

## Adsorption of monatomic hydrogen in icosahedral borides

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(Received 3 June 1991)

We have investigated adsorption of a single H atom onto a charge-neutral  $B_{12}H_{12}$  cluster, which simulates one of the subunits of an icosahedral boride. Five different paths of approach are considered for the H atom. At the level of fourth-order Moller-Plesset perturbation theory, only one of these paths leads to an equilibrium position in which the adsorption energy is positive. Although H can pass inside the icosahedral  $B_{12}$  cage, the most stable position is outside the cage, corresponding approximately to the position for which electronic charge transfer to the  $B_{12}$  cage is a maximum. A comparison is carried out between the charge densities and one-electron energy levels of the cluster in the absence and presence of the adsorbate.

### INTRODUCTION

The properties of the element boron make it of technological, as well as scientific, interest. In its bonding flexibility it is competitive with carbon, as demonstrated by the variety of lattice structures assumed by boron-based compounds.<sup>1</sup> There is an equally impressive range in the electronic properties associated with these compounds: from wide-gap semiconductors<sup>2</sup> to bipolaronic semiconductors,<sup>3</sup> narrow-gap semiconductors,<sup>4</sup> and metals.<sup>5</sup> As element number 5 in the Periodic Table, boron is very lightweight; many of the compounds are refractory as well [pure  $\beta$ -B, for example, has a melting temperature of  $\sim 2300$  K (Ref. 1)]. For all these reasons, boron-based compounds are increasingly being studied as high-temperature electronic materials.<sup>6</sup>

Despite this interest, the number of fundamental studies of boron and the borides is relatively small, although growing. Adsorption on B clusters or substrates is relatively unexplored from either the theoretical or experimental point of view,<sup>7-9</sup> in spite of the fact that the topic is of importance in, for instance, the deposition of boride films.<sup>10</sup> (Sykja and Lunell<sup>8</sup> have considered molecular  $H_2$  adsorption on a  $B_6$  half-icosahedron intended to simulate a boron surface; as there were no tie-off atoms, the resulting dangling bonds led to a situation quite different from the one considered here.) In addition, the very "open" lattice structures of many of the boron compounds (e.g., the icosahedral boron carbides, phosphides, and arsenides) can be expected to lead to uptake of interstitial atoms adsorbed at various sites within the lattice.<sup>11</sup> Efforts to make semiconducting devices based on doped borides<sup>12</sup> will obviously require knowledge of the positions of interstitials and their associated charge transfers.

Therefore, we have begun a series of studies of adsorption on clusters modeling the basic icosahedral subunit of several of the borides of interest (for instance,  $\alpha$ -B,  $\beta$ -B,  $B_{12}P_{12}$ ,  $B_{12}As_{12}$ , as the boron carbides). This is a model applicable to either adsorption at a boride surface or to the problem of interstitials. The present paper describes a series of such calculations for a single hydrogen atom and an icosahedral  $B_{12}$  unit with neutral "tie-off" atoms;

in future work we will consider other adsorbates, including diatomic molecular species.

### THEORY AND MODEL

Our basic model for the icosahedral unit is similar to that used in several recent papers dealing with bipolaron formation in the boron carbides.<sup>13</sup> The unique lattice structure of these and similar borides is based on a network of interconnected  $B_{12}$  units; while in elemental  $\alpha$ -B these units are directly linked to each other by means of two-center and three-center bonds, in the borides they are linked by two- or three-atom chains as well as two-center bonds.<sup>14</sup> The  $B_{12}$  unit is not quite a regular icosahedron, but is distorted slightly to  $D_{3d}$  symmetry; each B atom in the unit is bonded to an atom outside the unit.

