

Applying the B₁₂N₁₂ nanoparticle as the CO, CO₂, H₂O and NH₃ sensor

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ABSTRACT

In this study, the various properties including the stability energies, structural and electronic aspects of the hydrazine (N₂H₄), carbon monoxide (CO) water (H₂O) and ammonia (NH₃) molecules adsorptions on the top of the boron nitride nanoparticles (BNn) were studied through the Minnesota Functionals computations, DFT/M06-2X. The calculations clarify that the most stable adsorption configurations are those in which the oxygen, carbon, oxygen and nitrogen atoms of CO₂, CO, H₂O and NH₃ are closed to the boron atom of the nanoparticle, respectively. The absorption energies were obtained about -0.14, -0.15, -0.87 and -1.54 eV for absorption of CO₂, CO, H₂O and NH₃ gasses. The geometry optimizations, energy calculations and NBO charge transfer were used to evaluate the sensing ability of BNn for different analytes. The computed density of states (DOS) clarifies that a strong orbital hybridization takes place between CO₂, CO, H₂O and NH₃ and BNn in adsorption process. Finally, it is concluded that the BNn nanoparticle has greater response selectivity toward NH₃ compared to CO, CO₂ and H₂O.

1. Introduction

Boron is one of the very interesting elements in the periodic Table. Pure boron molecules are intermediate compounds between the materials with purely nonmetallic and metallic characteristics. This feature results into high chemical flexibility of boron rich molecules and it motivates many researchers to search the ground-state geometries of boron rich molecules and reveal their unique characteristics [1-8]. During the last decade, various experimental and theoretical efforts have been devoted to find the fullerene-like structures which formed of non-carbon elements [1-6]. In particular, the non-carbon elements in periodic table from III to V have been extensively applied in the fullerene-like cage and nanotube [7-13]. Especially, the group III nitrides have considerable importance to the science and technology aspects [14-16]. Boron nitride (BN) nanostructures such as nanotubes [17], nanocapsules [18] and electronic industry [19] have received much attention. The boron nitride nanostructures either nanocage or nanotubes are important due to their having temperature stability, high thermal conductivity and high resistance [17, 20-22]. The polar character of the B-N bonds in the boron nitride nanoparticles leads to a higher reactivity than

their carbon homologues. In addition, the considerable charge difference between the nitrogen and boron atoms, the boron and nitrogen atoms can play as a Lewis acid and base role, respectively. Therefore, we can conclude that the boron nitride nanoparticles can be regarded as a non-metal catalyst. In the boron nitride category, B₁₂N₁₂ (BNn) was reported to be the smallest stable nanocage particles. Recently, the scrutiny of the poisonous gases is of the most importance in both industrial and living environments [24-27]. The presence of gases like carbon monoxide, carbon dioxide, nitrogen oxides and ammonia at any concentrations are damaging in the living environments.

In the present research, we investigate the interactions between carbon monoxide (CO) carbon dioxide (CO₂), water (H₂O) and ammonia (NH₃) molecules and the BNn nanoparticle using M06-2X calculations. Evaluation of these gases is the basic function of the gas sensors [28]. The main purpose of this research is to obtain the fundamental outlooks into the efficacy of adsorbed gasses on the electronic aspects of the nanoparticles. The most valuable efforts are to use these effects to design more sensitive gas sensing devices.

2. Computational details

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The theoretical calculations on the CO, CO₂, H₂O and NH₃ gasses and their complexes with BN_n including CO_n-BN_n or H_nX-BN_n systems were carried out using a hybrid functional closed-shell M06-2X and 6-31++G** basis set, employing the Gaussian program package [16]. All the calculations were carried out in the gas phase under 1atm pressure and 298K temperature. The frequency calculations were performed at the mentioned level. No any pure imaginary frequency was obtained for the ground state at the same level of theory. Theoretical studies [17,18] proposed that the M06-2X method can give the best results to compute the absorption energies, strength of noncovalent interactions, and thermochemistry properties. The adsorption energies (E_{ad}) of the systems were computed using the M06-2X/6-31++G** level of theory.

The E_{ad} was obtained via differences between the total energies of the CO_n-BN_n or H_nX-BN_n systems and the energies of each monomer. The interaction energies were corrected for the basis set superposition error (BSSE) in all the complexes using the full counterpoise method [19].

