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Electronic Properties Calculation of CO and NO Adsorbed on BN Nanolayer, using Density Function Theory DFT

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Abstract: The properties of adsorption of monolayer hexagonal boron nitride were studied using Functional Density Theory (DFT). Where, the process of adsorption of gas with BN-sheet in different locations and studied the electronic characteristics such as the total energy, adsorption energy, the energy gap, density of state, HOMO AND LUMO. The results show that all adsorption of CO and NO on BN-sheet is weak physisorption indicating that BN-sheet could be a good CO or NO sensor to detect these gases at these sites, except in site F2 where the adsorption of NO on BN-sheet is a strong chemisorption. We can distinguish which of the adsorbate molecules is acting as acceptor or donor. This research show that the sensitivity of graphene based chemical gas sensors could be drastically improved by introducing appropriate dopant or defect.

Key words: Fullerene, gas adsorption, density functional theory, HOMO and LUMO, energy gap, physisorption

INTRODUCTION

Single layer of hexagonal Boron Nitride (BN) and graphene from two-dimensional crystals have lately been invented (Novoselov *et al*., 2005). Among them, only graphene has been studied extensively (Geim and Novoselov, 2002). Unlike graphene, 2-Dimensional (2D) graphenelike BN (Blase *et al*., 1995) is a wide forbidden energy gap semiconductor and is a hopeful material in optics and opto-electronics (Watanabe *et al*., 2004). Graphene was discovered in late 2004 at the focus for mesoscopic and nanotechnology directed by Novoselov *et al*. (2004). After the successful synthesis of graphene followed by a surge of studies novel two dimensional materials, a daunting quest was to obtain hexagonal Boron Nitride (BN).

Boron nitride is a dual chemical compound consisting of equal numbers of atoms of boron and nitrogen. The hexagonal structure of boron nitride is geometrically similar to that of graphite in carbon structures (Pease, 1952; Geick *et al*., 1966), since, in the periodic table, boron and nitrogen are neighboring to carbon (Pease, 1952). It is second only to diamond in hardness. Boron-Nitride (BN) in ionic honeycomb lattice which is the group 3-5 analogue of graphene has also been produced having desired insulator characteristics. Nevertheless, unlike the delocalized π electrons in graphite, the π electrons in BN are distributed more around N because of its stronger electronegativity. This strong directional effect of bonding confines the motion of the π electrons and thus results in a gap in h-BN. BN is the lightest 3-5 compound of those that are isoelectronic with 3-5 semiconductors such as GaAs but with a wider band gap with ionic bonding through significant charge transfer from B to N., i.e., Eg (BN) = 4.0-5.8 eV at temperature 25°C (Geick *et al*., 1966), compared with 1.42 eV of GaAs. Otherwise, it is think that the large forbidden gaps in this material may produce better electronic properties than those of carbon structures (Levinshtein *et al*., 2001).

MATERIALS AND METHODS

Computational details DFT: Our calculations are based on the use of DFT were performed using Gaussian 09 package (Rubio *et al*., 1994) with the Becke-three parameter density functional with Lee-Yang-Parr correlation functional (B3LYP) (Politzer and Seminario, 1995) was used with the 6-31G (d, p) basis sets progressively in order to save computation time.

Table 1 shows there are a difference between the HOMO and the LUMO energies of BN-sheet. The deduced values of Ionization Potential (IP), Electron Afinity (EA) are calculated by HOMO and LUMO energy, the IP, EA and Fermi Energy (E_F) for BN-sheet. The Energy gap (E_g) plays crucial role in the properties of a solid. Figure 1 shows the structure of pristine BN-sheet that is used in the present study, one can see from the figure that the structure of zigzag BN-sheet contains 32 atoms (16 boron+16 nitrogen). The optimized bond lengths for B-N are 1.40 Å for zigzag BN-sheet. These values are in agreement with other calculations for Boron/Nitrogen (BN) hybrid (Drissi *et al*., 2012). On the other hand, the B3LYP/6-31G (d, p) basis set is used for

Table 1: The structural and electronic properties of pristine BN-sheet

Properties	BN-sheet
E_{Tot}	-33047.9320
E_g	1.8060
IP = (-HOMO)	6.1331
EA = (-LUMO)	4.3260
E_F	-5.2290