The cluster model chosen for the present calculations consists of the basic  $B_{12}$  unit plus 12 "tie-off" atoms (taken to be hydrogenic) which are radially bonded to the B atoms in the unit and serve to represent the bonds to external atoms that would be present in the crystal (Fig. 1). Thus the possibility of dangling bonds, which would affect adsorption, is eliminated. The geometry of the  $B_{12}$  unit was taken from x-ray data on  $\alpha$ -B by Morosin *et al.*,<sup>14</sup> because of the distortion to  $D_{3d}$  symmetry, there are two inequivalent sets of six atoms each in the unit. Atoms in the polar triangles of the icosahedron are commonly referred to as B(2) atoms, while the remaining "equatorial" six are B(1) atoms. The B(1)-B(1) distance was taken to be 1.782 Å, the B(2)-B(2) distance 1.751 Å, and the B(1)-B(2) distance 1.803 Å. The distance from a B atom to its radially bonded hydrogenic tie-off atom was determined not from the crystal x-ray data, but from the criterion of charge neutrality. In the  $\alpha$ -B crystal, each  $B_{12}$  unit is equivalent and therefore neutral; but in a cluster model, hydrogenic tie-off atoms placed at the equilibrium B-H distance (about 1.2 Å) will tend to donate charge to the  $B_{12}$  unit, which is electron deficient. To minimize the charge transfer, we have increased the B-H distance to 2.62 Å; at this distance, the total charge on the 12 H atoms is  $0.10|e|$ .

The adsorbate H atom was allowed to approach the

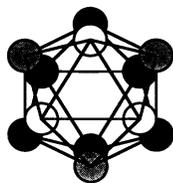


FIG. 1. The basic structure of the  $B_{12}$  cluster considered. The hydrogenic tie-off atoms are omitted for clarity. The view is along the threefold symmetry axis of the cluster, an icosahedron slightly distorted to  $D_{3d}$  symmetry.

$B_{12}H_{12}$  cluster along five distinct paths. Each path started at the center of the  $B_{12}$  cage, approached the cage along a line that was perpendicular to either one of the triangular faces of the cage or one of the edges, and extended in the same radial direction beyond the cage. The five paths considered were (a) through a B(2)-B(2)-B(2) face, (b) through a B(2)-B(1)-B(1) face, (c) through a B(2)-B(2) edge, (d) through a B(1)-B(1) edge, and (e) through a B(1)-B(2) edge.

At a number of points (at least five) along each path, an unrestricted Hartree-Fock (UHF) calculation was carried out on the  $(B_{12}H_{12}+H)$  cluster. When the total-energy minimum along each path was located, a second set of calculations, including correlation to the second-order (MP2), third-order (MP3), and fourth-order (MP4) Moller-Plesset level,<sup>15</sup> was carried out at that point. (A similar approach has been used<sup>16</sup> in studying chemisorption of H and O on Li clusters.) Results of these calculations, including total energies, charge densities, and one-electron energy levels, are discussed in the next section.

The GAUSSIAN 88 program package<sup>17</sup> was used to carry out all the calculations on a Cray Y-MP; the GAMESS package<sup>18</sup> was used to generate the charge densities used in plotting. The basis set chosen was 3-21G.<sup>19</sup> In this basis, the inner-shell atomic basis functions (here, the 1s) are represented by three Gaussians; the total set of valence basis functions (here, the 2s and 2p atomic orbitals) is divided into inner- and outer-shell functions. The former is represented by two Gaussians; the latter by a single Gaussian. Use of a more extensive basis set was prohibited by the size of the cluster; in particular, the amount of CPU time necessary for MP-level calculations is such that use of a larger basis would be impossible due to CPU-time limitations.

