ARTICLE

B_{12}N_{12} Nano-cage as Potential Sensor for NO_{2} Detection

Javad Beheshtian\textsuperscript{a}, Mohammad Kamfiroozi\textsuperscript{b}, Zargham Bagheri\textsuperscript{c}, Ali Ahmadi Peyghan\textsuperscript{d}\textsuperscript{*}

\textsuperscript{a}. Department of Chemistry, Shahid Rajaee Teacher Training University, P.O. Box: 16875-163, Tehran, Iran
\textsuperscript{b}. Department of Chemistry, Islamic Azad University, Shiraz Branch, Shiraz, Iran
\textsuperscript{c}. Science Department, Islamic Azad University, Islamshahr Branch, P.O. Box: 33135-369, Islamshahr, Tehran, Iran
\textsuperscript{d}. Young Researchers Club, Islamic Azad University, Islamshahr Branch, Tehran, Iran

(Dated: Received on August 29, 2011; Accepted on October 13, 2011)

The NO\textsubscript{2} molecule adsorption on B\textsubscript{12}N\textsubscript{12} nano-cage was investigated using density functional theory calculations in terms of adsorption energy, HOMO/LUMO energy gap (E\textsubscript{g}) changes, charge transfer, structural deformation, etc. Furthermore, some aspects of stability and properties of B\textsubscript{12}N\textsubscript{12} including calculation of binding electronic and Gibbs free energies, density of states, and molecular electrostatic potential surfaces are investigated. Three possible configurations for NO\textsubscript{2} adsorption on the B\textsubscript{12}N\textsubscript{12} nano-cage are energetically found. Interestingly, the results reveals that the E\textsubscript{g} of B\textsubscript{12}N\textsubscript{12} cluster is very sensitive to the presence of NO\textsubscript{2} molecules as its value reduces from 6.84 eV in free cluster to 3.23 eV in the most stable configuration of NO\textsubscript{2}/cluster complex. This phenomenon dramatically increases the electrical conductivity of the cluster, suggesting that the B\textsubscript{12}N\textsubscript{12} nano-cluster may be potential sensor for NO\textsubscript{2} gaseous molecule detection.

Key words: Nitrogen dioxide, Boron nitride nanocluster, Density functional theory, Adsorption, B\textsubscript{12}N\textsubscript{12}

I. INTRODUCTION

Air pollution is mainly result of releasing toxic substances such as noxious gases and very tiny particles, usually by burning of fossil fuels. Such noxious gases include carbon monoxide, nitrogen oxide and sulphur dioxide [1–3]. Nitrogen dioxide released from combustion facilities and automobiles is known to be extremely harmful to human body and is one of the main causes of air pollution. Nitrogen dioxide in the atmosphere is transferred to nitrous and nitric acid which leads to acid rain [4–7]. Thus, the development of NO\textsubscript{2} sensors is highly important for monitoring the nitrogen dioxide concentration in the atmosphere. One of the target places for installation of such sensors is in the exhaust systems in which they should have high-temperature durability [8–11].

The discovery of buckminsterfullerene C\textsubscript{60} [12] and carbon nanotubes (CNT) [13] has initiated a new era in supramolecular chemistry [14, 15]. Chemical sensors based on CNT have been utilized for detecting pollutant and toxic gases like NO\textsubscript{2} and CO. Such nano-scale assemblies can achieve high sensitivity and fast response time [16, 17]. The field of fullerene structures and their derivatives has become one of the most important issues in nanotechnology, because of possible important applications in electronic devices, imaging materials, magnetic recording, environmental processes, and so on [18–20].

Recently, several studies have been reported on boron nitride fullerene materials since they have excellent properties such as high-temperature stability which makes them suitable for NO\textsubscript{2} sensing, a low dielectric constant, large thermal conductivity, and oxidation resistance, leading to a number of potential applications as a structural or electronic material [21–23]. B\textsubscript{n}N\textsubscript{m} structures have been widely studied both theoretically and experimentally. Oku et al. have investigated hydrogenation of a BN nanocluster by using density functional theory (DFT) [23, 24]. Fowler et al. found that B\textsubscript{12}N\textsubscript{12}, B\textsubscript{16}N\textsubscript{16} and B\textsubscript{28}N\textsubscript{28} stand out as “magic” BN-fullerenes, and B\textsubscript{12}N\textsubscript{12} appears to be more stable than the others [25].