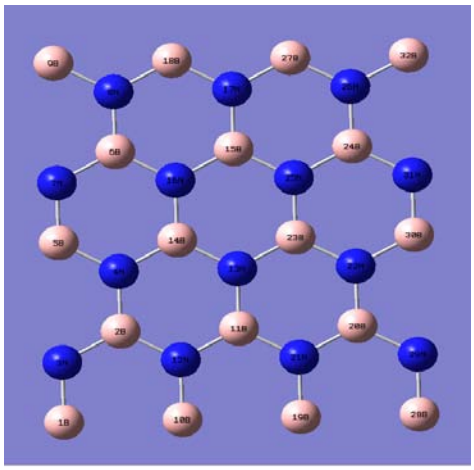

Fig. 1: Geometric structures of the BN-sheet

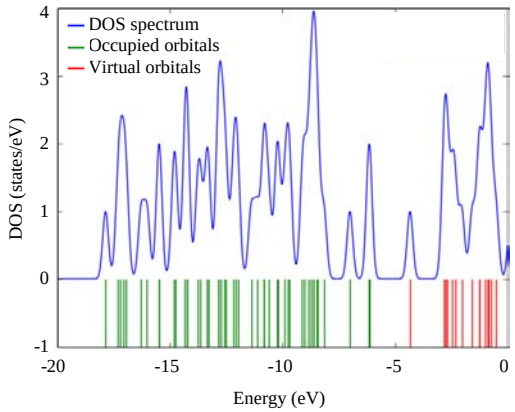

Fig. 2: Density of states (DOS) of BN-sheet

optimizations of the adsorption effect of CO and NO molecules on zigzag BN-sheet. The B3LYP/6-31G (d, p) is a reliable and commonly used level of theory for nanotube structures (Gan and Zhao, 2009; Ahmadi *et al*., 2012). We calculate the chemical potential or fermi Energy (E_F) of the complexes as given:

$$E_F = E_{HOMO} + E_{LUMO}/2 \quad (1)$$

Where:

E_{HOMO} = The Energy of the Highest Occupied Molecular Orbital

E_{LUMO} = The Energy of the Lowest Unoccupied Molecular Orbital

The energy gap in energy levels (E_g) of a system is defined as $E_g = E_{LUMO}-E_{HOMO}$. The adsorption Energy (E_{ads}) is estimated using the following approximate expression:

$$E_{ads} = E_{COMPLEX} - \left(E_{BN-Sheet} + E_{gas}\right) \quad (2)$$

Where:

$E_{COMPLEX}$ = Corresponds to the BN-sheet/gas complex in which the gas molecule has been adsorbed on the surface of BN-sheet

$E_{BN\text{-}sheet}$ and E_{gas} = The energy of the isolated BN-sheet and gas molecule

Figure 2 illustrated the density functional at 6-31G (d. p) basis set to investigate the adsorption effect of gas molecules CO and NO effect on the electronic structure BN-sheet.

RESULTS AND DISCUSSION

Electronic structure of pristine BN-sheet: Table 1 listed the calculated structural and electronic properties of BN-sheet. The HOMO is the orbital that primarily acts as an electron donor and the LUMO is the orbital that mostly acts as the electron acceptor play a significant role for Density of States (DOS) of BN-sheet. The highest number of degenerate states in the conduction and valence bands are shown as follows: 4 for Pristine BN-sheet, respectively. Since, that all Density of States (DOS) there are many main peaks, there are states available for occupation at high DOS for a specific energy level and no states can be occupied at a zero-density of states for energy level.

BN-sheet with CO and NO gas molecules adsorption: In order to find the favorable adsorption configuration, a comprehensive study on the adsorption of gas molecules (CO and NO) on BN-sheet is placed at two different occupation sites: The top (S1) site directly above the boron atom, top (S2) site directly above the nitrogen atom of CO gas molecule, the top (F1) site directly above the boron atom, top (F2) site directly above the nitrogen atom of NO gas molecule as shown in Fig. 3. Its known that CO is a non-disturbing and colorless gas when it enters the body of human, CO combines with blood haemoglobin that prohibit the union of oxygen and haemoglobin, leading to body tissue hypoxia and suffocation (Zhang *et al*., 2013).

