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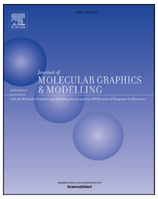

Boron fullerenes, B_n (n=20, 30, 38, 40, 50, 60): First principle calculations of electronic and optical properties

Siddheshwar Chopra*

Department of Physics, AIAS, Amity University, Noida, India

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Density functional theory (DFT) and time dependent density functional theory (TDDFT) at PBE0/6-311G* level are performed to examine the stability, electronic and optical properties of boron fullerenes (B_n, n = 20, 30, 38, 40, 50, 60). Amongst all the structures, B_{50} is found to be highly stable and has the least electronic gap. In general, all borofullerenes are found to be semiconducting in nature. Absorption wavelength shift in the photoabsorption spectra is reported with the increasing borofullerene size. Furthermore, the maximum absorption occurs within the visible range (for n = 30–50) characterized by deeper level excitations. Upon absorption, the electron delocalization is found to increase with the borofullerene, from natural transition orbital analysis (NTO) and exciton size analysis, respectively. Exciton size determination indicates a linear relationship between the number of borofullerene atoms and the exciton size. The excitons have been found to be Frenkel in nature.

1. Introduction

Fullerene research has been intensive since some time now, especially stimulated by the buckyball (C_{60}) which has a hollow cage structure [1,2]. Recently there are several research groups working on boron fullerenes, owing to their cage configurations possessing relatively high stability analogous to the carbon fullerenes. There are considerable computational [3,4] and experimental initiatives [5,6] for small boron clusters within 20 atoms range. These structures contain either pentagonal or hexagonal holes [7–9]. Considerable research interests in boron clusters are due to their potential applications as building blocks for nanomaterials and electro-optical nano devices [10–16]. Larger boron cluster B_{80} was theoretically predicted to form a fullerene-like structure [7,17] and its unusual stability was explained by the balance between three-center and two center bonds. Its applications include ozone sensing [16] and several others [18–21].

Several other studies demonstrated the stabilities of the theoretically predicted even membered boron clusters B_{32} [11], $B_{40/48}$ [10], $B_{30/36/40/42}$ [22]. Recently, the $B_{40}^{-/0}$ hollow cage boron fullerene with D2d symmetry was observed through a joint photoelectron spectroscopy and theoretical prediction [23]. Medium sized boron clusters (B_n, with n = 32, 48, 56, 64) with quadrangular holes in the 'snowdrop-like' fullerenes were reported by Su et al. [24]. Furthermore, an unusually stable B_{38} fullerene was reported through first principal calculations [25]. Mahdavifar et al. studied the stabilities of pristine and zinc doped B_n clusters (n = 20–60), and reported the B_{50} cluster to be most stable [26]. Other stability and electronic study of 32–56 atoms borofullerens was reported by Wang et al. [27] using first principles calculations. HOMO-LUMO gaps in this study were reported in the range 0.65–1.25eV. Titanium doped B_{40} fullerene was theoretically predicted to store up to 34 hydrogen molecules and was found to be a promising hydrogen storage material [28].

There have been very few reports on the optical absorption of boron fullerenes. The simulated absorption spectra of B_{40} fullerene were discussed by He et al. [29] and also for small sized B_n clusters (n = 12–36) by Koponen et al. [30]. Recently Li et al. studied the stabilities, photoelectron, infrared, Raman and electronic absorption spectra of B_{44}^{-} and metallo-borospherenes $MB_{44}^{0/-}$ (M = Li, Na, and K) using the density functional theory (DFT) and time-dependent density functional theory (TDDFT) calculations [31]. Our group has recently reported the study of electronic and optical properties of boron materials (pristine and metal doped boron nitride flakes) [32], and in another study we reported the in-depth analysis of the optical absorption spectra obtained in Ref. [32] including the natural transition orbital analysis and one particle transition density matrix based (1TDM) exciton size determination [33].

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* Corresponding author.
E-mail address: schopra1@amity.edu.

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In this study, it is planned to discuss the stabilities, electronic and optical properties of small to medium sized boron fullerenes, B_n (n = 20, 30, 38, 40, 50 and 60) using the first principles calculations. Primary focus will be on the study of optical absorption spectra based on the transition density matrix analysis in the light of natural transition orbital (NTO) and exciton size determination.

2. Methodology

Here, we present the density functional theory (DFT) and time dependent density functional theory (TDDFT) calculations performed in vacuum, on all-boron neutral clusters (B_n) of various sizes (n = 20, 30, 38,40,50 and 60). All the singlet ground state optimized configurations are shown in Fig. 1. DFT and TDDFT calculations were performed with the Firefly version 8.1.0, build number 8800 program code [34]. Self-consistent-field (SCF) all-electron electronic structure calculations are performed with unrestricted Kohn-Sham (UKS) level. The validity of UKS was checked by ensuring no spin contamination ($\langle S^2 \rangle = 0$) for all the structures. All structures were first relaxed using the conjugate gradient algorithm in Avogadro package [35]. Geometry optimizations were then performed with a 10^{-6} hartree convergence limit on the total energy.