The density of states (DOS), molecular electrostatic potential surface (MEP) and frontier molecular orbital analyses were calculated and presented using the M06-2X/6-31+G* level of theory.

3. Results and discussion

3.1. Adsorptions in the CO_n-BN_n ($n = 1$ and 2) or H_nX-BN_n ($n = 2$ and 3) systems

The fully optimized structure of isolated BN_n nanoparticle is presented in Fig. 1a. The bond length of B-N shared between two six-membered rings is about 1.48 Å and that is shared between a four-membered ring and a six-membered rings is 1.43 Å. The calculated HOMO-LUMO gap energy (E_g) of pure BN_n nanoparticle is to be about 9.15 eV, showing an insulator character. As shown in Fig. 3a, the HOMO and LUMO orbitals of pure BN_n are localized on the N and B atoms, respectively. Thus, the electron deficient boron atoms can be regarded as a Lewis acid, whereas the electron-rich nitrogen atoms play the role of a Lewis base. These are consistent with the results obtained in Ahmadi et al. studies [36]. Because of the large difference in electronegativity between B and N, ionic bonding is predominant in the BN_n nanoparticles. This can be seen from the surface electrostatic potentials (Fig. 2), where N sites receive electrons from B sites, resulting in positively charged B ions. These positively charged B ions on the cage surface become the available sites for adsorption of CO₂, CO, H₂O and NH₃ molecules. Also, the negatively charged N sites seem to be appropriate for adsorption H atoms of H₂O and NH₃ molecules. The interactions between the optimized structures of the BN_n nanoparticles and CO₂, CO, H₂O

and NH₃ is shown in Fig. 1 at the M062X/6-31+G* level of calculations. The calculated equilibrium molecule-cluster distance ($d_{\text{Molecule/B}_{12}\text{N}_{12}}$), adsorption energy (E_{ad}), NBO charge transfer, HOMO and LUMO energies, HOMO-LUMO gap energy (E_g) and change of E_g (ΔE_g) for each complex are presented in Table 1.

3.1.1. Adsorption of NH₃ on the nanoparticle

After the geometry optimization of the H₃N-BN_n complex, two stable configurations were obtained for NH₃ from its N-side and H-side close to the B and N atoms of BN_n nanoparticle, respectively which are presented in Figs. 1b and c. The adsorption energy and equilibrium distance of NH₃ from its N-side adsorption on the boron atom of BN_n nanoparticles is -1.54 eV and 1.62 Å, respectively. The adsorption energy and equilibrium distance for H-side of NH₃ adsorption on the nitrogen atom of cage was -0.07 eV and 2.43 Å, respectively that can be defined as a hydrogen bond (Table 1). The boron atoms of nanoparticle acts as Lewis acid site and the nitrogen atom of NH₃ molecule acts as Lewis base site. In Fig. 2, we represented electrostatic potentials at the 0.001 electrons per Bohr⁻³ isodensity surfaces of NH₃ adsorption on the BN_n were calculated at the same level of theory with WFA surface analysis suite [37]. Natural bond orbital (NBO) analysis for N-side and H-side are 0.56 and -0.01 e, respectively. The results clarify that the hydrogen bond leads to decrease in the intensity of electrons at a particular position. For molecule adsorption on the sites of the cage surface can be explained by considering the fact that the highest occupied molecular orbitals (HOMOs) of the BN_n are centered on the N sites, and the lowest unoccupied molecular orbitals (LUMOs) are located on the B sites (Fig. 3h). The NH₃ molecule can transfer the electrons to the LUMO on the N site of the cage through the electron lone pair of nitrogen atom and also hydrogen atom of NH₃ can accept electron from HOMO on the B site of the cage (Fig. 3j). The E_g for N-side and H-side of NH₃ are 7.72 and 5.91 eV, respectively (Table 1).

3.1.2. Adsorption of H₂O on the nanoparticle

The DFT calculations on the H₂O-BN_n complex indicate that there are two adsorption sites between the oxygen and hydrogen atoms of H₂O (O-side and H-side) and the B and N atoms of BN_n (Fig. 1d and 1e). In the H₂O adsorption systems, the bond lengths of B-O and N-H decrease by about 1.64 and 2.07 Å, respectively, that the adsorption energy (E_{ad}) are -0.87 and -0.18 eV, respectively (see Table 1). The NBO analysis shows that the oxygen and hydrogen atoms acquire positive and negative charges, respectively. This reveals that the charge is transferred from the H₂O molecule to the cage in the B-O bond formation while the in the N-H bond formation the charge transferred from the cage to the H₂O molecule (Table 1). Fig. 2 presents the molecular

electrostatic potentials $V(r)$ on the surface of the BNn–H₂O, which are computed on the 0.001 au contour of the molecule's electronic density. The calculated HOMO–LUMO gap (E_g) for H₂O–BNn (O–B) and BNn–H₂O (N–H) systems are 7.88 and 9.19 eV. The results clarify that the E_g of H₂O–BNn (O–B) is significantly decreased through the adsorption process.