The optimized adsorption structure of CO and NO adsorbed on BN-sheet is shown in Fig. 4, upon adsorption of CO and NO on BN-sheet, we find that C atom binds with the S1 site of BN-sheet with the C-B

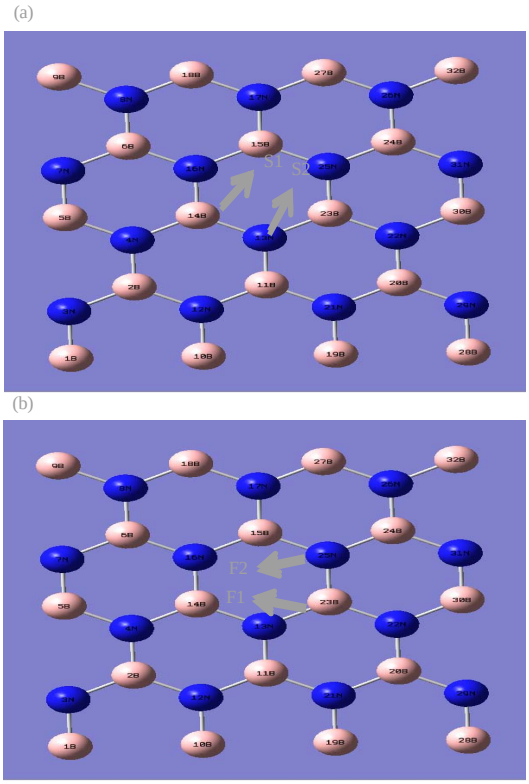

Fig. 3: The position of molecules on the BN-sheet; a) CO and b) NO

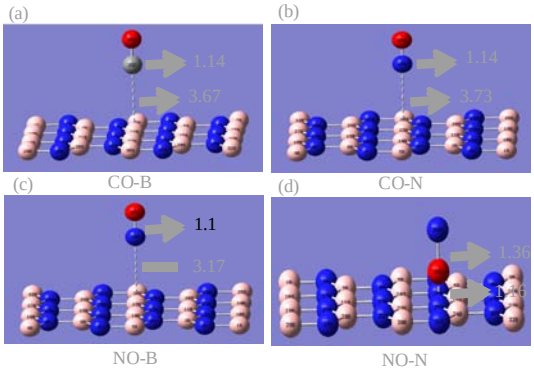

Fig. 4: Structural model of CO-BN-sheet and NO-BN-sheet adsorptive system; a) At site S1; b) At site S2; c) At site F1 and d) At site F2

of 3.17 Å while the N-C-O angle is 174.49, consistent with the other result (Imani *et al*., 2012; Jiang *et al*., 2015) mean while the bond length with S2 site N-C is 3.73 Å and the N-C-O angle is 165.8 , the bond length with F2 site O-N is 1.16 Å and the N-O-N angle is 180, consistent with the other result reported by Feng *et al*. (2014). If E_{ads}<0, the reaction is exothermic and spontaneous because the energy of the absorption system is less than the total energy of pristine BN-sheet and gas molecules. Greater

Table 2: Structural and electronic properties of adsorption of CO and NO molecule on BN-sheet

Properties	BN-sheet site S1	BN-sheet site S2	BN-sheet site F1	BN-sheet site F2
E_{Tot}	-36131.505	-36131.533	-36582.348	-36562.539
E_{ads}	-0.436	-0.464	-1.633	18.170
E_g	1.759	1.78	1.705	1.664
IP = (-HOMO)	6.067	6.062	6.048	6.369
EA = (-LUMO)	4.307	4.282	4.342	4.704
E_F	-5.187	-5.172	-5.195	-5.660

distance of 3.63 Å while the B-C-O angle is 172.8, N atom binds with the F1 site of BN-sheet with the N-B distance adsorption energy releases more energy during the reaction process. On the other hand, owing to the energy required when E_{ads}>0, it is comparatively difficult for the reaction to continue.