## RESULTS

In Fig. 2, we show total cluster energy (at the UHF level) versus adsorbate distance from the center of the icosahedron for each of the paths (a)-(e) listed above. Several general features are apparent: the center of the icosahedral cage is neither a minimum nor a saddle point in the energy; there is, however, always a local minimum inside the cage, roughly half an angstrom from the cage center (the cage radius is  $\sim 1.7$  Å). The most stable adsorbed position along any path is always outside the icosahedral cage. Energies at the positions of the minima outside the cage were recalculated at the MP2, MP3, and MP4 levels; results for the most stable positions along

each path are presented in Table I in terms of the calculated adsorption energy,  $\Delta E_{ad}$ :

$$\Delta E_{ad} = [E(B_{12}H_{12}) + E(H) - E(B_{12}H_{12} + H)],$$

i.e., the difference in the energy of the adsorbate-cluster complex at infinite separation and at the stable adsorbed position. (Energies for H and  $B_{12}H_{12}$  were calculated using the 3-21G basis set at all the relevant levels of correlation.) At the UHF level, adsorption energies are negative for all but two of the minima; at the MP2 level, all the adsorption energies are negative, but at the MP4 level,  $\Delta E_{ad}$  becomes less negative for all paths, going positive for the minimum outside the B(1)-B(2) edge only. For this latter case, the adsorption energy is  $\sim 0.26$  eV.

Since path (e) contains the only minimum for which  $\Delta E_{ad}$  is positive, we will consider this path in greater detail. Table II lists the Mulliken charge (at the UHF level) on the hydrogen adsorbate as a function of adsorbate distance from the cage center along path (e). (The position of the stable minimum is near 2.5 Å from the center.) We would initially expect the adsorbate to transfer electronic charge to the cage, based on consideration of the known electronic structure of the icosahedral borane ( $B_{12}H_{12}^{2-}$ ) molecule:<sup>20</sup> there are known to be 13 intraicosahedral bonding orbitals involving B 2s-2p hybridized wave functions. Since there are 36 boron valence electrons in all in the neutral state, and 12 of these are involved in bonding to the hydrogen atoms, only 24 electrons are available for intraicosahedral bonding. Two additional electrons are therefore necessary to fill the bonding orbitals, and the borane is thus stable as a dianion. The neutral  $B_{12}H_{12}$  structure is therefore electron deficient. We see however that when the adsorbate H atom in our calculation is at, or very near, the center of the cage, charge is actually transferred to the adsorbate. As it approaches the inside "surface" of the cage, its charge goes positive as expected; there is a drop in the net (positive) charge as the B(1)-B(2) edge is crossed, and the positive charge subsequently reaches a maximum near the position of the stable minimum.

The charge transfers can be considered from another perspective using the charge-density plots of Fig. 3. Total charge density in a plane is plotted for  $B_{12}H_{12}$ , and for  $(B_{12}H_{12}+H)$  on path (e) at the position of the stable minimum, in the xy, xz, and yz planes. The planes are taken to pass through the center of the icosahedral cage, which is the origin; the B(2)-B(2)-B(2) faces are parallel to the xy plane. The orientation is such that the upper B(2)-B(2)-B(2) triangle "points" in the positive-y direction, the lower triangle in the negative-y direction. The adsorbate atom lies in the yz plane. Note that for  $B_{12}H_{12}$ , the electronic charge density is largely confined to the outside of the cage; there is, however, a significant "trapped" charge at the center of the cage. This is presumably the charge that is transferred to the adsorbate atom when it is near the cage center, and accounts for the net negative charge on the H in those positions. Charge density is sixfold symmetric, as expected, in the xy plane; although no atoms lie in this plane, they are symmetrically located above and below  $z=0$ . Sixfold