3.1.3. Adsorption of CO₂ on the nanoparticle

It is found two configurations through adsorption of CO₂ at top of the nanoparticle surface: (i) the carbon side (configuration d) and (ii) the oxygen side (configuration e) of CO₂ adsorption on the top of the boron atom of the nanoparticle (Fig. 1d and 1e). The M062X calculations indicate that the adsorption of the CO₂ molecule from the carbon side and oxygen side on the cages (d and e) are an exothermic processes with negative E_{ads} of -0.14 and -0.03 eV and the interaction distances are 2.54 and 4.19 Å, respectively (Fig. 1a). The NBO analysis indicates the charge transfers are 0.00 and 0.04 e from CO₂ to the BNn nanoparticles surfaces in the configurations d and e (Table 1). This charge transfer indicates that the boron atoms of nanoparticle acts as Lewis acid site and the carbon and oxygen atoms of CO₂ molecule acts as Lewis base site. Fig. 2 reveals the electrostatic potential map of the BNn–CO₂ system that indicates the locations of the various most positive and most negative potentials, designated as $V_{S,max}$ and $V_{S,min}$, respectively. The DFT calculations indicate that in the configuration e, the interaction between the molecule and cage is much stronger in comparison to that of the d configuration. The calculated HOMO of CO₂ molecule is mainly located on the oxygen atom; thus this reveals that the electrons are transferred from CO₂ molecule to the BNn nanoparticle (Figs. 3d and 3e).

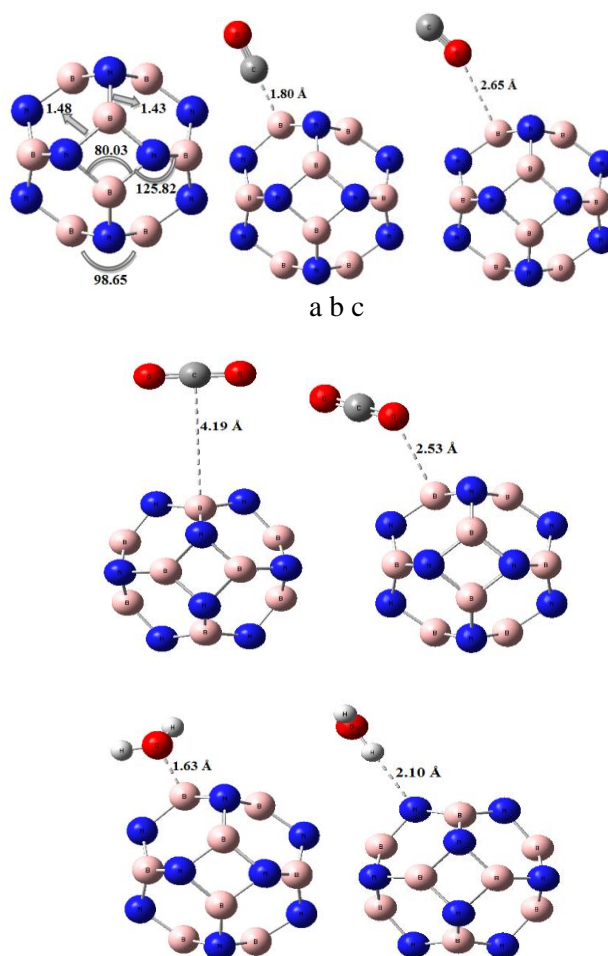
3.1.4. Adsorption of CO on the nanoparticle

Two configurations were selected to investigate in adsorption of CO at top of the nanoparticle. In the configuration b, the carbon atom of CO attaches to the boron atom of the cage and in the configuration c, the oxygen atom of CO binds to the boron atom of the cage (Fig. 1b and c). The computed adsorption energies (E_{ad}) and the equilibrium molecule–cage distance ($d_{Molecule/B12N12}$) for the two molecular adsorption configurations are -0.15 eV and 1.81 Å for configuration b and -0.09 eV and 2.66 Å for configuration c (Table 1). The interaction between CO and BNn leads to a charge transfer of 1.20 and 0.02 from the carbon and oxygen sides of CO to the nanoparticle, respectively (Table 1). There is a positive electrostatic potential and negative electrostatic potential for this configuration (Fig. 2). The HOMO of CO molecule is mainly occurred on the carbon atom respect to oxygen atom which leads to the stronger interaction in configuration b in comparison to the configuration c.

