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Research paper

Theoretical approach into potential possibility of efficient NO_2 detection via B_{40} and $Li@B_{40}$ fullerenes

Zeinab Maniei, Ehsan Shakerzadeh *, Zabiollah Mahdavifar

Chemistry Department, Faculty of Science, Shahid Chamran University of Ahvaz, Ahvaz, Iran

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ABSTRACT

The potential applicability of B_{40} and $Li@B_{40}$ fullerenes as chemical sensors for NO_2 pollutant detection is investigated by employing DFT calculations. The results indicate that NO_2 molecule is remarkably chemisorbed on the surface of both B_{40} and $Li@B_{40}$ fullerenes. It is found that electronic properties of B_{40} and $Li@B_{40}$ fullerenes change after NO_2 chemisorption. Although the highest occupied molecular orbital (HOMO)-lowest unoccupied molecular orbital (LUMO) energies gap (HLG) of B_{40} is considerably decreased after NO_2 chemisorption, the HLG of $Li@B_{40}$ are significantly enhanced after NO_2 adsorption. B_{40} and $Li@B_{40}$ fullerenes are introduced as novel promising chemical sensor for NO_2 pollutant.

1. Introduction

Nitrogen Dioxide (NO_2), which is released by the burning of fossil fuels, is extremely toxic gas [1,2]. The airways of the human respiratory system seriously hurt by NO_2 breathing. NO_2 exposures cause respiratory diseases such as lung cancer, coughing and wheezing [3,4]. NO_2 gas in the atmosphere can be the source of acid rain which is actually harmful for ecosystems and environment. Therefore, finding portable, highly sensitive, durable, and low cost NO_2 sensor is essential and valuable for scientist. There are several computational researches to develop chemical NO_2 sensor based on novel nanomaterials [5–10]. For example, Vessally and coworkers introduce a borazine doped nanographene as NO_2 sensor using DFT calculations [11]. Indeed, Chang et al. have explored the physisorption of NO_2 gas on the single-walled carbon nanotubes (CNTs) [12]. Dia et al. have shown that Al-doped graphene makes the electrical conductivity of the graphene more sensitive toward NO_2 gas [13]. Añez et al. investigated NO_2 adsorption on subsurface doped MgO (1 0 0) and BaO (1 0 0) surfaces through DFT calculations [14].

Boron materials have been attracted substantial attention due to their unique features and possible applications in material sciences, electronic industries and medicine [15–22]. Among boron materials, all-boron fullerenes are interesting structures because of their potential novel properties. Recently, Zhai et al. reported that the neutral B_{40} fullerene with D_{2d} symmetry is the most stable structure among the different B_{40} allotropes [23]. The simulated optical spectra of B_{40} fullerene with D_{2d} symmetry exhibit remarkable differences with other B_{40} isomers [24]. Recently, theoretical investigations are focused on the various properties and applications of B_{40} fullerene [25,26]. For instance, the structural stability of the encapsulated B_{40} via Li, Na, K, Ba, and Tl is examined using density functional theory (DFT) calculations [27]. Indeed, the efficient capture, storage and separation of CO_2 molecule via the B_{40} fullerene are theoretically investigated [28,29]. Also, ammonia adsorption and dissociation on B_{40} fullerene are investigated using density functional theory calculations and it is introduced as efficient NH_3 detectors [30]. Anota and coworkers have introduced the magnetic [BN fullerene:B_6 cluster]$^-$ nanocomposite as a promising vehicle for the delivery of dapsone [31]. The main purpose of the present quantum chemical research is to assess the ability of B_{40} fullerene to adsorb NO_2 as a promising chemical sensor. The results might offer innovative insights to the gas sensor nanotechnology based on boron nanomaterials.

2. Computational details

The geometry optimizations are carried out at B3LYP/6-31G(d) level of theory. To insure the determination of local minima, vibrational calculations are performed at the same computational level and no imaginary frequency is observed. It is noticeable that the geometry optimization and electronic structure of $NO_2@B_{40}$ complexes are taken into account through the spin-unrestricted approach. The $\langle S^2 \rangle$ values of $NO_2@B_{40}$ complexes are found to be very close the pure doublet state, ranging from 0.752 to 0.758.

