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DENSITY FUNCTIONAL THEORY STUDY: ADSORPTION OF SMALL GAS MOLECULES ON ALUMINIUM PHOSPHORENE MONOLAYER

Abstract: *The B3PLYP functional and 6-31G (d, p) basis set calculations were used to investigate the sensitive properties of small toxic gas molecules (CO, CO_2, NO, NO_2) on an aluminum phosphorene monolayer. These gases, which play a significant role in environmental degradation. Adsorption energy, adsorption distance, and charge transfer parameters all supported us in determining the best adsorption point among three adsorption sites: Center, Al, and Bridge. We may infer from the adsorption energy and electron localization function results that these (CO, CO_2, NO and NO_2) gas molecules are chemically adsorbed on an aluminum phosphorene monolayer. Our findings also reveal that after adsorption, there is a significant amount of charge transfer between CO molecules and an aluminum phosphorene monolayer .This indicates that an aluminum phosphorene monolayer is more susceptible to CO, CO_2, NO and NO_2 adsorption than pristine and doped graphene. Furthermore, it is clear that small gas molecule adsorption will modulate the bandgap and work function of an aluminum phosphorene monolayer to varying degrees. Our research will provide theoretical direction for practical applications.*

Key words: *aluminium phosphorene, gas adsorption, DFT, HOMO, LUMO.*
Language: *English*
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Introduction

As a result of the rapid growth in modern chemical industries, the environment has become vulnerable to pollution as a result of toxic and dangerous gases (CO, CO_2, NO, NO_2) that factories emit in large quantities into the atmosphere, and this emission leads to problems including smog and acid rain in addition to other substances that are dangerous to humans and the environment. This is reflected in the ozone layer by depletion as a result of this, so it was necessary to find gas sensors to sense toxic gas particles and monitor air pollution[1,2,3].

To treat these problems, the researcher needs to search for this type of material that represents low energy consumption, fast response and high sensitivity to gases[4]. So we were found that two-dimensional monolayers possess a large surface area and these materials are from a new generation of sensors [5, 6], whereby examining monolayer graphene which shows good properties [7, 8], and

developing super-sensitive sensors based on theoretical and experimental studies [9].

AlP monolayer is a layer of aluminum and phosphorous atoms arranged in two dimensions, the thickness of which is equivalent to the diameter of a phosphorus atom or aluminium and its structure is hexagonal. AlP monolayer consists of aluminum and phosphorous atoms, which are arranged in a regular hexagonal network similar to compact bee houses and resemble graphene[1]. The aim of the current study is to find a gas sensor for toxic gases emitted using a monolayer AlP.

II. MODELING AND COMPUTATIONAL DETAILS

In this work, DFT calculations were completed using Gaussian 09 package [10]. This software package is using the standard and modern quantum mechanics basics and there are different types from these. The functional base set B3LYP / 6-31G (d, p) is used to make complete geometry optimizations of the absorption effect of single-layer AlP molecules on CO, CO_2, NO, and NO_2 gas[11]. The B3LYP / 6-31G functional level (d, p) is one of the theory levels commonly used for nanotube structures.[12]. The chemical potential or Fermi energy (E_F) of the complexes was obtained, as shown below:

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

Where:

-E_{HOMO}: is the energy of the higher occupied molecular orbital.

-E_{LUMO}: is the energy of the lower unoccupied molecular orbital.

In addition, the energy gap in the energy levels (for example) of the system is recognized as follows:

$$E_g = E_{LUMO} - E_{HOMO} \quad \text{..... (2)}$$

The adsorption energy (E_{ads}) was calculated using the following pretty close expression:

$$E_{ads} = E(COMPLEX) - (E(MOLECULE) + E(GAS)) \quad \text{..... (3)}$$

Where:

- E(COMPLEX): The actual molecule energy with gas adsorption.
- E(MOLECULE): The total energy without absorption of the studied molecule.
- E(GAS): Gas molecule's total energy [13].