The all-electron basis set 6-311G* and hybrid generalized gradient approximation (GGA) based Perdew-Burke-Ernzerhof (PBE0 or also called PBE1PBE) functional [36] is employed for the exchange correlation potential, for the geometry optimizations of all the structures and later for the study of absorption spectra, respectively. The validity of the basis set and functional used in the current study has been verified for boron clusters by several others [25,29]. The optimized ground state geometries were confirmed as global minima by checking for the absence of negative frequencies in the computed hessian. Furthermore, to obtain the vertical excitation energies, single point energy calculations were performed on the ground state optimized geometries of all the structures at the PBE0/6-311G* level of theory, for 20 lowest singlet excited states using TDDFT calculations under Tamm-Dancoff approximation. No symmetry constraints were imposed for both the DFT and TDDFT calculations. Afterwards, photo-absorption spectra were analyzed to determine the dominant molecular orbital transitions along with their oscillator strengths and absorption wavelengths, using the Gaussum 3.0 package [37]. Furthermore, the natural transition orbitals (NTO) and exciton sizes were calculated from the transition density matrix (obtained from TDDFT response vectors) using the recently developed post processing tool for the analysis of excited state wavefunctions, TheoDORE [38]. TheoDORE uses the cclib library for parsing data [37] and the Jmol package for plotting [39].

3. Results and discussion

3.1. Stability and electronic study

The ground state all-boron neutral clusters B_n (n = 20, 30, 38, 40, 50, 60) were optimized at PBE0/6-311G* level of theory. The boron fullerenes obtained in this study represent irregular cage structures (with triangle facets), which was also reported earlier by Wang et al. [27]. Such irregular cages (32–56 atoms) were concluded to be energetically more favorable than their symmetric counterparts [27]. It is worthy to calculate some chemical parameters of these borofullerenes. We calculate the first vertical ionization potential (IP), electron affinity (EA) electronic chemical potential (μ), electronegativity (χ), hardness (η), and electrophilicity index (ω); given by the following relations [40–42]:

$$IP \sim -E_H \quad (1)$$

$$EA \sim -E_L \quad (2)$$

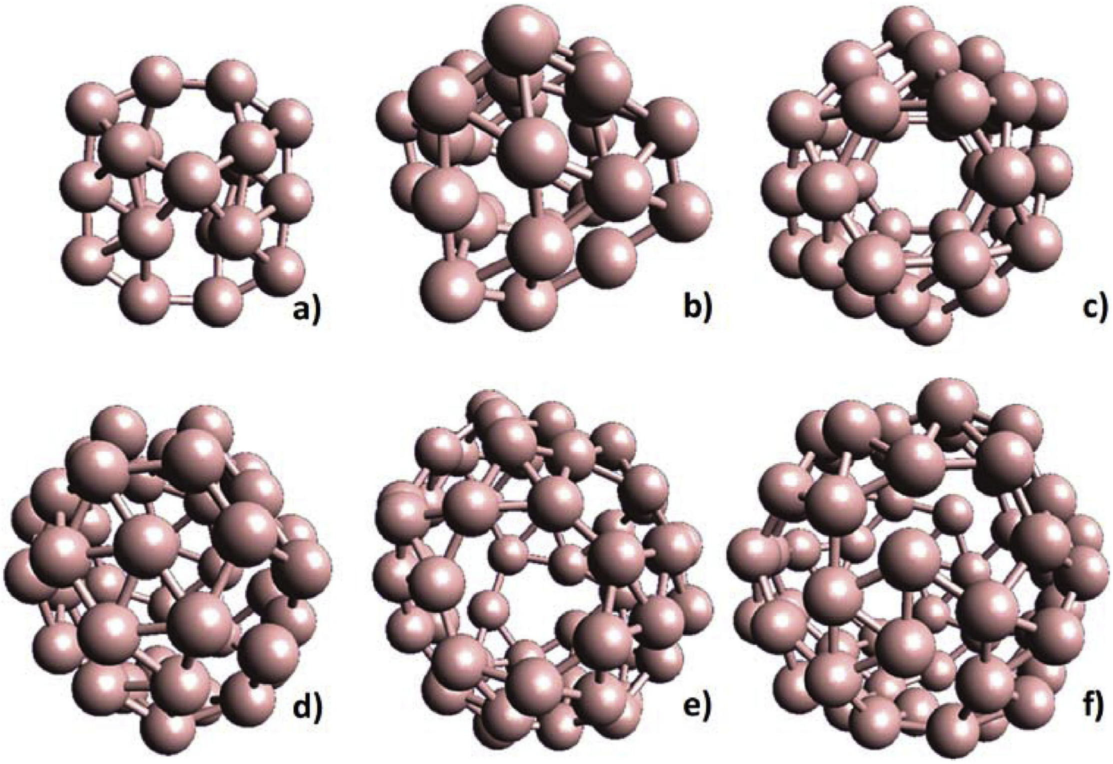

Fig. 1. Optimized ground state configurations (at PBE0/6-311G* level of theory) of the Borofullerenes: a) B_{20}, b) B_{30}, c) B_{38}, d) B_{40}, e) B_{50} and f) B_{60}.