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* Corresponding author at: Chemistry Department, Faculty of Science, Shahid Chamran University of Ahvaz, Ahvaz, Iran.

E-mail address: e.shakerzadeh@scu.ac.ir (E. Shakerzadeh).

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Thus, the negligible spin contamination confirms the reliability of the computational approach. All calculations are performed using Gaussian 09 quantum chemistry code [32] with default convergence criteria. The SCF convergence criteria are set to 10^{-8} Hartree on the density (SCF = Tight) as well as the convergence of geometric optimizations are adjusted to maximum force and root-mean-square (rms) force of 4.5×10^{-4} and 3.0×10^{-4} Hartree Bohr^{-1}, respectively, as well as maximum and rms displacements of 1.8 $\times 10^{-3}$ and 1.2×10^{-3} Bohr, respectively.

The HOMO-LUMO gap (*HLG*) of the considered systems defines as:

$$HLG = (\varepsilon_L - \varepsilon_H) \tag{1}$$

where ε_H and ε_L are the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energies, respectively. The singly occupied molecular orbital (SOMO) is considered for the *HLG* calculation of the NO_2@B_{40} complexes.

The adsorption energy (E_{ads}) due to the interaction of NO_2 with the B_{40} fullerene is computed as:

$$E_{ads} = E_{NO_2@B_{40}} - (E_{B_{40}} + E_{NO_2}) + E_{BSSE} \tag{2}$$

$E_{NO_2@B_{40}}$ stands for the total energy of the total energy of the adduct B_{40} fullerene with the NO_2 molecule as well as $E_{B_{40}}$ and E_{NO_2} are the energies of the isolated B_{40} and NO_2, respectively. The E_{BSSE} is the basis set superposition errors which is evaluated using counterpoise method. It is noteworthy that the structures of NO_2 molecule and B_{40} fullerene are relatively distorted to provide effective interaction during the adsorption process. Therefore the following definition is applied to evaluate deformation energy:

$$E_{def} = \left(E^{sp}_{B_{40}} - E^{iso}_{B_{40}}\right) + \left(E^{sp}_{NO_2} - E^{iso}_{NO_2}\right) = E^{B_{40}}_{def} + E^{NO_2}_{def} \tag{3}$$

where the $E^{sp}_{B_{40}}$ and $E^{sp}_{NO_2}$ are the total energies of the B_{40} and NO_2 molecule in their relaxed geometries, respectively. The deformation energies include the deformation energies of B_{40} fullerene ($E^{B_{40}}_{def}$) and NO_2 molecule ($E^{NO_2}_{def}$). Actually the deformation energy is the amount of energy that the B_{40} fullerene and NO_2 molecule need to adapt themselves for favorable interaction.