III. RESULTS AND DISCUSSIONS

1. Adsorption configurations

The AlP monolayer has a single layer, as seen in Fig. 1. There are three types of adsorption sites in the AlP monolayer. The distance between the AlP substrate and the gas molecules is initially set to 2.5 Å. Furthermore, the gas molecule's original orientation is perpendicular to the substrate.

As gas molecules are absorbed in various configurations, several insertion geometries have to be considered. To that end, one (NO, NO_2, CO, and CO_2) gas molecule at a distance from 2.5 Å over Al atom, center and bridge. On the other hand, one original orientation of the triatomic (NO_2), CO_2 is taken into account. The N molecular atom points to Al in the first direction towards the Al-P bridge in the second direction, towards the central ring in the third direction while the C atoms of CO_2 point towards the AlP layer in the same directions. All systems can then relax completely.

The molecules' absorption energies will be used to determine how they interact with the AlP layer. Based on the equation. The higher the adsorption of gas molecules onto the AlP, the lower the Ead value. For further research, the most energy-appropriate adsorption configurations are selected.

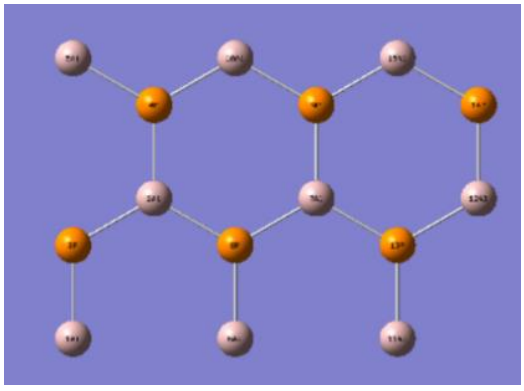


Fig. 1. Geometric structures of AlP monolayer.

After improving the geometry, the adsorption energy (E_{ads}), electronic properties of the studied molecules such as HOMO, LUMO, total energy (E_{tot}), energy gap (E_g) and Fermi Energy (E_F) were found as shown in Table 1.

Table 1: Structural and electronic properties of AlP monolayer.

Model	Site	HOMO	LOMO	E_g eV	E_F e.v
CO	Bridge	-0.19474	-0.15009	1.2149265	-4.69141215
	Al	-0.19472	-0.15003	1.2160149	-4.69032375
	Center	-0.2010	-0.13304	1.8491916	-4.5446142
CO_2	Bridge	-0.19344	-0.12136	1.9612968	-4.282854
	Al	-0.18334	-0.12698	1.5335556	-4.2219036
	Center	-0.19060	-0.13241	1.5833499	-4.39455105
NO	Bridge	-0.19434	-0.13129	1.7155905	-4.43019615
	Al	-0.1949	-0.15287	1.1436363	-4.73141085
	Center	-0.19363	-0.13222	1.6709661	-4.43318925
NO_2	Bridge	-0.17548	-0.13659	1.0581969	-4.2457123
	Al	-0.19563	-0.12327	1.9689156	-4.3386345
	Center	-0.18585	-0.14578	1.0903047	-4.5118261

Table 1 summarizes the adsorption energies of different gas molecules thought about in this work on AlP. We do not take into account the different orientations of adsorbed gas molecules since we are specifically interested in the influence of gas adsorption on the electronic structure of the AlP monolayer. The study of electronic structure, on the other hand, is virtually separate of direction and adsorption sites.

CO, CO_2, NO, and NO_2 adsorption energies, are much higher, indicating a good binding between these two molecules and the AlP layer.

Here, it is useful to compare the adsorption energy of these molecules in graphene as they have been shown to have excellent chemical sensing properties. The E_{ad} values are Studied to be 0.8-1.4 eV for CO on graphene-based on GGA functional. These results are less than those adsorbed on AlP as specific in Table 1. However, the E_{ad} values for NO and NO_2 on AlP are relevance. Q is defined as the total Mulliken charge on the molecules and negative number means charge move from AlP to molecule as shown in Table 2.