It can be noticed from Table 2, that the total energy of adsorbed BN-sheet are larger than those of pristine BN-sheet. The energy gap E_g of adsorbed BN-sheet are less than those of pristine BN-sheet. This indicates that E_g decreases with the adsorption of CO and NO to BN-sheet while the total energy increase (in magnitude) with increasing the number of atoms. The computed IP and E_F for adsorbed BN-sheet at sites (S1, S2, F1) are less than pristine. The computed EA for adsorbed BN-sheet at site (S1, S2) are less than pristine.

The adsorption energy of in site (F2) larger than 1 eV corresponding to strong chemisorption (Huang *et al*., 2008). The adsorption energy of BN-sheet at sites (S1, S2, F1) are less than 0.5 eV in agreement to weak physisorption to weak physisorption (Pashangpour, 2010). In general, the adsorption energy in the results indicate that BN-sheet is strongly reactive to NO in site F2, the adsorption energies in this site equal to 18.17 eV, corresponding to a strong chemisorption Therefore, due to gases slow desorption from BN-sheet, the BN-sheet is not suitable as the sensor of NO at site F2. Nevertheless, BN-sheet could catalyse or activate this adsorbate due to the strong interaction, suggesting the possibility of BN-sheet as a metal-free catalyst. For BN-sheet at sites (S1, S2, F1), the binding strength of CO and NO with BN-sheet is intermediate with the adsorption energy of -0.463, -0.464, -1.633 eV, respectively. Thus, BN-sheet can be used to detect CO and NO, since, the adsorption-desorption equilibrium of CO and NO BN-sheet at those sites is easily built.

Table 2 indicated that that E_{HOMO} and E_{LUMO} of pristine BN-sheet are larger than the CO and NO adsorption on BN-sheet except in some site. We found that high value of E_{HOMO} is -6.396 eV this value indicates a tendency of the molecule to donate electrons while the lower the value of E_{LUMO} is -4.282 eV this value indicate a tendency of the molecule to accept electrons.

Figure 5 shows that in the LUMO and HOMO lobes are concentrated around the atoms of the BN-sheet molecule near atom bind of the gas molecule.