In the present work, we perform DFT calculations to study the interaction of B\textsubscript{12}N\textsubscript{12} and NO\textsubscript{2} molecules. The results show that the B\textsubscript{12}N\textsubscript{12} molecule is highly sensitive to NO\textsubscript{2} and could be a potential candidate for serving as a sensor of this molecule. To our knowledge, no prior theoretical investigations have been reported on potential application of nanocage clusters as a gas sensor.
II. COMPUTATIONAL METHODS

All calculations were performed using DFT within spin-unrestricted B3LYP hybrid functional. Since this method is known to reproduce accurate geometries and thermo-chemistries and has been widely used in the nanostructure studies [26–30], 6-31G* all electron basis sets were used for the optimization, natural bond orbital (NBO), density of states (DOS), frontier molecular orbital (FMO) analyses, and energy calculations. The adsorption energy ($E_{\text{ads}}$) of NO$_2$ molecule on the pure B$_{12}$N$_{12}$ cluster was obtained using the following equation

$$E_{\text{ads}} = E(\text{B}_{12}\text{N}_{12}/\text{NO}_2) - E(\text{B}_{12}\text{N}_{12}) - E(\text{NO}_2) \quad (1)$$

$E(\text{B}_{12}\text{N}_{12}/\text{NO}_2)$ is the total energy of B$_{12}$N$_{12}$/NO$_2$ complex, and $E(\text{B}_{12}\text{N}_{12})$ or $E(\text{NO}_2)$ is referred to the energy of an isolated B$_{12}$N$_{12}$ or NO$_2$ molecule, respectively. Negative values for $E_{\text{ads}}$ reveal that the adsorption is exothermic. All calculations were implemented in Gaussian 98 package of programs [31].

III. RESULTS AND DISCUSSION

A. Structure optimization and geometry

At first, accuracy of the method used in this work has been tested to describe properties of NO$_2$ molecule in gas phase. In the present approach, the bond length of individual N–O and angle of free NO$_2$ are 1.20 Å and 133.85°, respectively, which are in good agreement with the experimental values of 1.19 Å and 134.1° [32].

The optimized structure and geometry parameters of B$_{12}$N$_{12}$ nanocluster are shown in Fig.1. In a structural view, the cluster is made of six squares and eight hexagons. The calculated NMR spectrum of cluster consists of two single peaks showing T$_h$ symmetry. These results are the same as the results of Ref.[25]. Structurally, there are two types of individual B–N bond among the 36 B–N bonds in B$_{12}$N$_{12}$: one is shared by two six-membered rings (6-MR, H bond), and the other by 4- and 6-MR (S bond, Fig.1). The S bond (1.486 Å) is slightly longer than H bond (1.439 Å). The lengths of these bonds are exactly equal to those obtained by Wang et al. [33], but slightly differ from those reported in Ref.[25]. However, the method used in Ref.[33] is the same as what was used in the present work while is not the same as that in Ref.[33] . The calculated IR frequencies are 323.9–1446.3 cm$^{-1}$, indicating that this structure is a true stationary point on the potential energy surface. The range of vibration frequencies calculated within the DFTB method in Ref.[25] is 320–1456 cm$^{-1}$ which is rather in good agreement with our results.

The binding electronic energy ($\Delta E_b$) is calculated, using the following expression (as Lee et al. have used [34]):

$$\Delta E_b = \frac{1}{24} [E_{\text{tot}}(\text{B}_{12}\text{N}_{12}) - 12(E_{\text{B}} + E_{\text{N}})] \quad (2)$$

where $E_{\text{tot}}$ is total energy of B$_{12}$N$_{12}$ cluster, 12 is the number of B and N atoms involved, and $E_{\text{B}}$ and $E_{\text{N}}$ are the energies of an isolated B and N atom, respectively. The calculated value is $-303$ meV. To examine the entropic effect on cluster stability, the binding Gibbs free energy ($\Delta G_b$) is calculated by using following expression:

$$\Delta G_b = \frac{1}{24} [G_{\text{tot}}(\text{B}_{12}\text{N}_{12}) - 12(G_{\text{B}} + G_{\text{N}})] \quad (3)$$

where $G_{\text{tot}}$ is total Gibbs free energy of B$_{12}$N$_{12}$ cluster, and $G_{\text{B}}$ and $G_{\text{N}}$ are Gibbs free energies of an isolated B or N atom, respectively. The calculated value is $-289$ meV confirming more stability of B$_{12}$N$_{12}$ cluster.