Table 2: Adsorption energies, adsorption height and transfer charges for adsorption configurations.

Model	Site	D °A	r °A	E_{ad} eV	Q |e|
CO	Bridge	3.214	3.54	-0.754	+0.19
	Al	2.165	3.54	-1.749	+0.18
	Center	1.946	3.54	-1.945	+0.2
CO_2	Bridge	2.276	3.54	-0.62	+0.27
	Al	2.89	3.54	-0.733	+0.3
	Center	1.962	3.36	-0.7 33	+0.3
NO	Bridge	1.950	3.39	-3.5	-0.2
	Al	2.002	3.39	-3.6	-0.3
	Center	1.937	3.39	-3.5	-0.2
NO_2	Bridge	1.974	3.39	-1.11	-0.2
	Al	1.889	3.39	-0.408	-0.1
	Center	1.919	3.39	-0.71	-0.1

1. CO **Adsorption on AlP monolayer.**

The CO gas molecule adsorption process on the AlP monolayer is examined. Fig.2 depicts the most robust adsorption structure of the CO-AlP complex. The CO molecule is positioned perpendicular to the AlP plane at different positions, namely the Al atom, the middle ring, and the Al-P bridge. Adsorption energies are -0.754, -1.749, and -1.945 eV, respectively. The mean atom-atom distance (C-Al bond length) between CO and AlP is 2.165,

which is less than the AL-C dimer bond length (3.54), and minimum distance of atom-atom from CO to the bridge Al-P is 3.214, which is less than the length of the AL-C dimer bond (3.54). The minimal atom-atom distance between the CO and the middle ring Al-P is 1.946, which is less than the length of the AL-C dimer bond (3.54). These findings indicate that the CO is chemically adsorbing on the AlP layer. The determined E_{ad} of CO on AlP is substantially greater than the values recorded for CO adsorption on AlP monolayer (0.112 eV), N-doped graphene (0.40 eV), and B-doped graphene (0.14 eV)[14]. Furthermore, the relationship of CO and AlP results in a charge shift of 0.2e from the AlP layer to CO. CO molecule's C and O atoms lose and gain electronic charges of 0.05 and 0.15e, respectively.