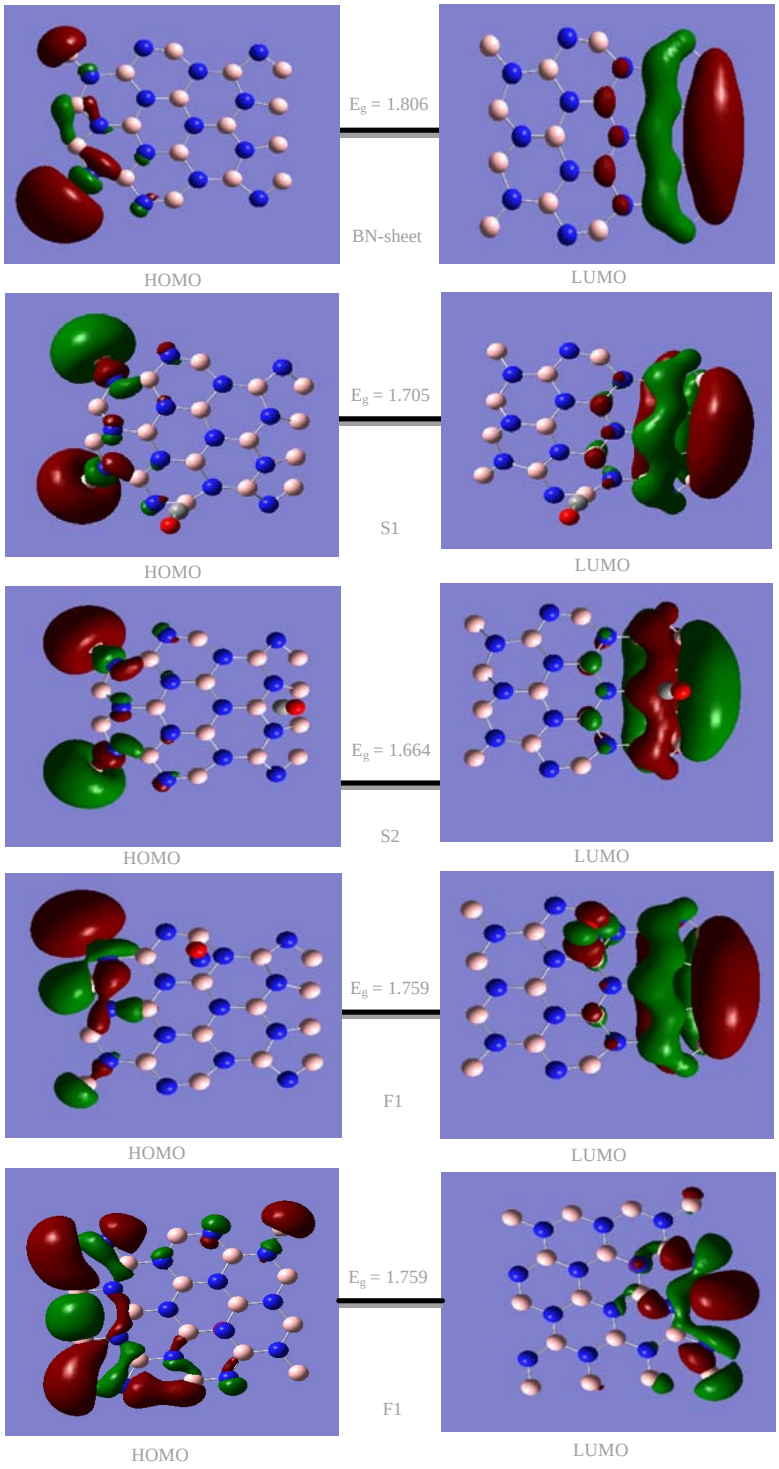

Fig. 5: The DFT calculation of HOMO and LUMO shapes for studied molecules

Figure 6 illustrated DOS of CO and NO adsorption on BN-sheet, the figure show that the DOS of BN-sheet with the adsorption of gas molecules are different from the corresponding pristine BN-sheet. In the adsorption of gas molecules CO and NO on BN-sheet, the highest of peaks becomes less at cases (c, d) in comparison with pristine BN-sheet, i.e., the conduction and valence bands are less with the highest number of density of states.

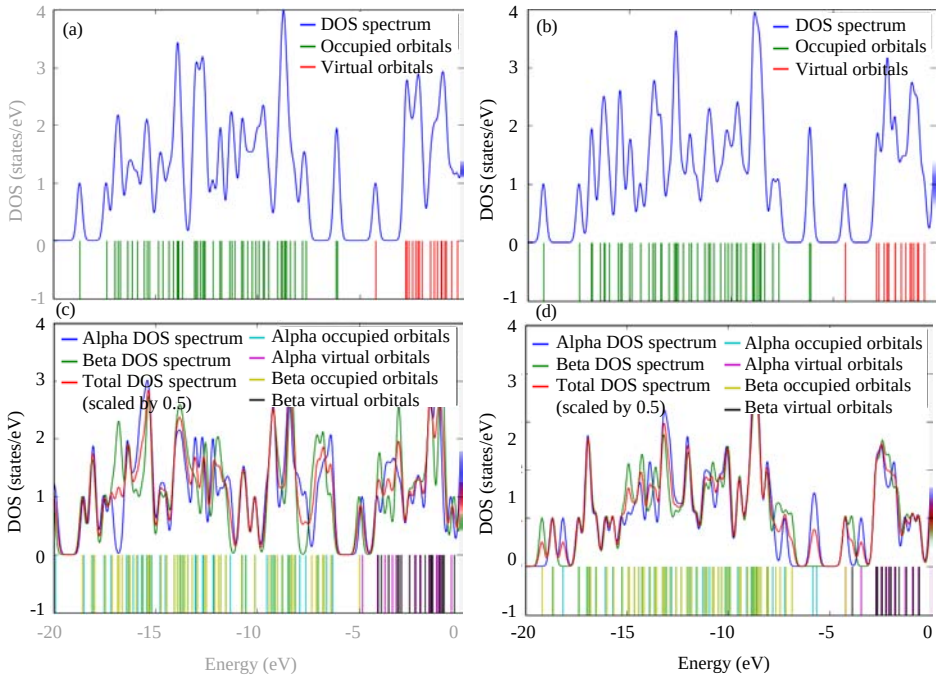

Fig. 6: Density of States (DOS) of CO and NO BN-sheet for: a) CO-B; b) CO-N; c) NO-B and d) NO-N

