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Vibrational stability and electronic structure of a B_{80} fullerene

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We investigate the vibrational stability and the electronic structure of the proposed icosahedral fullerenelike cage structure of B_{80} [N. G. Szwacki, A. Sadrzadeh, and B. I. 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 seven imaginary frequencies. The equilibrium structure has T_h symmetry and a *smaller* gap of 0.96 eV between the highest occupied and the lowest unoccupied molecular orbital energy levels compared to the icosahedral structure. The static dipole polarizability of a 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 a useful candidate as electron acceptor if it is synthesized. The infrared and Raman spectra of the highly symmetric structure are characterized by a few absorption peaks.

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I. INTRODUCTION

Since the discovery of C_{60}, numerous studies have shown possible existence of hollow inorganic cagelike structures.[1–11] Recent work by Szwacki *et al.*[12] added boron to the list of elements that can form fullerenelike hollow cage structure. Several studies have reported stable clusters, rings, and nanotubes of boron.[8,13–22] Small boron clusters containing less than 20 atoms tend to prefer planar or quasiplanar structures. The planar to three-dimensional structural transition in a boron cluster seems to occur at B_{20}.[23] The honeycomb sheet of boron, i.e., the graphene equivalent of boron, is found to be unstable. Boron prefers the buckled triangular planar sheet over the hexagonal honeycomb structure.[24] Recent density-functional calculations by Tang and Ismail-Beigi,[25] however, show that boron sheets made up of triangular and hexagonal motifs are more stable than both the honeycomb and buckled triangular sheet. These sheets can be thought of as triangular sheets doped with holes and are suggested to be precursors of boron nanotubes. The stability of these boron sheets is explained using the concept of three-center bonding. Previous studies on the formation and chemical bonding in boron nanotubes was reviewed by Quandt and Boustani.[21,26] The structural models of boron fullerenes was proposed earlier by Boustani.[27] The recent report of B_{80} fullerene by Szwacki *et al.*[12] shows that the B_{80} fullerene is 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 (cf. one). It is known that the boron analog of C_{60} is not a stable structure. However, these additional 20 boron atoms at the centers of the hexagonal rings stabilize the B_{60} to form a stable B_{80} fullerene with a binding energy of 5.77 eV per atom. The structure of a B_{80} cluster was suggested by Szwacki *et al.* to maintain the same icosahedral point group symmetry as in the 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 found that the highest occupied molecular orbital (HOMO) belongs to the t_{2u} irreducible representation.[12]

The purpose of the present article is to investigate various electronic structure related properties of this boron cluster within density-functional formalism by an all electron linear combination of atomic orbital method. We first show that the equilibrium structure of the B_{80} fullerene has T_h symmetry. We then study its response to applied static electric field and compare its chemical reactivity with that of the C_{60} fullerene using density-functional indicators of reactivity. Finally, the infrared and Raman spectra of B_{80} is provided for its possible detection.

II. COMPUTATIONAL DETAILS

Our calculations are performed using the NRLMOL suite of codes[28,29] in which the Kohn-Sham molecular orbitals are expressed as linear combination of Gaussians. The exchange-correlation effects are treated within the generalized gradient approximation using the Perdew-Burke-Ernzerhof[30] parametrization. We use a large polarized Gaussian basis set that is specifically optimized[31] for the Perdew-Burke-Ernzerhof[30] parametrization. The exchange-correlation contributions to the Hamiltonian matrix and energy are obtained using efficient optimal numerical grids.[28,29] The structural optimization is performed by the limited memory Broyden-Fletcher-Goldfarb-Shanno algorithm. The vibrational frequencies are obtained by diagonalizing the dynamical matrix built by finite difference approximation.

III. RESULTS

We have first optimized the structure of B_{80} (see Fig. 1) using the icosahedral point group by the NRLMOL code.[28,29] The resultant electronic structure shows some discrepancy

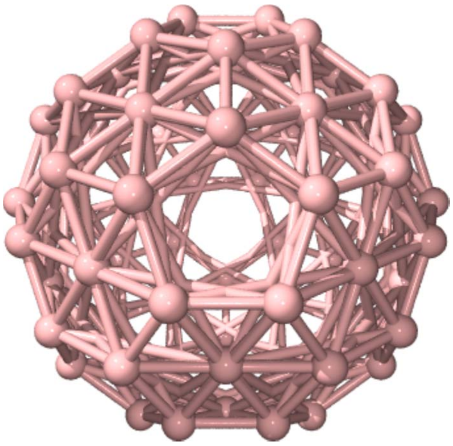

FIG. 1. (Color online) Optimized geometry of a B_{80} cage.

with respect to the previous study by Szwacki.[12] The HOMO level is fivefold degenerate and belongs to the h_u 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 the 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 fourfold degenerate and the other one is a threefold 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 unconstrained relaxation of B_{80} cluster shows that the cluster has T_h symmetry. This result is consistent with a recent study, which reports the T_h B_{80} cluster.[32] Our study shows that 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, 2.5093, 6.6176). The positions of all atoms in the B_{80} cluster can be obtained using the position of the nonequivalent atoms and using the symmetry operations of T_h. The four threefold symmetry axes are along the (111) directions.

