The vibrational stability and electronic structure of B$_{80}$ fullerene-like cage

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(Dated: March 20, 2008)

We investigate the vibrational stability and the electronic structure of the proposed icosahedral fullerene-like cage structure of B$_{80}$ [Szwacki, Sadrzadeh, and Yakobson, Phys. Rev. Lett. 98, 166804 (2007)] by an all electron density functional theory using polarized Gaussian basis functions containing 41 basis functions per atom. The vibrational analysis of B$_{80}$ indicates that the icosahedral structure is vibrationally unstable with 7 imaginary frequencies. The equilibrium structure has $T_h$ symmetry and a smaller gap of 0.96 eV between the highest occupied and lowest unoccupied molecular orbital energy levels compared to the icosahedral structure. The static dipole polarizability of B$_{80}$ cage is 149 Å$^3$ and the first ionization energy is 6.4 eV. The B$_{80}$ cage has rather large electron affinity of 3 eV making it useful candidate as electron acceptor if it is synthesized. The infra-red and Raman spectra of the highly symmetric structure are characterized by a few absorption peaks.

PACS numbers:
Keywords:

Since the discovery of C$_{60}$, several studies have reported possible existence of hollow inorganic cage-like structures. Recent work by Szwacki et al. added boron to the list of elements that can form fullerene-like hollow cage structure. While several studies have reported stable clusters, rings, and nanotubes of boron, a hollow fullerene-like cage cluster containing only boron has not yet been found. Using density functional theory Szwacki et al. showed that a boron cluster containing 80 atoms can form a stable hollow cage. The basic structure of this cluster is similar to that of C$_{60}$ with 12 pentagonal and 20 hexagonal rings. The B$_{80}$ cluster has an additional boron atom at the center of each hexagon. It is known that the boron analogue of C$_{60}$ is not a stable structure. However, these additional 20 boron atoms at the centers of the hexagonal rings stabilize the B$_{80}$ to form a stable B$_{80}$ fullerene with a binding energy of 5.77 eV per atom. The structure of B$_{80}$ cluster has been suggested by Szwacki et al. to maintain the same icosahedral point group symmetry as in C$_{60}$ fullerene. They also predicted that the icosahedral B$_{80}$, as in the case of C$_{60}$, has the lowest unoccupied molecular orbital (LUMO) of t$_{1u}$ symmetry. However they find that the highest molecular orbital (HOMO) however belongs to the t$_{2u}$ irreducible representation.

The purpose of the present article is to further investigate the electronic structure of this novel boron cluster, focusing particularly on its response to applied electric field. To this end, we calculate the dipole polarizability of the B$_{80}$ cluster using the linear combination of atomic orbital approach within the density functional formalism. In addition to the dipole polarizability we also compute the first ionization energies and the electron affinity. We also provide the infra-red and Raman spectra for possible detection. We use large polarized Gaussian basis sets to express the Kohn-Sham molecular orbitals. The exchange-correlation effects are treated within the generalized gradient approximation using the Perdew-Burke-Ernzerhof parametrization. We have first optimized the structure of B$_{80}$ using the icosahedral point group by the NRLMOL code. The resultant electronic structure shows some discrepancy with respect to the previous study by Szwacki. The HOMO level is 5 fold degenerate and belongs to the h$_{1u}$ irreducible representation instead of t$_{2u}$ as reported earlier. Besides, this small discrepancy, the present calculation also revealed that a more stable B$_{80}$ cluster has symmetry lower than the icosahedral symmetry as reported by Szwacki et al. To verify if this lower symmetry structure is due to symmetry breaking distortion of icosahedral cage, full vibrational frequency calculations were performed within the harmonic approximation. These calculations show that the icosahedral B$_{80}$ cluster is vibrationally unstable with...
two sets of imaginary frequencies. One of the two sets of modes is four fold degenerate and the the other one is a three fold degenerate mode. The vibrational motions of atoms in these two modes are depicted in Fig. 2. These modes are the out of plane motion of the boron atoms capping hexagons.