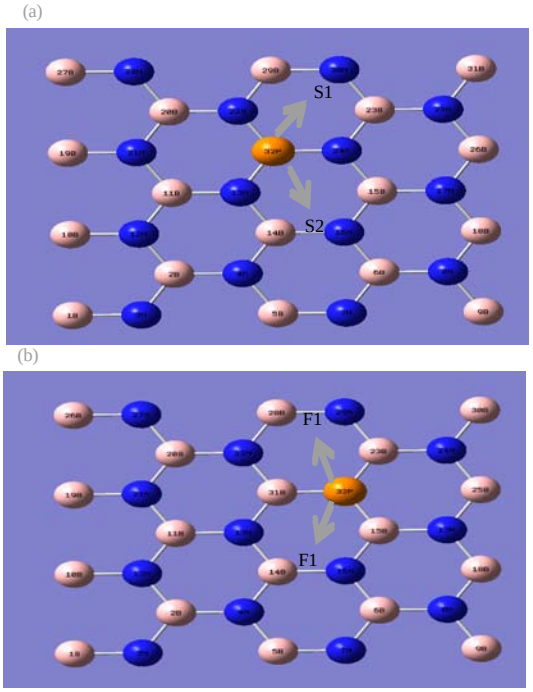

Fig. 7: The position of molecules on the BN-sheet: a) CO and b) NO

BN-sheet with CO and NO gas molecules adsorption: Figure 7 shows the most stable configuration are CO

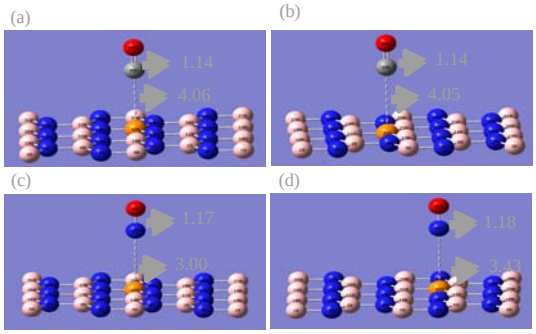

Fig. 8: Structural Model of CO-BN-sheet and NO-BN-sheet adsorptive system: a) At site S1; b) At site S2; c) At site F1 and d) At site F2

and NO gas molecule adsorbed on the surface of BN-sheet doping one atom from Phosphorus (P) in two sites. First site (S1), Phosphorus atom instead of boron atom of BN-sheet and in the second site (S2), Phosphorus atom instead of nitrogen atom of BN-sheet with CO gas molecules (Fig. 8). In the same way doped P atom in two sites (F1, F2) instead of boron atom from BN-sheet (F1) and nitrogen atom from BN-sheet (F2) and adsorbed with NO molecule gas.

The optimized adsorption structure of CO and NO adsorbed on BN-sheet is shown in Fig. 8, upon adsorption of CO and NO on BN-sheet, we find that P