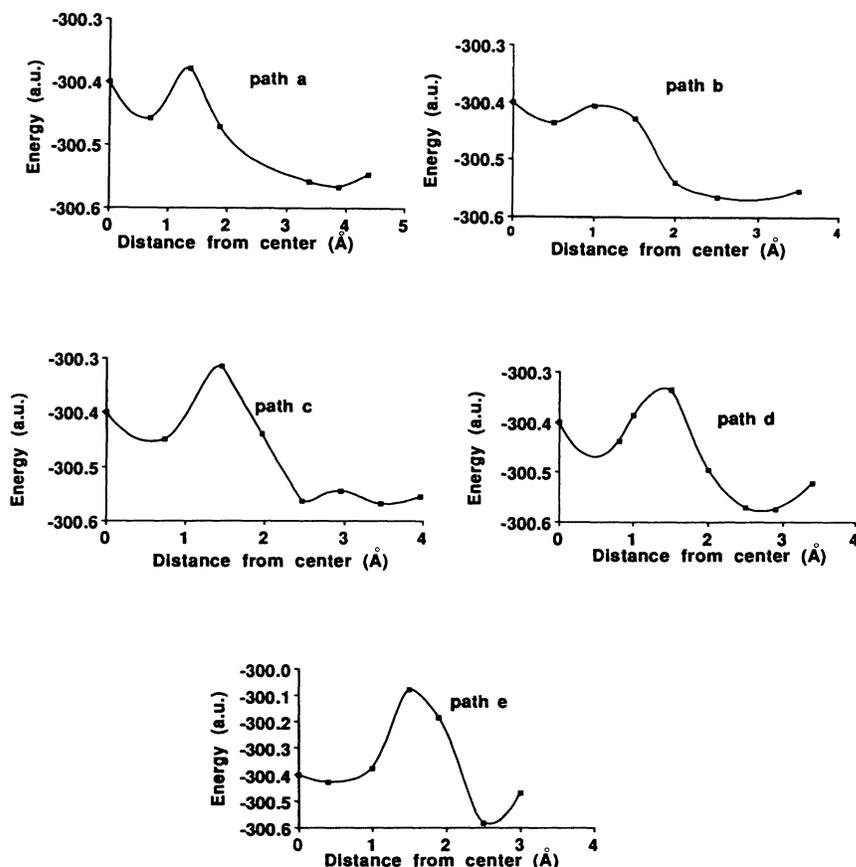


FIG. 2. Total energy, at the UHF level, for the  $(B_{12}H_{12}+H)$  cluster as a function of distance of the adsorbate H from the cluster center along the five paths (a)–(e) described in the text. Points denoted by a square are those at which the total-energy calculation was performed; a fit to these points resulted in the continuous curve.

symmetry is broken in the  $xz$  plane; the four external lobes of charge belong to four of the H atoms attached to B(2) atoms, two above and two below the plane. Again, no atoms lie exactly in the  $xz$  plane. However, two B(2) and two B(1) atoms, plus their tie-off hydrogens, lie in the  $yz$  plane; while the net Mulliken charges on the H tie-off hydrogens are all positive, the magnitude of the charge on the B(1)-attached H atoms is over an order of magnitude smaller. Thus these H atoms show up on the charge-density plot for the  $yz$  plane as two distinct regions of charge density external to the cage.

The charge density in the  $xy$  plane for the  $(B_{12}H_{12}+H)$  cluster retains, very nearly, its sixfold symmetry; addition of the adsorbate causes charge to be transferred outward to the tie-off atoms, although only four actually have a

net negative charge. In the  $xz$  plane, we see additional evidence that some of the cage charge has been displaced; in the  $yz$  plane, severe distortion of the charge density has taken place in the presence of the adsorbate, at the top of the plot. One important feature of all these plots is the delocalized nature of the electronic charge density over the  $B_{12}$  cage itself; while individual H atoms lying in a plane give rise to a distinct and identifiable charge density, B atoms in the cage are not distinguishable, even if they lie in the plane of the plot.

Finally, we consider the one-electron energy levels (generated from the UHF calculations) of  $B_{12}H_{12}$  versus  $(B_{12}H_{12}+H)$  for the most stable position along path (e). Figure 4 displays the spin-up and spin-down levels in the vicinity of the gap between highest-occupied and lowest-

TABLE I. Adsorption energies  $\Delta E_{ad}$  at the positions of the most stable minima for paths (a)–(e).