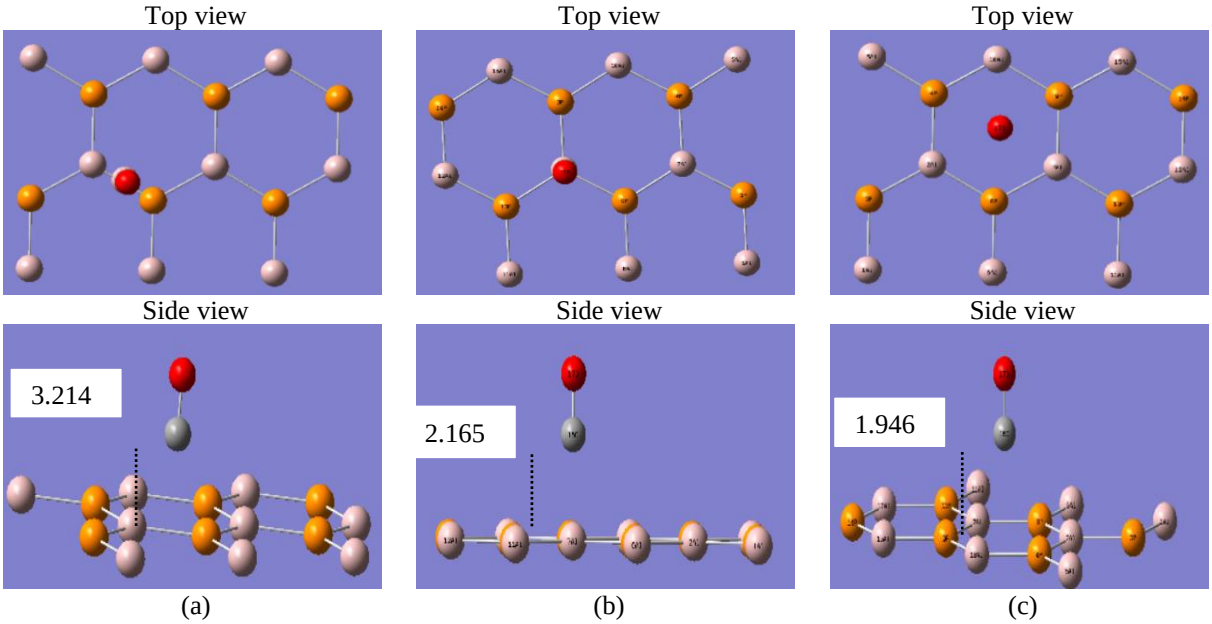


Fig.2: Top views and side views of most stable configurations of (a) bridge, (b) Al -atoms (c) center, AlP monolayer molecule adsorbed CO on the top site of AlP.

2. CO_2 **Adsorption on AlP monolayer.**

The mechanism of absorption of CO_2 on AlP is further complex than the else molecules studied. The AlP plates and the CO_2 molecule undergo significant structural variations upon adsorption on AlP.

Fig.3 represents the CO_2-AlP complex's most stable adsorption structure. The CO_2 molecule is vertical to the AlP plane at three points: the Al atom, the middle ring, and the Al-P bridge. The corresponding adsorption energies are -0.62, -0.733, and -0.733 eV. The average atom-atom distance (C-Al bond length) between CO and AlP is 2.8, which is less than the AL-C dimer bond length (3.54), and the minimum atom-atom distance between CO_2 and the bridge Al-P is 2.214, which is less than the AL-C dimer bond length (3.54). The atom-atom distance between CO_2 and the middle ring Al-P is 1.962, which is less than the length of the AL-C dimer bond (3.54). These results suggest that CO_2 is chemically adsorbing on the AlP substrate. Furthermore, the CO-AlP reaction causes the charge of 0.3e to be transferred from the AlP layer to the CO. The C and O atoms lose the CO molecule and gain an electrical charge of 0.05 and 0.25e, respectively.