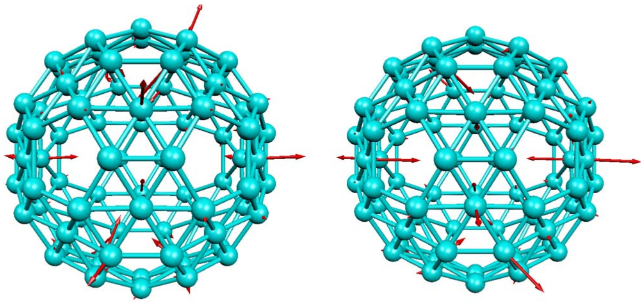

FIG. 2. (Color online) Unstable vibrational modes of an icosahedral B_{80} cage.

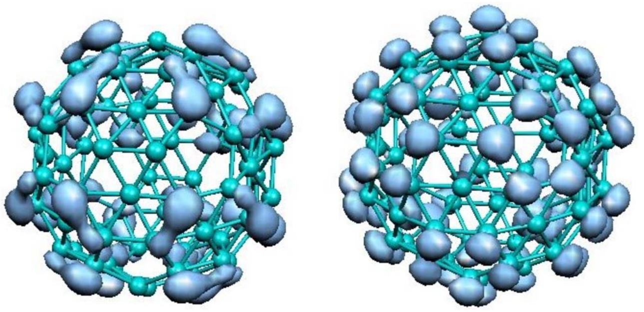

FIG. 3. (Color online) The orbital densities of the HOMO (left) and LUMO (right) of the B_{80} cluster.

The total energy of the T_h structure is lower by 0.05 eV compared to the icosahedral structure. Its electronic structure is $7a_u$, $12a_g$, $22e_g$, $22t_g$, $27t_u$, and $12e_u$. The h_u symmetry of the HOMO of the icosahedral structure is split into a threefold degenerate t_u and two degenerate e_u levels in the T_h structure. The splitting also reduces the HOMO-LUMO gap in the T_h structure from 1.1 to 0.96 eV. The doubly degenerate HOMO belongs to e_u irreducible representation. The threefold degenerate LUMO is of t_u symmetry. The HOMO and LUMO orbital densities are shown in Fig. 3. The HOMO density is mostly localized on the bonds shared by two hexagonal rings. The C_{60} fullerene can be built from the graphene sheet by introducing pentagonal rings. These pentagonal rings are defects that introduce curvature in the planar sheet, and 12 pentagons make the structure closed. The C_{60} is the smallest fullerene in which the pentagonal rings are isolated. In analogy with C_{60}, the structure of the B_{80} fullerene can also be thought to be derived from the triangular boron sheet. However, its structure is also compatible with the hole doped triangular sheet.[25] As in C_{60}, the 12 pentagonal rings in B_{80} are isolated. The bonding in B_{80} can also be explained using the three-center bonding.[25]

Apart from the structural similarity, both the B_{80} and C_{60} have 240 valence electrons. Thus, it is interesting to examine the similarity in their electronic properties. One such property is the static dipole polarizability, which characterizes systems 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.[33–37] 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 a linear combination of atomic orbitals requires 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 the polarizability calculation. More details about the construction and performance of the basis set can be found in Refs. 31, 38, and 39. Due to the quasispherical symmetry of the B_{80} cluster, the off-diagonal elements of the polarizability