Path	Adsorbate distance from cage center (Å)	Adsorption Energy (a.u.)			
		UHF	MP2	MP3	MP4
a	3.9	-0.0131	-0.0534	-0.0285	-0.0307
b	2.5	-0.0118	-0.0304	-0.0083	-0.0107
c	3.5	-0.0130	-0.0261	-0.0055	-0.0071
d	2.9	+0.0007	-0.0227	-0.0001	-0.0033
e	2.5	+0.0057	-0.0109	+0.0134	+0.0095

unoccupied molecular orbitals (the HOMO-LUMO gap) for both clusters. The gap width for the spin-up levels is relatively unaffected by the presence of the adsorbate, going from 7.91 to 7.69 eV; the spin-down gap is more

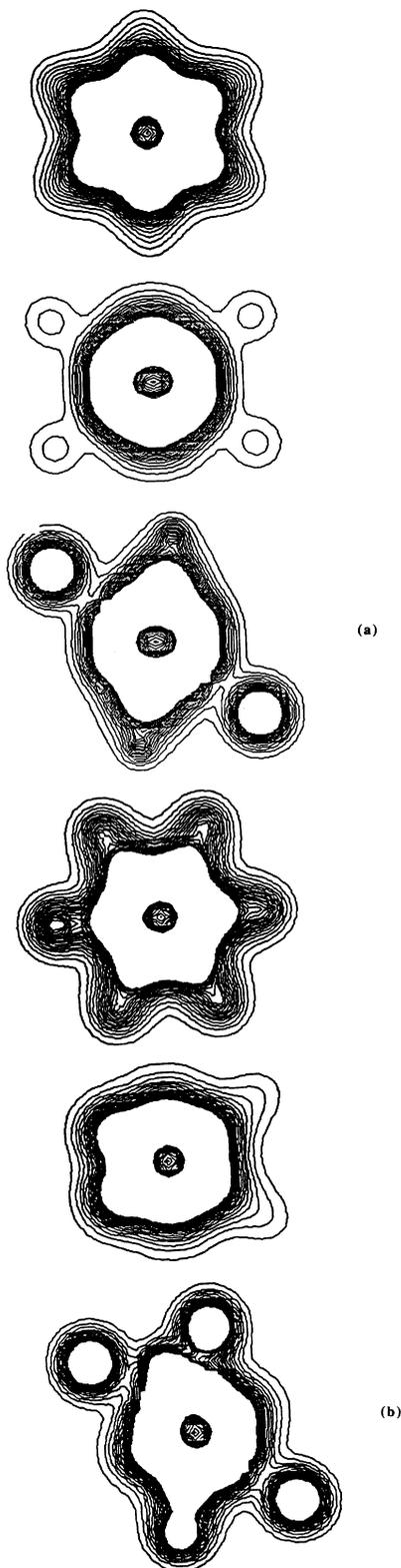


FIG. 3. Total charge densities, in the  $xy$ ,  $xz$ , and  $yz$  planes, for the  $B_{12}H_{12}$  cluster (a) and the  $(B_{12}H_{12} + H)$  cluster (b).

TABLE II. Adsorbate Mulliken charge as a function of distance for path (e).

Distance ( $\text{\AA}$ )	Charge on H (in units of electron charge)
0.0	-0.237
0.4	-0.158
1.0	+0.132
1.5	0.210
1.9	0.014
2.5	0.253
3.0	0.356
3.5	0.114
4.0	0.014

affected, going from 6.66 to 6.15 eV (the adsorbate electron goes into a spin-down level). However, no mid-gap level is introduced. The principal effect of the adsorbate is to break the  $D_{3d}$  symmetry of the  $B_{12}H_{12}$  cluster and therefore split the degeneracy of the one-electron levels (doubly degenerate levels are indicated by a single line in the case of  $B_{12}H_{12}$ ).

