H. Schwarz, Int. J. Mass Spectrom. **237**, 75 (2004).
[17] S. F. Li and X. G. Gong, J. Chem. Phys. **122**, 174311 (2005).
[18] M. J. Frisch, G. W. Trucks, H. B. Schlegel et al., GAUSSIAN 03, Revision C.02, Gaussian, Inc., Wallingford CT, 2004.
[19] A. Ricca and C. W. Bauschlicher, Chem. Phys. **208**, 233 (1996).
[20] F. L. Gu, X. Yang, A. Ang, H. Jiao, P. Von, and R. Schleyer, J. Comput. Chem. **19**, 203 (1998).
[21] J. E. Fowler and J. M. Ugalde, J. Phys. Chem. A **104**, 397 (2000).
[22] J. Aihara, J. Phys. Chem. A **105**, 5486 (2001).
[23] J. Aihara, H. Kanno, and T. Ishida, J. Am. Chem. Soc. **127**, 13324 (2005).
[24] B. Kiran, G. G. Kumar, M. T. Nguyen, A. K. Kandalam, and P. Jena, Inorg. Chem. **48**, 9965 (2009).
[25] Handbook of Chemistry and Physics, 51st ed. (The Chemical Rubber Co., U.S.A., 1970).
[26] H. Zhai, B. Kiran, J. Li, and L. Wang, Nature Mater. **2**, 827 (2003).
[27] R. Burgert, H. Schnockel, A. Grubusic, X. Li, S. T. Stokes, K. H. Bowen, G. F. Gantefor, B. Kiran, and P. Jena, Science **319**, 438 (2008).
[28] A. C. Reber, S. N. Khanna, P. J. Roach, W. H. Woodward, and A. W. Castleman, J. Am. Chem. Soc. **129**, 16098 (2007).