Full symmetry unconstrained relaxation of $B_{80}$ cluster show that the cluster has $T_h$ symmetry. The $T_h$ cluster is vibrationally stable. The $T_h$ $B_{80}$ cluster has five inequivalent atoms whose positions in Bohr are (0.0000, 7.9117, 1.6024), (4.3303, 4.3303, 4.3303), (2.6304, 6.8420, 3.2061), (5.1888, -5.8587, -1.6209), and (0.0000, 2.5903, 6.6176). The position of all atoms in $B_{80}$ cluster can be obtained using the position of the nonequivalent atoms and using the symmetry operations of $T_h$. The 4 three fold symmetry axes are along the 111 directions.

The energy of $T_h$ structure is lower by 0.05 eV compared to the icosahedral structure. Its electronic structure is 7a_u, 12a_g, 22e_g, 22t_v, 27t_u, 12e_u. The $h_u$ symmetry level of the HOMO of the icosahedral structure is split into a three-fold degenerate $t_u$ and a two fold degenerate $e_u$ level in the $T_h$ structure. The splitting also reduces the HOMO-LUMO gap in the $T_h$ structure. The HOMO is two fold degenerate and belongs to $e_u$ irreducible representation. The LUMO is three fold degenerate to $t_u$ type. The HOMO and LUMO orbital densities are shown in Fig. 3.

The static dipole polarizability is an important physical property that characterizes the system’s response to an applied static electric field to the first order. A number of methods have been developed to compute the dipole and higher polarizabilities. In this work, we use the finite-field method. In the finite-field method the total energies and/or dipole moments are computed self-consistently for various values of the applied electric field [13, 16, 17, 18, 19, 20]. The polarizability tensor is then built from well converged total energies or dipole moments using the finite-difference approximation. An accurate estimate of the polarizability using the linear combination of atomic orbitals requires the use of a large basis set supplemented with diffuse functions. The Gaussian basis set used in this work consists of 5 s-, 4 p-, and 3 d- type Gaussians each contracted from 12 primitive functions. This basis is augmented with 6 d- type functions. Thus, in total 3280 basis functions are used in polarizability calculation. More details about construction and the performance of basis set can be found in Ref. 11, 21, 22. Due to the quasi spherical symmetry of $B_{80}$ cluster, the off-diagonal elements of the polarizability tensor are zero. The mean polarizability obtained by finite-field method is 149 Å³. The mean polarizability of $C_{60}$ fullerene determined using the same set of approximations is 82 Å³. The larger polarizability of $B_{80}$ cluster is principally due to its larger volume. Using classical electrostatics, the polarizability of a spherical shell of radius $R$ can be shown to be $R^3$. Unlike the $C_{60}$ fullerene which in all atoms are at same distance from its center of mass, the atoms in $B_{80}$ cluster are at slightly different distances (3.74-4.27 Å) from the center of $B_{80}$ cluster. Using the radius of the outermost atoms, the volume of $B_{80}$ cluster can be estimated to be roughly 1.74 times that of the $C_{60}$ fullerene. Using 1.74 as a scaling factor, the polarizability of $C_{60}$ fullerene can be used to estimate polarizability of $B_{80}$ cluster. This rough estimate is 143Å³, in good agreement with the polarizability obtained by finite-field method. The finite-field (screened) polarizability does not change due to symmetry lowering of the $B_{80}$ cluster. The unscreened polarizability however show significant change upon symmetry lowering. It increases from 631Å³ to 897 Å³ due to the decrease in the HOMO-LUMO gap and due to changes in low-lying dipole allowed transitions. These transitions must be strongly screened to give identical values of polarizability for $I_h$ and $T_h$ clusters.