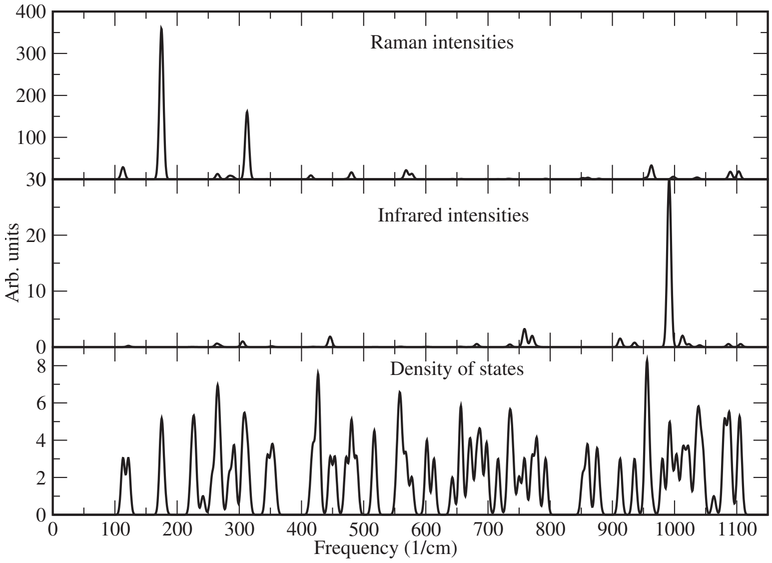

FIG. 4. The vibrational density of states, infrared absorption intensity and the Raman scattering intensities of the B_{80} cluster with T_h structure.

tensor are zero. The mean polarizability obtained by the finite-field method is 149 Å^3. The mean polarizability of C_{60} fullerene determined using the same set of approximations is 82 Å^3. The larger polarizability of the B_{80} cluster is principally due to its large 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 in which all atoms are at same distance from its center of mass, the atoms in the B_{80} cluster are at slightly different distances (3.74–4.27 Å) from the center of the B_{80} cluster. Using the radius of the outermost atoms, the volume of the 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 the C_{60} fullerene can be used to estimate the polarizability of the B_{80} cluster. This rough estimate is 143 Å^3, in good agreement with the polarizability obtained by the finite-field method. The finite-field (screened) polarizability does not change due to symmetry lowering of the B_{80} cluster. The unscreened polarizability, however, shows significant change upon symmetry lowering. It increases from 421 to 598 Å^3 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 is shown in Fig. 4. The bottom panel shows the density of states and the upper two panels show the infrared and Raman activity of the B_{80} cluster, respectively. 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 peak is seen at 963 cm^{-1}.

The vibrational frequencies determined in analysis of the vibrational stability of the B_{80} cluster can 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[40] is given as

$$\alpha_{i,j}^{\mathrm{vib}} = \sum_{\mu} Z_{i,\mu}\omega_{\mu}^{-2}Z_{j,\mu}^{T}.$$

Here, ω_{μ}^{-2} is the frequency of the μth vibrational mode and $Z_{i,\mu}$ is the effective charge tensor (see Ref. 40 for more details). The vibrational contribution to polarizability is 5.5 Å^3, which is much smaller than the electronic contribution but is larger than that observed in carbon fullerenes.[40]

To understand the reactivity of the 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 outermost electron. It can be determined from the self-consistent total energy difference of the B_{80} cluster and its singly charged cation.[41] The calculated ionization energy is 6.4 eV and is smaller than that of C_{60} (7.6 eV). Similarly, the electron affinity can be computed from self-consistent total energy difference of the neutral cluster and its anion. The calculated electron affinity is 3 eV. The reported electron affinity and ionization potential are vertical quantities, that is, they are determined at the fixed geometry of the neutral B_{80} cluster. The effect of the cluster reorganization upon addition of an electron is small in this highly symmetric cluster. The chemical hardness is an indicator of the reactivity of the molecule. In the density functional theory, the hardness is the second derivative of total energy (E) with respect to the number of electrons (N) at constant external potential. It can be approximated as half of the difference between the ionization potential and electron affinity. This definition immediately points out that the B_{80} cluster is more reactive than the C_{60} fullerene. The rather large electron affinity makes the B_{80} cluster, if synthesized, an interesting candidate as an electron receptor. The larger electron affinity also suggests the possibility of coating this 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 the recently reported B_{80} cluster is examined by computing the harmonic vibrational frequencies. The B_{80} cluster is found to be unstable in icosahedral symmetry but stable in the reduced T_h symmetry. The electronic structure of B_{80} cluster changes upon symmetry lowering. The symmetry lowering decreases the HOMO-LUMO gap from 1.1 (in I_h structure) to 0.96 eV. Its static dipole polarizability (149 Å^3), however, does not alter appreciably. Its ionization potential is 6.4 eV. The T_h structure has large electron affinity of 3 eV making it a candidate as an electron receptor. Using chemical hardness as an indicator of reactivity, B_{80} is found to be more reactive than the C_{60} fullerene. The infrared and Raman spectra are provided.

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