Based on Mulliken population analysis, the point charge of boron and nitrogen in B$_{12}$N$_{12}$ cluster is +0.44 e and $-0.44$ e, respectively, which is in agreement with our calculated MEP. As shown by the mapped-MEP of B$_{12}$N$_{12}$ in Fig.2(a), the B atoms are positively charged (blue colors) while the N atoms are negatively charged (red colors) in B–N bonding. Electronically,
FIG. 2 (a) The calculated molecular electrostatic potential surface and (b) the lowest unoccupied molecular orbital of B$_{12}$N$_{12}$ cluster. The red color is referred to the high electron density on nitrogen atoms and the blue one is referred to the positive sites (B atoms). For the color, the reader can refer to the web along this article legend.

calculated DOS of the B$_{12}$N$_{12}$ is shown in Fig.1(c). Obviously, HOMO/LUMO energy gap ($E_g$) of 6.84 eV for the cluster is obtained that is wider than BNNT (5.5 eV) [35].

B. NO$_2$ adsorption

As shown in Fig.2(b), calculated LUMO for B$_{12}$N$_{12}$ cluster reveals that it is more localized on the boron atoms. Thus, it seems that these atoms are suitable sites for nucleophilic attack of NO$_2$ molecules. In order to determine the minimum energy adsorption structure for NO$_2$ on exterior surface of the considered cluster, a number of distinct starting structures were used for optimization including both the nitrogen and oxygen atoms of NO$_2$ close to two B atoms, oxygen atom close to B atom, two oxygen atoms at top of two B atoms located on a square and two oxygen atoms at top of two B atoms located on a hexagon.

To ensure that the most stable adsorption configuration can be achieved, the initial distance between the molecule and the cluster was adjusted several times from 1.0 Å to 3.0 Å. Full structural relaxation was then performed with each initial molecule-cluster distance. After careful structural optimization, we obtain three stable and one unstable adsorption configurations depicted in Fig.3.

Among the four considered configurations (Fig.3), R is thermodynamically unstable with positive $E_{ads}$ of 0.59 eV and distance of 1.63 Å between NO$_2$ and the cluster. The Q configuration stands for the interaction between one of the oxygen atoms of NO$_2$ molecule and the B atom of the nanocluster, $D_{B-O}=2.75$ Å. In this configuration, a net charge about 0.036 electrons transfers from gas to the cluster and its corresponding calculated $E_{ads}$ value (Table I) is about −0.06 eV. The most stable configuration is Z, in which one of the nitrogen atoms of NO$_2$ is close to a B atom of the cluster by a distance of 2.57 Å. This configuration has an $E_{ads}$ of −0.13 eV and a charge transfer of 0.22 e from the cluster to the molecule. In the P configuration, a locally structural deformation at the adsorption site can be observed after the NO$_2$ adsorption, where the adsorbing boron atom is slightly pulled out of the surface and the corresponding two B−N bonds in square side (S bond) are thus considerably elongated. The $D_{B\text{−bond}}$ increases from 1.439 Å in the pristine model to 1.513 Å in the P model (Fig.3). Also molecular angle of NO$_2$ decreased from 133.84° in the pristine model to 110.9° in the adsorbed model.

Further indication of the degree of deformation in the geometry of NO$_2$ as a result of adsorption process is given by the bond reorganization energy ($E_{Re}$), calculated as the energy difference between the geometry of NO$_2$ after adsorption and the full relaxed molecule. For this configuration, the $E_{Re}$ of NO$_2$ is about 1.31 eV which confirms the strong interaction. It is noteworthy to mention here that despite the smaller distance between NO$_2$ and the cluster in configuration P, its $E_{ads}$ is less in comparison to that of configuration Q. It is thought to be due to more structural deformation in configuration P.

C. Electronic properties

Table II summarizes the energy of HOMO, LUMO, and $E_g$ values of the studied stable configurations. Since a small change of $E_g$ can modify the electrical conductivity of a sorbent, these changes ($\Delta E_g$) upon the adsorption process are related to the sensitivity of

<table>
<thead>
<tr>
<th>Configuration</th>
<th>$E_{HOMO}$/eV</th>
<th>$E_{LUMO}$/eV</th>
<th>$E_g$/eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine</td>
<td>−7.70</td>
<td>−0.86</td>
<td>6.84</td>
</tr>
<tr>
<td>P</td>
<td>−7.21</td>
<td>−2.12</td>
<td>5.09</td>
</tr>
<tr>
<td>Q</td>
<td>−7.02</td>
<td>−3.83</td>
<td>3.19</td>
</tr>
<tr>
<td>Z</td>
<td>−7.61</td>
<td>−4.38</td>
<td>3.23</td>
</tr>
</tbody>
</table>

*a* Equilibrium tube-molecule distance.
*b* $Q$ is the total Mulliken charge on the molecules and negative number means charge transfer from tube to molecule.
*c* Equilibrium distance of adsorbed oxygen to nitrogen in NO$_2$.