Comparative investigation of the adsorption energy in the CO_n–BNn ($n = 1$ and 2) or HnX–BNn ($n = 2$ and 3) systems reveals that BNn has greater response to NH₃ (from N side) than that of CO₂ (from C side), CO₂ (from O side), CO (from C side), CO (from O side) and H₂O (from O side) (Table 2). A relatively large difference of adsorption energy between CO_n–BNn or HnX–BNn complexes can be described based on the electronegativity difference, p character, and dipole moment in the molecules (see Table 2).

Table 1. Calculated adsorption energy (E_{ad} : eV), HOMO energies (E_{HOMO}), LUMO energies (E_{LUMO}) and HOMO–LUMO energy gap (E_g).

Comp.	E_{ad}	E_{HOMO} (eV)	E_{LUMO} (eV)	E_g (eV)	$\% \Delta E_g$ (eV)
BN	–	-9.51	-0.36	9.15	–
BN–NH ₃	-1.54	-8.68	-0.95	7.72	142.59
BNn–H ₃ N	-0.07	-7.19	-1.28	5.91	324.18
BNn–OH ₂	-0.87	-8.86	-0.99	7.88	127.05
BNn–H ₂ O	-0.15	-8.11	-1.41	6.70	245.29
BNn–CO ₂	-0.03	-9.53	-0.47	9.06	8.68
BNn–O ₂ C	-0.14	-9.44	-0.44	9.00	14.69
BNn–CO	-0.15	-9.14	-0.05	9.09	5.87
BNn–OC	-0.09	-9.45	-0.01	9.44	29.01



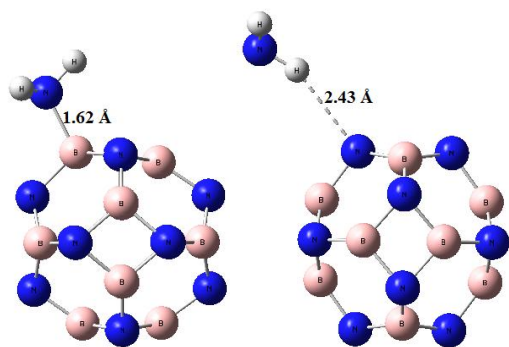


Fig. 1. Geometric parameters of isolated BN_n and small molecule-adsorbed BN_n nanoparticle. Distances in Å and angles in degrees.