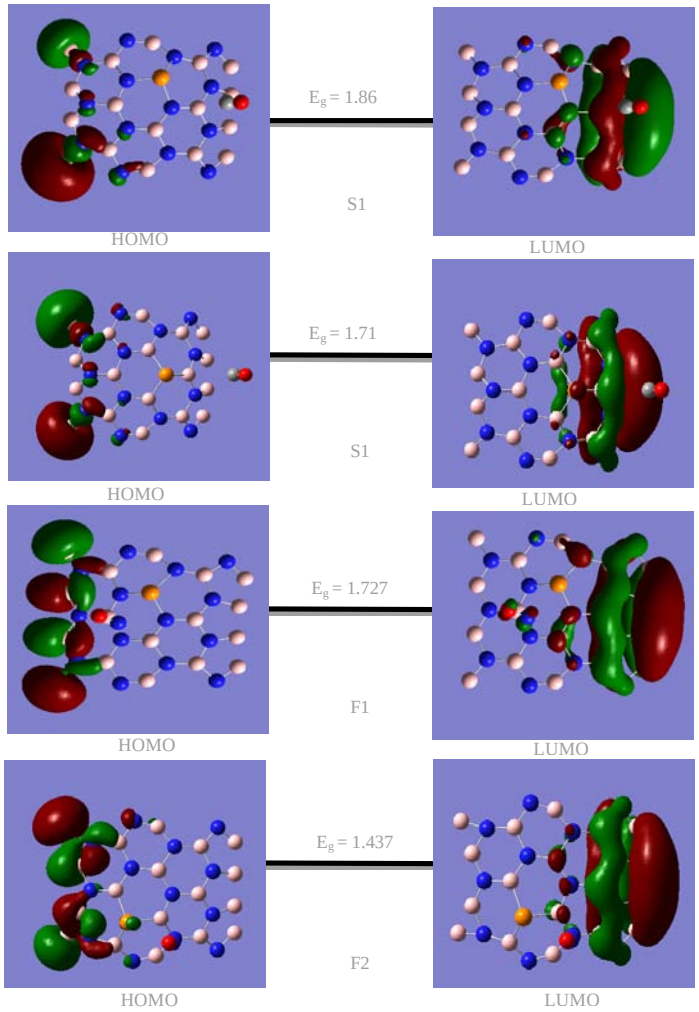

Fig. 9: The DFT calculation of HOMO and LUMO shapes for studied molecules

atom binds at site S1 with CO gas molecules of the P-C distance of 4.06 A° while the P-C- O angle is 149.92 and P atom binds at site S2 with CO gas molecules of the P-C distance of 4.05 A° while the P-C-O angle is 136.98. P atom binds at site F1 with NO gas molecule of the P-N distance of 3.00 A° while the P-N-O angle is 122.74 and P atom binds at site F2 with NO gas molecule of the P-N distance of 3.43 A° while the P-N-O angle is 119.43. The total energy of adsorbed BN-sheet are larger than those of pristine BN-sheet. The energy gap E_g of adsorbed BN-sheet are less than those of pristine BN-sheet, except in site S1 This indicates that E_g decreases with the adsorption of CO and NO to BN-sheet while the total energy increase (in magnitude) with increasing the number of atoms. The computed IP, EA and EF for adsorbed BN-sheet at sites (S1, F1, F2) are less than pristine.

The adsorption energy of BN-sheet at all sites are less than 0.5 eV in agreement to weak physisorption (Pashangpour, 2010). In general, the adsorption energies for BN-sheet at all sites (S1, S2, F1, F2), the binding strength of CO and NO with BN-sheet is intermediate with the adsorption energy of -30.503, -11.592, -31.427, -13.795 eV, respectively. Thus, BN-sheet can be used to detect CO and NO, since, the adsorption desorption equilibrium of CO and NO BN-sheet at those sites is easily built.

Table 3 indicated that that E_{HOMO} and E_{LUMO} of pristine BN-sheet are larger than the CO and NO adsorption on BN-sheet, except the E_{LUMO} in site S2. We found that high value of E_{HOMO} is -6.097 eV this value indicates a tendency of the molecule to donate electrons while the lower the value of E_{LUMO} is -4.217 eV this value indicate a tendency of the molecule to accept electrons.

Figure 9 shows that in the LUMO and HOMO lobes are concentrated around the atoms of the BN-sheet molecule near atom bind of the gas molecule, except the HOMO at sites S1, S2 concentrated the atoms of the