One point of comparison for our calculations is the previous consideration by Beckel and Howard<sup>9</sup> of the stable positions of a Mg atom relative to an icosahedral borane. The partial retention of diatomic differential

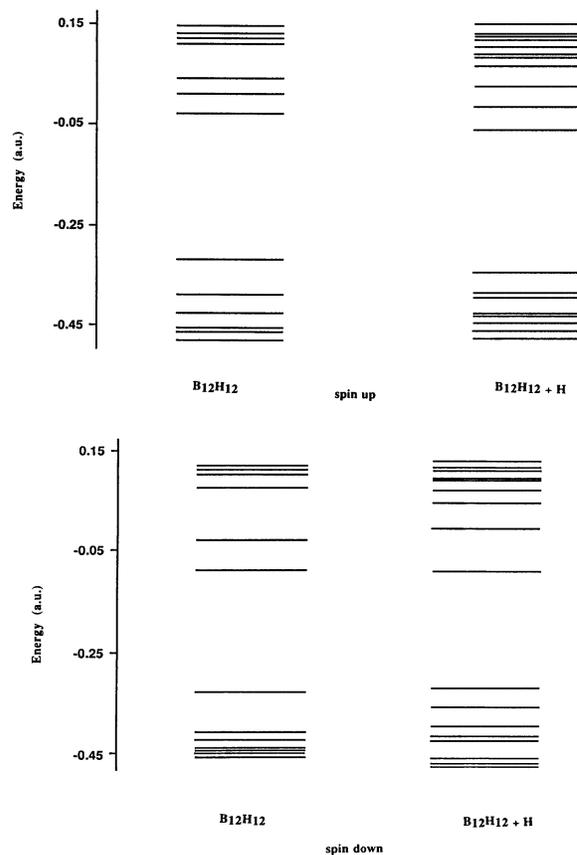


FIG. 4. Spin-up and spin-down one-electron energy levels near the HOMO-LUMO gap for  $B_{12}H_{12}$  and for  $(B_{12}H_{12} + H)$  with H at the most stable position along path (e).

overlap method,<sup>21</sup> which uses a minimum basis set of Slater-type orbitals on the B and H atoms, was employed. It was found that in this case, the cage center was a stable position for the adsorbate; there was also another local energy minimum outside the cage. The relative depth of the two minima depended on whether Mg 3*d* basis functions were included; in the presence of 3*d* functions, the deepest minimum appeared to be at the cage center. Although adsorption energies were not explicitly calculated, they appear, from the shape of the energy versus distance curve, to be positive for both minima. Since Mg is rather easily ionized to Mg<sup>2+</sup>, it can supply the two electrons the electron-deficient B<sub>12</sub> cage lacks; therefore the Mg + B<sub>12</sub>H<sub>12</sub> complex is probably more stable, in general, than the H + B<sub>12</sub>H<sub>12</sub> complex.

The results of our calculations lead to several conclusions on the nature of hydrogen adsorption or interstitials in  $\alpha$ -B. At the levels of correlation included in this calculation, adsorption is energetically favored only for

an adsorbate position outside the cage and centered on a B(1)-B(2) bond. We note that since the trend in going from the MP2 to MP4 level is to make the adsorption energies less negative, it is possible that inclusion of higher-order correlation effects may result in positive adsorption energies at additional adsorbate positions. In addition, basis-set restriction tends to overestimate barrier heights; although use of a larger basis than 3-21G is prohibitive here due to CPU time requirements, it might reduce the barrier heights between the inside and outside of the cage.

#### ACKNOWLEDGMENTS

Partial support from the Welch Foundation, Houston, Texas (Grant No. Y-1092) is gratefully acknowledged. The authors also acknowledge computational support from the University of Texas Center for High Performance Computing.

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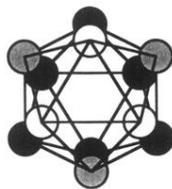


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