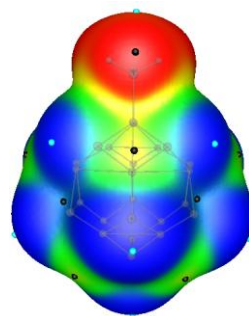
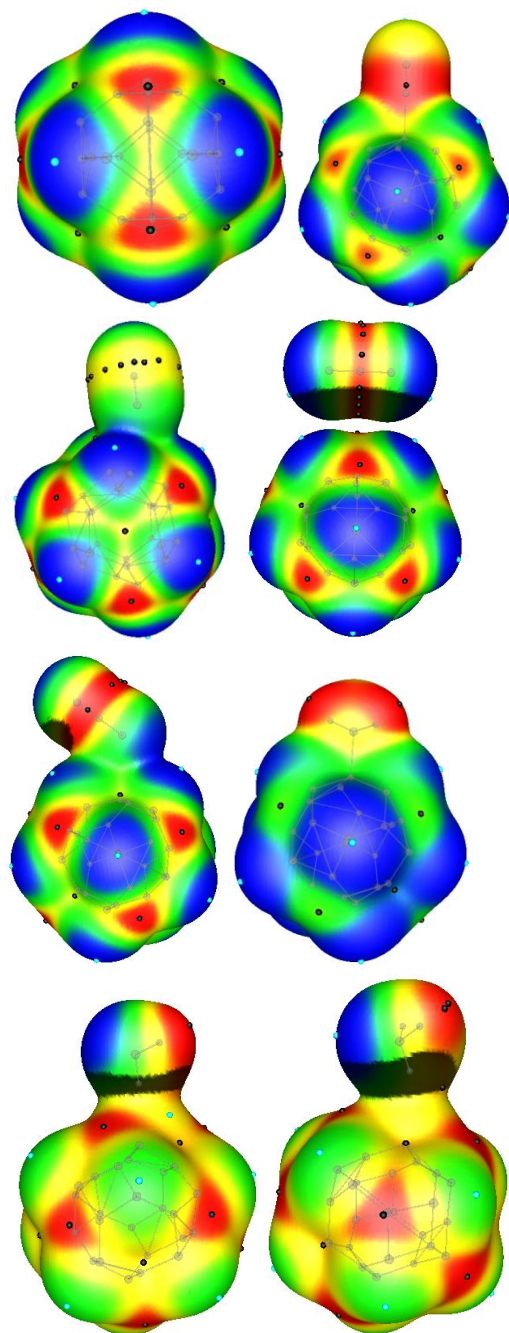
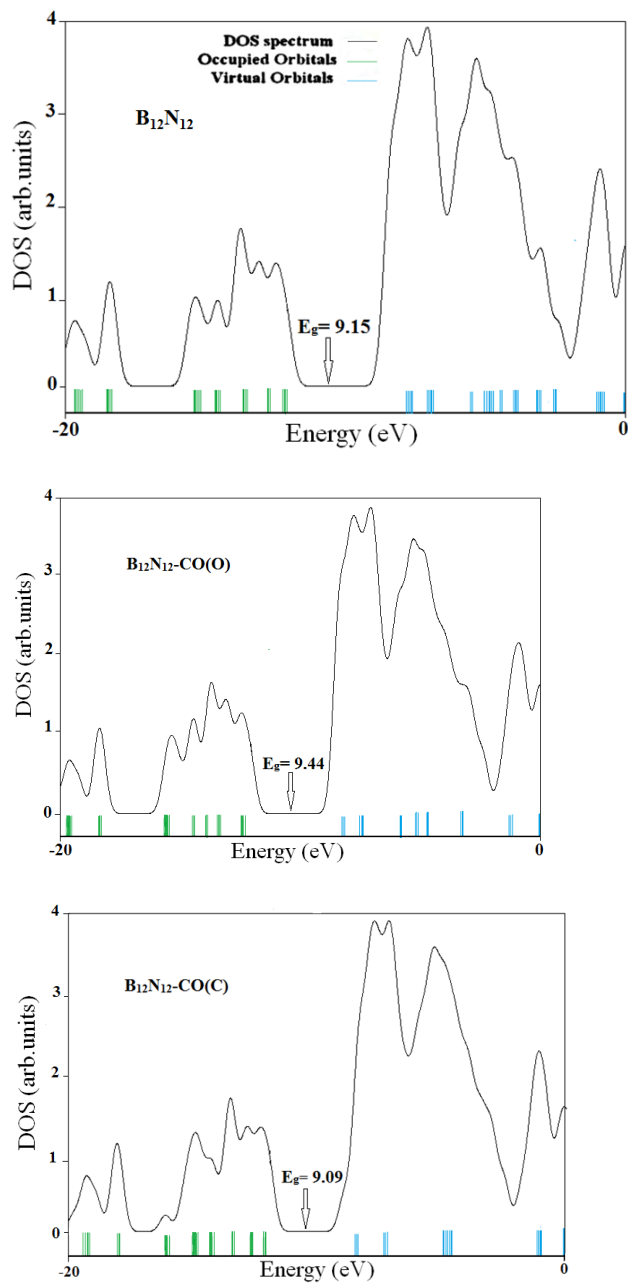


Fig. 2. The molecular electrostatic potentials $V(r)$ on the surface of the BN_n -Complexes.