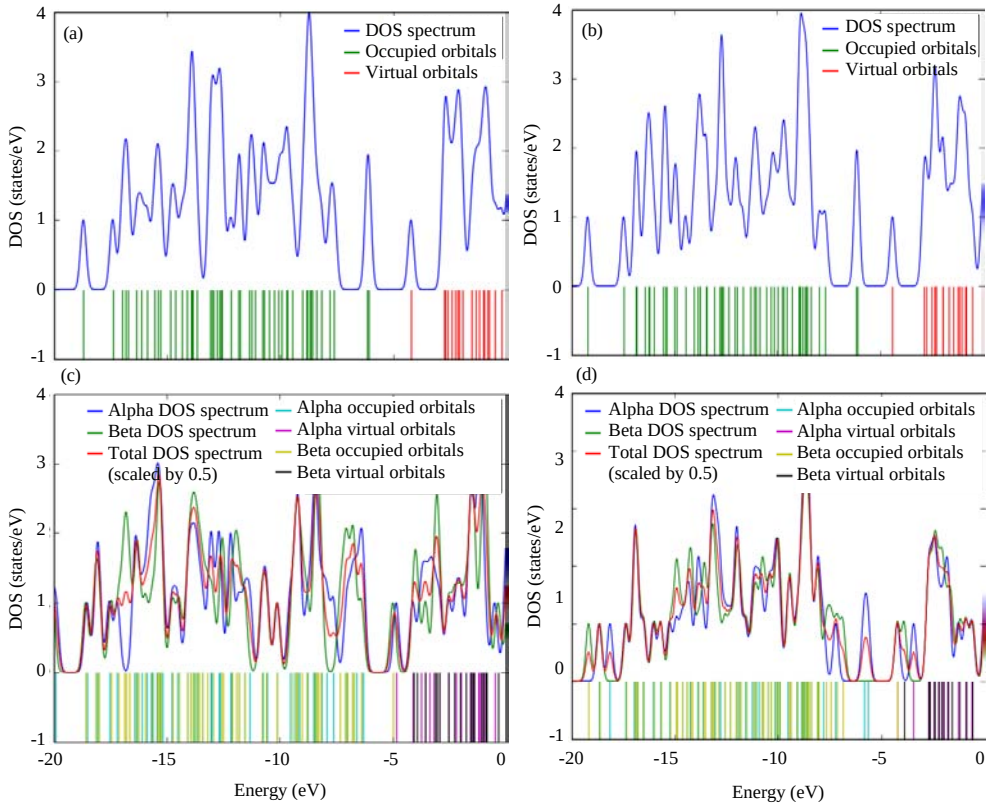

Fig. 10: Density of States (DOS) of CO and NO BN-Sheet for: a) CO-P-B; b) CO-P-N; c) NO-P-B and d) NO-P-N

Table 3: Structural and electronic properties of adsorption of CO and NO molecule on BNP-sheet

Properties	BN-sheet site S1	BN-sheet site S2	BN-sheet site F1	BN-sheet site F2
E_{Tot}	-44740.423	-43927.007	-45190.993	-44378.856
E_{ads}	-30.503	-11.592	-31.427	-13.795
E_g	1.860	1.710	1.727	1.430
IP = (-HOMO)	6.081	6.097	5.994	5.648
EA = (-LUMO)	4.217	4.386	4.266	4.217
E_F	-5.149	-5.241	-5.130	-4.932

BN-sheet molecule out of atom bind of the gas molecule. Figure 10 illustrated DOS of CO and NO adsorption on BN-sheet, the figure show that the DOS of BN-sheet with the adsorption of gas molecules are different from the corresponding pristine BN-sheet. In the adsorption of gas molecules CO and NO on BN-sheet, the highest of peaks becomes less at cases (c, d) in comparison with pristine BN-sheet, i.e., the conduction and valence bands are less with the highest number of density of states.

CONCLUSION

We explore the adsorption of CO and NO on the surface of Pristine PN-sheet and doping PN-sheet by DFT calculation at B3LYP/6-31G (d, p) level of theory. In general, the adsorption energy in the results indicate that Pristine PN-sheet is strongly reactive to NO in site F2 because gases slow desorption from Pristine PN-sheet, the Pristine PN-sheet is not suitable as the sensor of NO. However, Pristine PN-sheet could catalyse or activate this adsorbate due to the strong interaction, suggesting the possibility of Pristine PN-sheet as a metal-free catalyst. For Pristine PN-sheet at sites (S1, S2, F1) can be used to detect CO, since, the adsorption-desorption equilibrium of CO, on Pristine PN-sheet and at this sites is easily built (the adsorption energy = (-0.436, -0.464, -1.633 eV), respectively. The adsorption energy for all adsorption of CO and NO on doping PN-sheet is a weak physisorption in all sites (S1, S2, F1, F2). Thus, doping PN-sheet can be used to detect NO at this site.

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