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Study of Hafnium Diboride Clusters Using Density Functional Theory

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Abstract

Using Density Functional Theory, the lowest energy equilibrium structure, vibrational spectra, and natural orbital analysis were obtained for Hafnium diboride clusters [$(HfB_2)_x$ for x = 1, 2, and 3]. For comparison, boron clusters [Bx for x = 2, 4, and 6] were also considered. TheHfB_2 and $(HfB_2)_2$ showed equilibrium structures with the boron atoms in arrangements similar to what was obtained for pure boron atoms, whereas, for $(HfB_2)_3$, a different arrangement of boron was obtained. From the NBO analysis, it is shown that larger electronic density in a specific plane increases the superconductivity behavior of this material, then it can be expected that these clusters should exhibit a similar super conducting behavior.

Keywords: Density Functional Theory, conducting behavior, electronic density

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INTRODUCTION

Materials composed of diborides have attracted the attention of researchers in recent years because of its superconductivity properties [1, 2]. In particular, it has been found that MgB2 behaves as a superconductor at relatively high critical temperature, Tc = 40 K. Although Tc for this material is not as high as other oxides with super conducting properties, its preparation is less expensive and it has a lower anisotropy, making smoother grain boundaries and hence increasing current flow [3]. Non-oxide ceramics, such as carbides, nitrides and borides represent one of the fastest growing classes of new advanced materials to be considered and pursued by today’s industries. The economic and technological significance of using these ceramics to improve present material structures and designs is now well documented. Transition metals ceramic diborides, such as titanium, hafnium and zirconium diborides, are members of a family of materials with extremely high melting temperatures, high thermal and electrical conductivity, excellent thermal shock resistance, high hardness and chemical inertness. These compounds, also referred to as Ultra High Temperature Ceramics (UHTCs), constitute a class of promising materials for use in high performance applications, where high temperatures, high thermal fluxes, severe surface stresses are involved. These conditions are met in the design of sharp edges on re-entry vehicles, thermal insulations in combustion chambers, special inserts in advanced brakes, cutting tools and plasma arc electrodes [4]. The lowest energy equilibrium structure was obtained and corroborated with a harmonic vibrational analysis. Natural orbital analysis was performed in order to characterize the electron density of the system. Boron clusters were also considered for comparison purposes with the results obtained being in agreement with recent studies [5].

Computational Methods

The theoretical methods used in this study were based on ab-initio methods within the density functional theory [6] approximation using the three-parameter hybrid functional B3LYP/LANL2DZ [7,8] as the basis set. The standard LanL2DZ basis as effective core potential with no symmetry constraint is employed here. This basis set provides an effective way to solve two-electron integrals even in case of heavy elements. The previous calculations [9-12] revealed that LanL2DZ basis sets of the effective core potential theory were proven to be reliable for the geometries, stabilities, and electronic properties of Si_nTM (TM = transition metals) clusters.

For all systems, a full geometry optimization was performed and various initial geometries were used to guarantee the determination of the lowest energy equilibrium structure. Harmonic vibrational analysis was performed for each system not only to obtain the vibrational frequencies, but also to characterize the nature of the structure obtained in the potential energy surface (PES). All calculations were performed using the Gaussian 98 software package [13]. In order to analyze the charge distribution in the system, natural bond orbital (NBO) analysis was performed on the optimized wave function using the NBO program of the Gaussian 03 package. This analysis provides an improvement to the Mulliken population analysis usually used in the description of the charge distribution.

RESULTS AND DISCUSSION

The equilibrium bond lengths of all the optimized structures are presented in Table 1 and the structures are shown in Figures 1 and 2. Table 2 shows the harmonic vibrational spectrum of HfB2 and B2 and it can be observed that all frequencies obtained have a positive sign, which means that the global minimum was obtained.