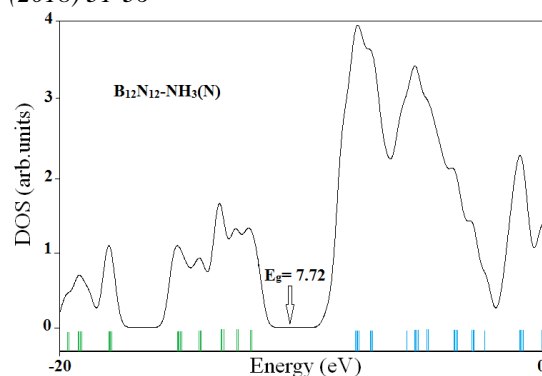
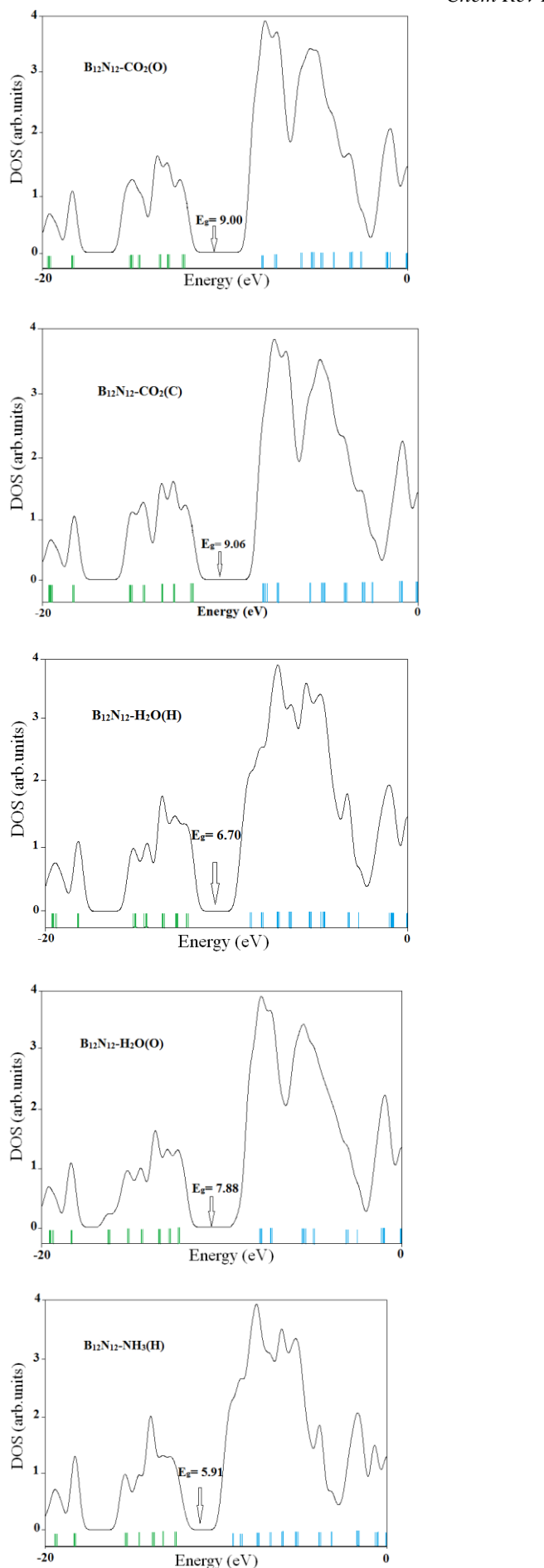


Fig. 3. Computed density of states (DOS) for pure BNN and the BNN- CO(C), BNN-CO(O), BNN-CO₂(C), BNN-CO₂(O), BNN-NH₃(N), BNN- H₂O(O), BNN-NH₃(H) and BNN- H₂O(H) complexes

3.2. Density of state (DOS) analysis

Computed density of state (DOS) maps indicate that the energy gaps of BNn is 9.15 eV and of CO_n-BNn or HnX-BNn with CO₂ (C-side interaction), CO₂ (O-side interaction), CO (C-side interaction), CO (O-side interaction), NH₃ (N-side interaction), H₂O (O-side interaction) NH₃ (H-side interaction) and H₂O (H-side interaction) complexes are 9.15, 9.06, 9.00, 9.09, 9.44, 7.88, 7.72, 5.91 and 6.70 eV, respectively at the M06-2X/6-31++G** method (Fig. 3). The ΔE_g in the adsorption process is associated to the sensitivity of an absorbent for a particular molecule. As seen in Table 1, the ΔE_g of BNn is 8.68% and of CO_n-BNn or HnX-BNn with CO₂ (C-side interaction), CO₂ (O-side interaction), CO (C-side interaction), CO (O-side interaction), NH₃ (N-side interaction), H₂O (O-side interaction) NH₃ (H-side interaction) and H₂O (H-side interaction) complexes are 14.69%, 5.87%, 29.01%, 127.05%, 142.59%, 324.18% and 245.29%, respectively. The computed DOS indicates that the E_g amount is reduced compared to the isolated BNn. It is known that the E_g is a major factor in determination of the electrical conductivity of BNn which will improve in the existence of the molecules with respect to the following equation [38]:

$$\sigma \propto \exp\left(\frac{-E_g}{2KT}\right)$$

in where σ is the electrical conductivity and k is the Boltzmann's constant. According to the equation, the smaller E_g amount leads to increase the conductivity at a given temperature. However, it can be conclude that the BNn nanoparticle selectively acts as a gas sensor device between CO₂, CO, H₂O and NH₃ which acts as the most suitable gas sensor for the NH₃ molecule.

4. Conclusions

The M06-2X calculations are used to studied the equilibrium distances, stabilities, and electronic

properties of CO₂, CO, NH₃ and H₂O molecules which adsorbed at top of the BN_n nanoparticle. The results reveal that the CO₂, CO, NH₃ and H₂O molecules can be strongly adsorbed on the BN_n with a good adsorption energies. The CO and CO₂ molecules interactions to BN_n from the carbon and oxygen atoms of CO and CO₂ are more prominent compared to the interaction with the oxygen and carbon atoms, respectively. A relatively large difference of adsorption energy between CO_n-BN_n (n = 1 and 2) or HnX-BN_n (n = 2 and 3) complexes can be described on the basis of electronegativity difference, p character, and dipole moment in molecules. The most stable configuration was BN_n-NH₃ with E_{ad} and E_g about -1.54 and 7.72 eV and 142.59% change of the E_g. Finally, it is concluded that BN_n nanoparticle has greater response selectivity toward NH₃ compared to CO, CO₂ and H₂O, a wide variety of investigations have been done upon the adsorption of this molecule both theoretically and experimentally.