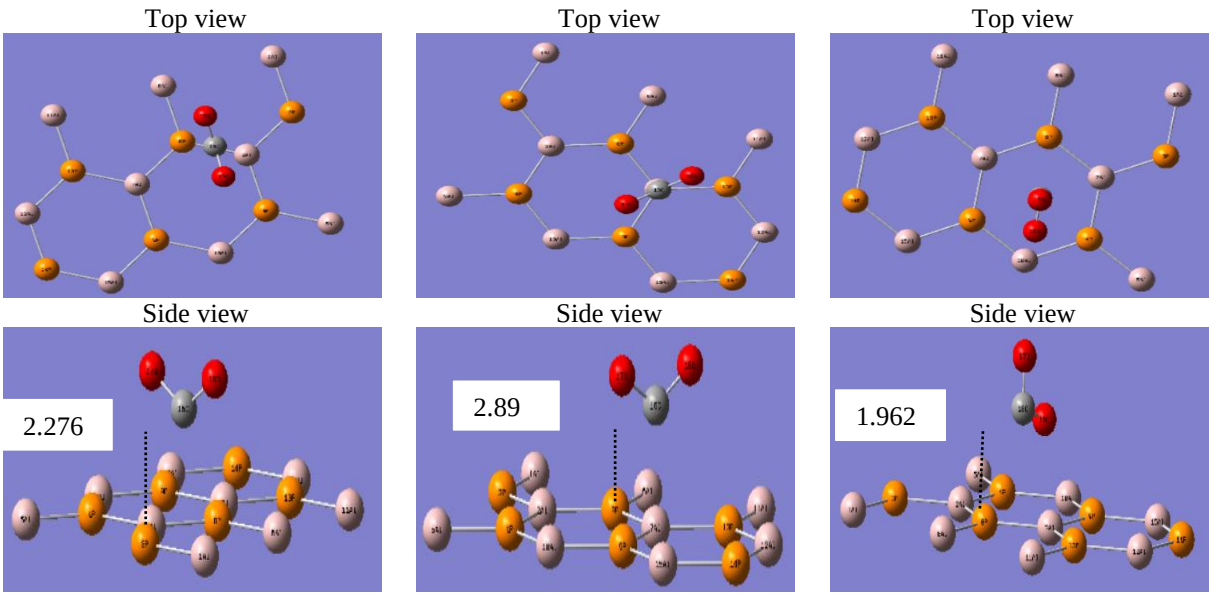


Fig.3: Top views and side views of most stable configurations of (a) bridge, (b) Al -atoms (c) center, AlP monolayer molecule adsorbed CO_2 on the top site of AlP.

3. NO Adsorption on AlP monolayer

When NO is exposed to the AlP layer, it adopts an oblique direction with respect to the level of AlP, seen in Fig. 3. The N atom of the NO atom indicates Al atom in the AlP. The angle of O-N-Al is 129.51 degrees. The interaction of the electron-lacking Al atom with the electron-donated N atom of NO results in a strong absorption energy of (-3.5 to -0.61)eV and the creation of a strong N-Al bond (2 Å), which implies that NO is a chemical adsorption on the AlP layer. It must be remembered that the distance of Al-N (2 Å) in NO-AlP complex is smaller than length of the Al-N bond, and the monolayer is completely different from that of graphene. For NO, the E_{ad} values on AlP were Specific to be 3.5-3.6 eV and are greater than those on graphene with 1.1-2.9 eV[14].

Demonstration of the covalent bonding amid AlP and NO Adsorption leads to a strong artificial pull between the molecule and its adsorbents. Table 1 summarizes the adsorption energies of the different structures. The adsorption energy obtained for NO on AlP is much higher than that recorded for native graphene (0.30eV) and N-doped graphene (0.40eV) [14]. It's also comparable with the NO absorption energy recorded on B-doped graphene (1.07 eV) [14]. When NO is absorbed onto the AlP sheet, a clear charge of 0.35e of NO is transferred to the AlP sheet.