3. Results and discussions

The optimized geometry of the B_{40} fullerene is exhibited in Fig. S1. The B_{40} fullerene with D_{2d} symmetry is composed of interwoven double chains with two hexagons at the top and bottom, and four heptagons in the side surface. The obtained HOMO, LUMO and HOMO-LUMO gap (HLG) energies of the B_{40} fullerene are calculated to be −5.834, −2.901 and 2.932 eV, respectively. The obtained HOMO-LUMO gap which is comparable to that of C_{60} (3.020 eV), is in well agreement with the result of Zhai et al. of 3.130 eV [23]. In order to investigate the NO_2 adsorption on the exterior surface of the B_{40} fullerene, it is located in different initial positions including: atop center of a hexagon or heptagon, atop six different boron atoms and the bridges of bonds. After full geometry optimization, six minima are predicted in for NO_2@B_{40} complex, which are the most energetically favorable. The geometries of these stable complexes with all real vibrational frequencies are presented as panels **A**–**F** in Fig. 1. The NO_2 adsorb on a boron atom of a heptagon and hexagon of B_{40} fullerene through one of its oxygen atom in **A** and **B** complexes, respectively. In **C** and **D** complexes, NO_2 molecule adsorbs through both oxygen atoms on two beside boron atoms of heptagon and hexagon of B_{40} fullerene, respectively. The NO_2 adsorbs on a boron atom of a heptagon of B_{40} fullerene through its nitrogen atom in **E** complex; while it adsorbs through both oxygen atoms on two vis-a-vis boron atoms of heptagon of B_{40} fullerene in **F** complex. The adsorption energies, HOMO, LUMO and HLG values of the complexes are listed in Table 1. The appreciable adsorption energies imply to chemisorption of NO_2 molecule on the surface of B_{40} fullerene. The obtained adsorption energies are −1.332, −1.499, −1.967, −1.702, −1.106 and −0.408 eV for **A**, **B**, **C**, **D**, **E**, and **F** complexes, respectively. The deformation energies are also calculated to be 2.902, 1.414, 4.605, 1.779, 0.550 and 4.733 eV for **A, B**, **C**, **D**, **E**, and **F** complexes, respectively. It is noticeable that both B_{40} fullerene and NO_2 molecule significantly distort during chemisorption process. The deformation energies of B_{40} fullerene in **A, B**, **C**, **D**, **E**, and **F** complexes are 1.441, 0.479, 2.537, 0.765, 0.349 and 2.430 eV, respectively; whereas the corresponding values for NO_2 molecule are 1.461, 0.935, 2.067, 1.013, 0.200 and 2.302 eV. Due to the NO_2 adsorption onto B_{40}, the boron atom at the adsorption site protrudes out of plane in order to efficiently interact with NO_2 molecule. This causes the elongation of the bond lengths at the adsorption site. Some structural parameters such as bond lengths, angles and dihedral angles for the considered complexes are summarized in Table 2. The values of the isolated systems are also listed in this table for comparison. The results of this table demonstrate the considerable variations of these parameters during the chemisorption process of NO_2 molecule onto B_{40} surface. Thus, both B_{40} and NO_2 remarkably distort to be favorable for chemisorption process. These results are in accordance with the substantial deformation energies of the B_{40} and NO_2.

Furthermore, to consider the importance of van der Waals interactions and ensure non-dependence on the basis set in these structures, the obtained complexes are re-optimized though a set of levels of theory including: B3LYP/6-311+G(d), HSEh1PBE/6-31G(d), HSEh1PBE/6-311+G(d), M06-2X/6-31G(d), M06-2X/6-311+G (d). The Heyd, Scuseria, and Ernzerhof (HSEh1PBE), which is derived from the PBE method is able for considering dispersion forces as the main constituent part of a van der Waals interaction [33,34]. The M06-2X functional is a high nonlocality functional with double the amount of nonlocal exchange (2X) to consider dispersion forces [35]. The adsorption energies for the considered complexes through these levels are gathered in Table 3. It is obvious that the obtained values are nearly the same as those calculated by B3LYP/6-31G(d). The linear regression graph of adsorption energies calculated from B3LYP/6-31G(d) versus those obtained with the mentioned levels are depicted in Fig. S2 of supplementary materials. All these methods predict the same trend for the adsorption energies of the considered complexes with significant regression coefficients. These results are anticipated since the interactions are sufficiently strong in which van der Waals interactions could be ignored in their interactions. Therefore the dispersion energies are not considerable as well as the basis set independency is confirmed.

The electronic properties of B_{40} fullerene change after NO_2 chemisorption. The HOMO, LUMO and HLG values of these complexes are collected in Table 1. The energy gaps of **A**, **B**, **C**, **D**, **E** and **F** complexes are calculated to be 1.245, 1.280, 2.138, 1.263, 1.194 and 1.888 eV, respectively. The corresponding HLG values are decreased by 58%, 56%, 27%, 57%, 52% and 52% with respect to pristine B_{40} fullerene (HLG = 2.932 eV). The NO_2 interaction via B_{40} fullerene leads to new LUMO level at nearly 4 eV, which is located between the original HOMO and LUMO of pristine B_{40}. The LUMO level shift to upper energies and the HLG is remarkably decreased.

It is well known that the energy gap (E_g) is a major factor determining the electrical conductivity of a material and there is a classic relation between them as follows [36]:

$$\sigma \propto \exp\left(\frac{-E_g}{2kT}\right) \tag{4}$$