TABLE I Calculated structural parameters and adsorption energies of nitrate adsorbed on the SWCNT in vacuum and water medium.

<table>
<thead>
<tr>
<th>Configuration</th>
<th>$D^*/\text{Å}$</th>
<th>$E_{ads}$/eV</th>
<th>$Q^b$/e</th>
<th>$D_{N−O}^c$/Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>P</td>
<td>1.42</td>
<td>−0.06</td>
<td>−0.341</td>
<td>1.42</td>
</tr>
<tr>
<td>Q</td>
<td>2.75</td>
<td>−0.09</td>
<td>0.036</td>
<td>1.20</td>
</tr>
<tr>
<td>Z</td>
<td>2.57</td>
<td>−0.13</td>
<td>−0.220</td>
<td>1.20</td>
</tr>
</tbody>
</table>

DOI:10.1088/1674-0068/25/01/60-64 ©2012 Chinese Physical Society
Nano-cage as Potential Sensor for NO\textsubscript{2} Detection

FIG. 3 Models for four stable different adsorption states for a NO\textsubscript{2} molecule on B\textsubscript{12}N\textsubscript{12}. Bonds length in Å and bond angles in (°).

FIG. 4 DOSs for three stable configurations of NO\textsubscript{2}/nanocluster.

the adsorbent for a particular analyte.

To gain an in-depth understanding of the changes of electronic properties of B\textsubscript{12}N\textsubscript{12} nanoclusters, it is essential to calculate the DOSs of the cluster before and after NO\textsubscript{2} molecule adsorption. Figure 4 shows DOS of three possible exothermic NO\textsubscript{2} adsorptions on the cluster. For example, in the configuration Z (as the most stable), the DOSs near the conduction level have a distinct change compared to that of the pristine B\textsubscript{12}N\textsubscript{12}, so that three peaks of virtual orbital states are generated. The energy level of the lowest generated state is about −4.38 eV, revealing that $E_G$ of the cluster decreases from 6.84 eV in free state to 3.23 eV (58% change) in adsorbed form; Consequently, the electrical conductivity of the B\textsubscript{12}N\textsubscript{12} increases dramatically with even one adsorbed-NO\textsubscript{2} molecule.

Therefore, the presence of the toxic molecule, NO\textsubscript{2}, can be detected by calculating the conductivity change of B\textsubscript{12}N\textsubscript{12} before and after the adsorption process. This behavior suggested that B\textsubscript{12}N\textsubscript{12} may be a very sensitive NO\textsubscript{2} gas sensor compared with a few suggested nanomaterials. For example, Xiao et al. have considered chemisorptions of NO\textsubscript{2} on silicon carbide (SiC) nanotubes [36]. They found that NO\textsubscript{2} interacts strongly with SiC ($E_{\text{ads}}>1$ eV), but upon a single NO\textsubscript{2} molecule adsorption on the tube, $E_G$ is decreased from 1.36 eV to 1.19 eV, leads to 12.5% change in $E_G$ [36]. Moreover, using this cluster as NO\textsubscript{2} sensor has the advantage of not having such a strong interaction that prevents the recovery of the device. Finally, similar trend was found for the other configurations as shown in Fig.4.

IV. CONCLUSION

The NO\textsubscript{2} molecule adsorption on B\textsubscript{12}N\textsubscript{12} nanocluster, using DFT calculations by means of adsorption energy, HOMO/LUMO energy gap changes, charge transfer, structural deformation, etc. was explored. Three possible configurations for NO\textsubscript{2} adsorption on B\textsubscript{12}N\textsubscript{12} nano-cage energetically were found. The calculations demonstrated that the $E_G$ of B\textsubscript{12}N\textsubscript{12} nanocluster is very high sensitive to the presence of NO\textsubscript{2} molecules, as its value changes from 6.84 eV in free cluster to 3.23 eV in the most stable configuration of NO\textsubscript{2}/cluster complex, suggesting that B\textsubscript{12}N\textsubscript{12} nano-cluster may be a potential sensor to detect the NO\textsubscript{2} molecules.