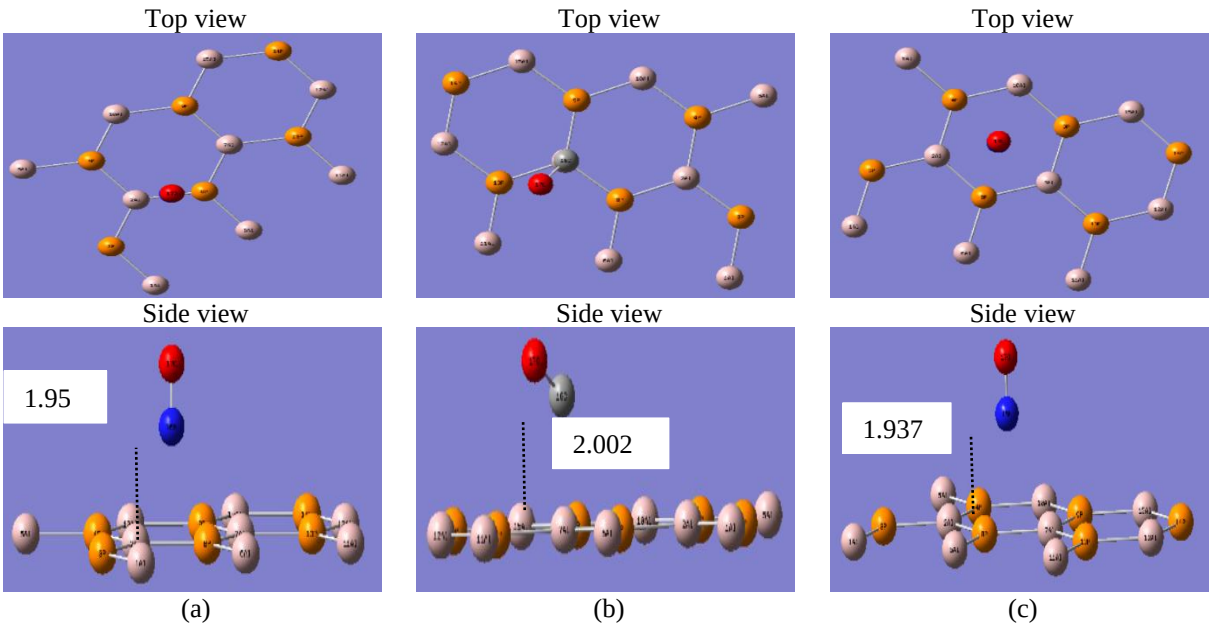


Fig.4: Top views and side views of most stable configurations of (a) bridge, (b) Al -atoms (c) center, AlP monolayer molecule adsorbed NO on the top site of AlP.

4. NO_2 **Adsorption on AlP monolayer**

The adsorption mechanism NO_2 over AlP is more complex than the other molecules considered above. Absorption on the AlP causes major structural modifications in both the AlP layer and the NO_2 molecule. The bond lengths N-O, NO_2 are increased isolated (1.21) to 1.79 and 3.11, this means that during absorption in the NO and O species the molecule is completely separated. N-O-N binding angle of NO_2 isolated decreases from 133.06 to 95.04 that after complexing with AlP. The atom of the O-molecule form a covalent bond of 1.38 and 1.40 length with the Al and P atoms in AlP sheet respectively..

The bond angle between Al -O- P is 100.68, the NO part of the NO_2 molecule, on the other hand, forms an N-P covalent bond with another Al atom in the same Al-p hexagon. The chemical absorption NO separated on AlP is very close to the NO molecule on the AlP layer. The O-N-Al angle is 130.15, and the N-Al bond thickness is 1.65. The NO_2 absorption energies on the AlP sheet, and the adsorption energy measured for NO_2-AlP is higher than that calculated for NO and CO molecules. Most interestingly, the E_{ad} scale of NO_2 on AlP is greater than that recorded for NO_2 absorption on graphene (0.48 eV). N-doped graphene (0.98 V), B-doped graphene (1.37 V)[14]. Furthermore, a large charge of 0.2 e of NO2 molecule is transferred to the AlP layer. This wide charge transfer corresponds to high NO_2 absorption energies over AlP.