The calculation of the vibrational frequencies establishes the stability of the $T_h$ structure. The vibrational density of states of the $B_{80}$ cluster are shown in fig. 4. The bottom panel shows the density of states and the upper two panels show respectively the infrared and Raman activity of the $B_{80}$ cluster. The cluster shows a very strong infrared peak at 991 cm⁻¹. The other significant peaks occur at 446, 759, 771, 912, and 1012 cm⁻¹. The Raman spectrum shows a few low frequency modes with strong peaks at 112, 174, 176, and 312 cm⁻¹. Another prominent peak is seen at 963 cm⁻¹. The vibrational frequencies determined in analysis of the vibrational stability of $B_{80}$ cluster can be also be used to compute the vibrational contribution to the dipole polarizability. In general, the vibrational polarizability is the second largest contribution to the total polarizability tensor. For the case of ionic and hydrogen bonded systems, the vibrational contribution may be comparable to or even larger than the electronic contribution. The vibrational contribution to the polarizability tensor within
the double harmonic approximation [22] is given as
\[ \alpha_{i,j}^{\text{vib}} = \sum_{\mu} Z_{i,\mu} \omega_{\mu}^{-2} Z_{j,\mu}^T \]

Here, \( \omega_{\mu}^{-2} \) is the frequency of the \( \mu \)-th vibrational mode, \( Z_{i,\mu} \) is the effective charge tensor (See. Ref. [22] for more details). The vibrational contribution to polarizability is 5.5 Å² which is much smaller the electronic contribution but is larger than that observed in carbon fullerenes [22].

To understand the reactivity of the \( \text{B}_{80} \) cluster, we have calculated its ionization potential and the electron affinity. The first ionization energy is the minimum energy required to remove an electron. It can be determined from the self-consistent total energy difference of the \( \text{B}_{80} \) cluster and its singly charged cation [23]. The calculated ionization energy is 6.5 eV and is smaller than that of \( \text{C}_{60} \) (7.6 eV). Similarly, the electron affinity can be computed from self-consistent total energy difference of neutral cluster and its anion. The calculated electron affinity is 3 eV. Our calculations also indicated that the cluster reorganization upon addition of an electron is also small in this highly symmetric cluster. The chemical hardness is an indicator of the reactivity of the molecule. It can be approximated as half of the difference between the ionization potential and electron affinity [24]. This definition immediately points out that the \( \text{B}_{80} \) cluster is more reactive than the \( \text{C}_{60} \) fullerene. The rather large electron affinity makes \( \text{B}_{80} \) cluster, if synthesized, an interesting candidate as an electron receptor. The larger electron affinity also suggests possibility of coating these cluster with alkali or transition atoms, which then can be tested as hydrogen storage materials. Other possibilities are using it as a building block in ionic cluster assembled materials or as an electron receptor in a photovoltaic device.

To summarize, the vibrational stability of recently reported \( \text{B}_{80} \) cluster is examined by computing the harmonic vibrational frequencies. The \( \text{B}_{80} \) cluster is found to be unstable in icosahedral symmetry but stable in the reduced \( T_h \) symmetry. The electronic structure of \( \text{B}_{80} \) cluster changes upon symmetry lowering. The symmetry lowering decreases the HOMO-LUMO gap from 1.1 eV (in \( T_h \) structure) to 0.97 eV. Its static dipole polarizability (149 Å³) however does not alter appreciably. Its ionization potential is 6.5 eV. The \( T_h \) structure has large electron affinity of 3 eV making it a candidate as an electron receptor. Using the chemical hardness as an indicator of reactivity the \( \text{B}_{80} \) is found to be larger than the \( \text{C}_{60} \) fullerene. The infra-red and Raman spectra are provided.

This work is supported in part by the National Science Foundation through CREST grant, by the University of Texas at El Paso (UTEP startup funds, University research institute grant) and partly the Office of Naval Research, directly and through the Naval Research Laboratory. Authors acknowledge the computer time at the UTEP Cray acquired using ONR 05PR07548-00 grant.

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