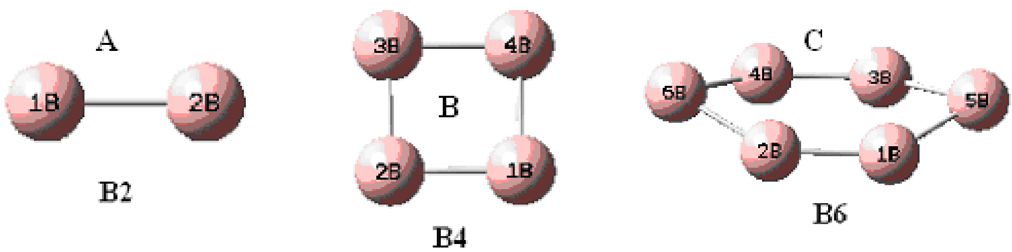

FIG-1 Optimized structures of Boron Clusters

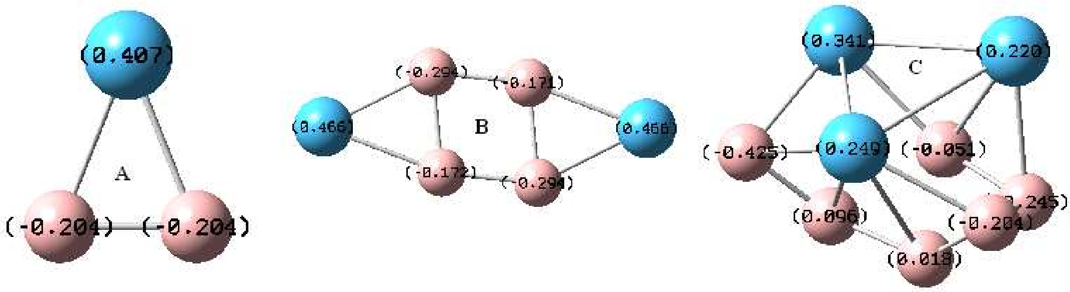

FIG-2 Optimized structures of Hafnium Diboride Clusters

Table-1: Optimized bond lengths in angstrom

HfB2	$(HfB_2)_2$	$(HfB_2)_3$	B2	B4	B6
R (1-2)=2.10	R (1-2)=1.67	R (1-2)=1.63	R (1-2)=1.68	R (1-2)= 1.56	R (1-2)=1.60
R (1-3)=2.10	R (1-3)=1.73	R (1-6)=1.73	-	R (1-4)= 1.56	R (1-5)=1.60
R (2-3)=1.55	R (1-5)=2.09	R (1-7)=2.26	-	R (2-3)= 1.56	R (2-6)=1.60
-	R (2-4)=1.73	R (2-3)=1.66	-	R (3-4)= 1.56	R (4-6)=1.60
-	R (2-6)=2.17	R (2-6)=1.68	-	-	R (3-4)=1.60
-	R (4-6)=2.09	R (2-9)=2.28	-	-	R (3-5)=1.60
-	R (3-4)=1.67	R (3-8)=2.19	-	-	-
-	R (3-5)=2.17	R (3-9)=2.36	-	-	-
-	-	R (4-5)=1.59		-	-
-	-	R (4-6)=1.64	-	-	-
-	-	R (4-7)=2.54	-	-	-
-	-	R (5-7)=2.31	-	-	-
-	-	R (5-8)=2.20	-	-	-
-	-	R (6-7)=2.42	-	-	-
-	-	R (7-8)=2.86	-	-	-
-	-	R (7-9)=2.88	-	-	-
-	-	R (8-9)=2.90	-	-	-

In the case of HfB2, the frequency that corresponds to the diboride stretching vibration, frequency, is 17% higher than in the B2 molecule because the bond shortening. Figures 1(B) and 2(B) show the lowest energy for equilibrium structure of $(HfB_2)_2$ and B4, respectively. Both structures show a planar arrangement of atoms, with the boron atoms in a two-dimensional unsymmetrical rhombic arrangement for $(HfB_2)_2$ and a perfect square for B4. Specifically, two of the boron-boron bonds in $(HfB_2)_{2,}$ the molecular species do not change and the other two were stretched by 0.06 A^o. The Hafnium atoms were accommodated at a relatively long distance when compared to the separation of the boron atoms. The vibrational frequency analysis shown in Table 2 demonstrates that the structure is a minimum in the PES. A direct comparison between the modes in the molecular species and the pure boron clusters was not possible. Figure 2(B) shows the NBO density analysis for the dimer and it can be observed that all the boron atoms forming the 2D rhombic arrangement have a negative charge. The boron atoms, which are closer to the Hf atoms, showed larger value of electron density than the other atoms, which has the Hafnium at a larger distance. Hence, the electron density is being concentrated on the boron atoms in a nonsymmetrical fashion and is being donated by the Hf atoms. Figures 1(C) and 2(C) show the lowest energy equilibrium structure of B6 and $(HfB_2)_3$. Boron atoms form a nonsymmetrical nonplanar arrangement. Although the B6 do not show a planar structure, the arrangement of atoms is different to the one obtained in the molecular species. The vibrational analysis shows all positive frequencies and similar to the previous system, it is not possible to correlate the frequencies between the B6 and the molecular system. The NBO analysis for the molecular systems shows a similar electronic distribution to the one observed for the dimer, namely, the electronic distribution is located on the boron atoms. Two of the boron atoms show a larger electronic distribution (-0.425) because of their closeness to the Hafnium atoms.

Table-2: Vibrational frequencies of stable structures

HfB2	**$(HfB_2)_2$**	**$(HfB_2)_3$**	**B2**	**B4**	**B6**
585	91	95	913	234	123
626	119	126	-	320	134
1103	171	147	-	1015	336
-	174	187	-	1162	431
-	222	202	-	1182	475
-	382	231	-	1212	489
-	549	287	-	-	663
-	555	342	-	-	802
-	812	380	-	-	1009
-	842	417	-	-	1019
-	1032	435	-	-	1304
-	1036	467	-	-	1353
-	-	500	-	-	-
-	-	526	-	-	-
-	-	559	-	-	-
-	-	607	-	-	-
-	-	714	-	-	-
-	-	825	-	-	-
-	-	979	-	-	-
-	-	1014	-	-	-
-	-	1141	-	-	-

CONCLUSION

In all cases considered, the lowest energy equilibrium structure for HfB2 clusters showed an arrangement of boron atoms that are two-dimensional or quasi-two dimensional. The electron densities concentrated on the boron atoms and hence the hafnium atoms are acting as electronic donating species. The larger electronic density in a specific plane increases the superconductivity behavior of this material, then it can be expected that these clusters should exhibit a similar super conducting behavior.

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