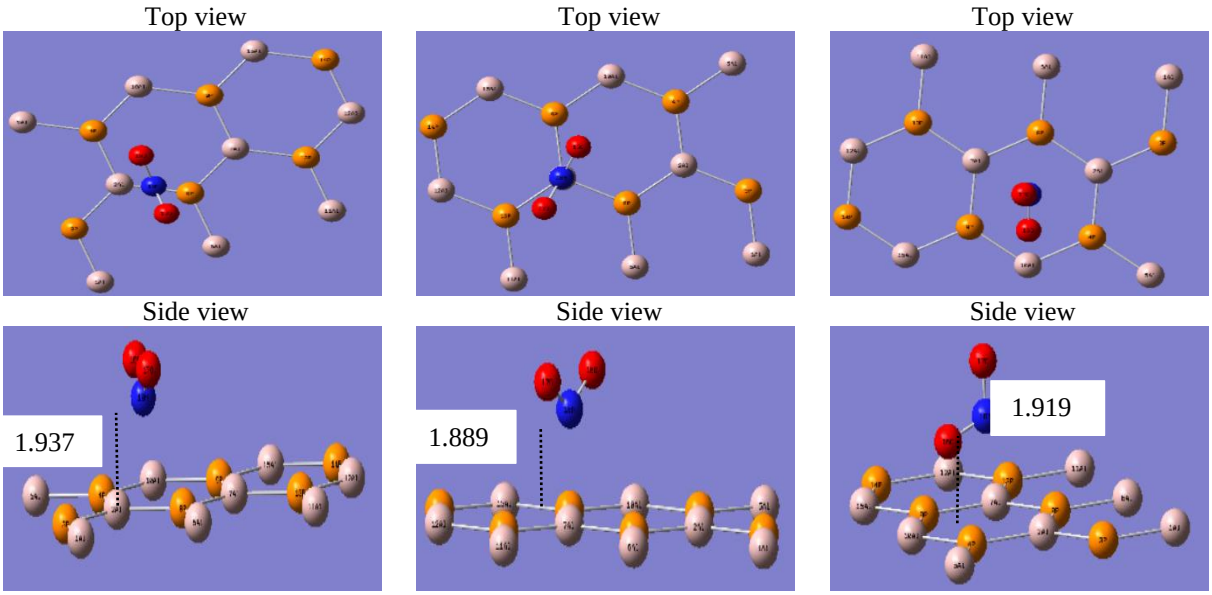


Fig.5: Top views and side views of most stable configurations of (a) bridge, (b) Al -atoms (c) center, AlP monolayer molecule adsorbed NO_2 on the top site of AlP.

The initial distance between the gas molecule and the substrate is set to 2.5 for each adsorption formation. The adsorption distance is calculated, which is defined as the shortest distance from atom to atom between the gas molecule and the substrate (see Fig.6). Adsorption distances of 1.95 on the bridge, 2.0 on the Al atom, and 1.93 in the center of the NO molecule of the system on the AlP layer.

For NO_2, adsorption distances of 1.97, 1.88, and 1.91 are calculated, respectively. The smaller the adsorption distance, the stronger the interaction. For CO, adsorption distances of 3.21, 2.16, and 1.94 are measured on the AlP layer, respectively. As a result, chemical bonds develop between the AlP layer structure and gas molecules. Chemical bonds form in the case of CO_2 gas molecule when the adsorption distances of 2.27 on the bridge, 2.0 on atom Al, and 1.96 in the middle are less than number of the corresponding atom covalent radii (3.54).

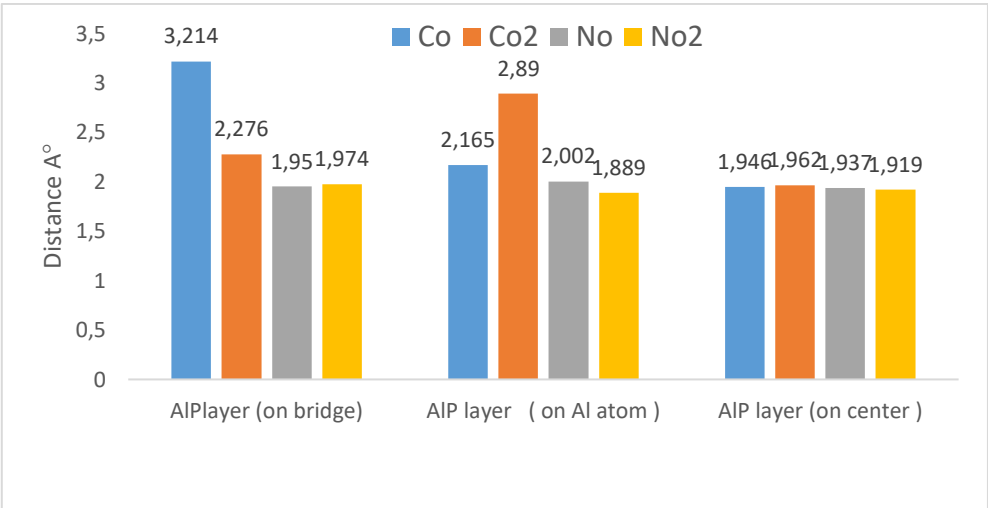


Fig. 6. The absorption distance of gas molecules on AlP layer system.