References

- [1] J. Beheshtian, M. Kamfiroozi, Z. Bagheri, A. Ahmadi, *Comp. Mater. Sci.* 54 (2012) 115–118.
- [2] A. Ahmadi, N.L. Hadipour, M. Kamfiroozi, Z. Bagheri, *Sens. Actuat. B-Chem.* 161 (2012) 1025–1029.
- [3] S. HaiJun, *Comp. Mater. Sci.* 47 (2009) 220–224.
- [4] D. Golberg, Y. Bando, *Appl. Phys. Lett.* 73 (1998) 2441–2443.
- [5] H. Omidvar, S. Goodarzi, A. Seif, A.R. Azadmehr, *Superlattice. Microst.* 50 (2011) 26–39.
- [6] S.K. Jain, P. Srivastava, *Comp. Mater. Sci.* 50 (2011) 3038–3042.
- [7] J. Beheshtian, Z. Bagheri, M. Kamfiroozi, A. Ahmadi, *J. Mol. Model.* 18 (2012) 2653–2658.
- [8] G. Seifert, E. Hernandez, *Chem. Phys. Lett.* 318 (2000) 355–360.
- [9] H.S. Wu, F.Q. Zhang, X.H. Xu, C.J. Zhang, H. Jiao, *J. Phys. Chem. A* 107 (2003) 204–209.
- [10] Y.R. Hacoheh, E. Grunbaum, R. Tenne, J.L. Hutchison, *Nature* 395 (1998) 336–337.
- [11] Y. Feldman, E. Wasserman, D.J. Srolovitz, R. Tenne, *Science* 267 (1995) 222–225.
- [12] C. Balasubramanian, S. Belluci, P. Castrucci, M.D. Crescenzi, S.V. Bhoraskar, *Chem. Phys. Lett.* 383 (2004) 188–191.
- [13] L. Bourgeois, Y. Bando, W.Q. Han, T. Sato, *Phys. Rev. B* 61 (2000) 7686–7691.
- [14] D.A. Neumayer, J.G. Ekerdt, *Chem. Mater.* 8 (1996) 9–25.
- [15] W.H. Goh, G. Patriarche, P.L. Bonanno, S. Gautier, T. Moudakir, M. Abid, G. Orsal, A.A. Sirenko, Z.H. Cai, A. Martinez, A. Ramdane, L. Le Gratiot, D. Troadec, A. Soltani, A. Ougazzaden, *J. Cryst. Growth* 315 (2011) 160–163.
- [16] E. Silva Pinto, R. de Paiva, L.C. de Carvalho, H.W.L. Alves, J.L.A. Alves, *Microelectr. J.* 34 (2003) 721–724.
- [17] N.G. Chopra, R. J. Luyken, K. Cherrey, V. H. Crespi, M.L. Cohen, S.G. Louie, A. Zettl, *Science*, 269 (1995) 966.
- [18] I. Narita, T. Oku, *Diamond Relat. Mater.*, 12 (2003) 1146.
- [19] S. Iijima, C. J. Brabec, A.Maiti, J. Bernholc, *J. Chem. Phys.*, 104 (1996) 2089.
- [20] D. Golberg, Y. Bando, O. Stephan, K. Kurashima, *Appl. Phys. Lett.*, 73 (1998) 2441.
- [21] D. Golberg, Y. Bando, K. Kurashima, T. Sato, *Scr. Mater.*, 44 (2001) 1561.
- [22] D. B. Zhang, E. Akatyeva, T. Dumitrica, *Phys. Rev., B* 84 (2011) 115431.
- [23] T. Oku, A. Nishiwaki, I. Narita, M. Gonda, *Chem. Phys. Lett.* 380 (2003) 620.
- [24] M. Neek-Amal, J. Beheshtian, A. Sadeghi, K. Michel, F.M. Peeters, *J. Phys. Chem. C* 117 (2013) 13261–13267.
- [25] D. Kohl, *J. Phys. D34* (2001) R125–R149.
- [26] A. Dubbe, *Sens. Actuators B* 88 (2003) 138 – 148.
- [27] Q. Wan, Q.H. Li, Y.J. Chen, T.H. Wang, X.L. He, J.P. Li, C.L. Lin, *Nature* 424 (2003) 171–174.
- [28] H. Ullah, K. Ayub, Z. Ullah, M. Hanif, R. Nawaz, A.A. Shah, S. Bilal, *Synth. Met.* 172 (2013) 14–20.
- [29] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G.A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H.P. Hratchian, A.F. Izmaylov, J. Bloino, G. Zheng, J.L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J.A. Montgomery Jr., J.E. Peralta, F. Ogliaro, M. Bearpark, J.J. Heyd, E. Brothers, K.N. Kudin, V.N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J.C. Burant, S.S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J.M. Millam, M. Klene, J.E. Knox, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, R.L. Martin, K. Morokuma, V. G. Zakrzewski, G.A. Voth, P. Salvador, J.J. Dannenberg, S. Dapprich, A.D. Daniels, Ö. Farkas, J.B. Foresman, J.V. Ortiz, J. Cioslowski, D.J. Fox, Gaussian, Gaussian Inc., Wallingford, CT, (2009).
- [30] S. Kozuch, J.M.L. Martin, *J. Chem. Theory Comput.* 9 (2013) 1918.
- [31] M.D. Esrafil, R. Nurazar, *Comput. Mater. Sci.* 92 (2014) 172.
- [32] M.W. Schmidt, K.K. Baldrige, J.A. Boatz, S.T. Elbert, M.S. Gordon, J.H. Jensen, S. Koseki, N. Matsunaga, K.A. Nguyen, S.J. Su, T.L. Windus, M. Dupuis, J.A. Montgomery, *J. Comput. Chem.* 14 (1993) 1347–1363.
- [33] F. Weinhold, C.R. Landis, *Discovering Chemistry With Natural Bond Orbitals*, John Wiley & Sons, (2012).
- [34] Z. Jin, Y. Su, Y. Duan, *Sens. Actuators B.* 72 (2001) 75–79.
- [35] N. O’Boyle, A. Tenderholt and K. Langner, cclib: A library for package independent computational chemistry algorithms. *J. Comput. Chem.* 29 (2008) 839–845.
- [36] Javad Beheshtian, Zargham Bagheri, Mohammad Kamfiroozi, Ali Ahmadi, *Microelectr. J.* 42 (2011) 1400–1403.
- [37] Bulat FA, Toro-Labbe A, Brinck T, Murray JS, Politzer P Quantitative analysis of molecular surfaces: areas, volumes, electrostatic potentials and average local ionization energies. *J. Mol. Model.* 16 (2010) 1679–1691.
- [38] S.S. Li, *Semiconductor physical electronics*, 2nd edn. Springer, Heidelberg (2006).