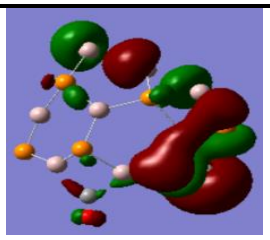
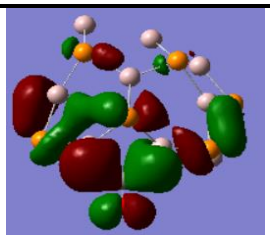
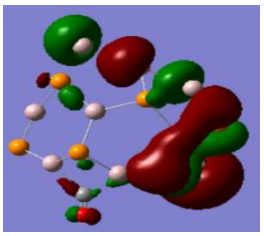
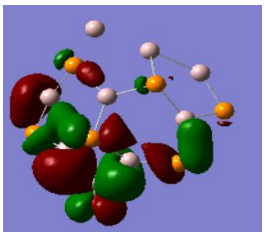
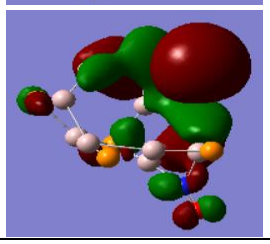
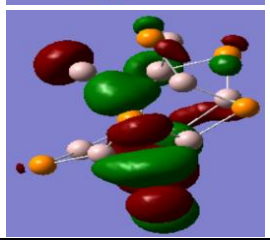
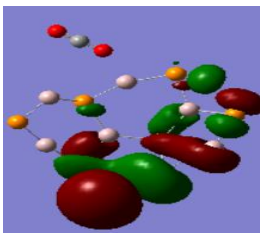
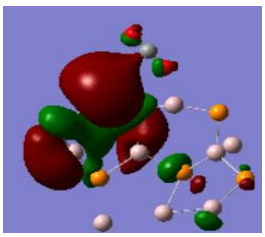
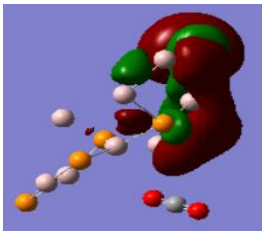
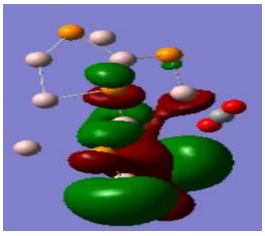
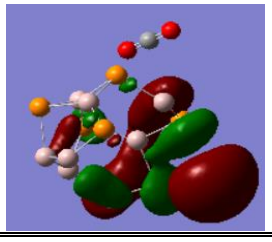
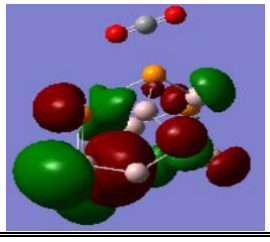
5. **The electronic structure of the AlP monolayer**

The HOMO and LUMO orbit are located next to the Fermi plane, which helped us know the acquaintance of electron states near the Fermi surface and the acquaintance from the transported electrons. Fig.7. shows the distribution of the HOMO and LUMO orbital. We found that the electron cloud distribution meaning in these two orbits is

concentrated in the edge region of pure graphene, where the electron states were mainly near the Fermi surface.

Fig.7. Demonstrates the HOMO and LUMO energies of the AlP mechanism after gas absorption. Because of the short absorption distance, high charge transfer, low absorption energy, CO_2, CO, NO, and NO_2 have no effect on the AlP system's E_f. gives that the Fermi level the same to the -4.69 eV Though there appears bandgap at the level of about 1.216 eV.

After CO absorption, the band structure is almost identical to that of AlP away from the Fermi level seen in Fig.7, a bandgap of about 1.22 volts appears after complete relaxation, and Fermi level is almost unchanged due to the valence electrons from the introduced Al atom are Below is a C atom, indicating that the atom can act as a p-type impure.

Model	Site	HOMO		LOMO
CO	Bridge		E_g eV 1.2149265	
	Al		E_g eV 1.2160149	
	Center		E_g eV 1.8491916	
CO_2	Bridge		E_g eV 1.9612968	
	Al		E_g eV 1.5335556	
	Center		E_g eV 1.5833499	

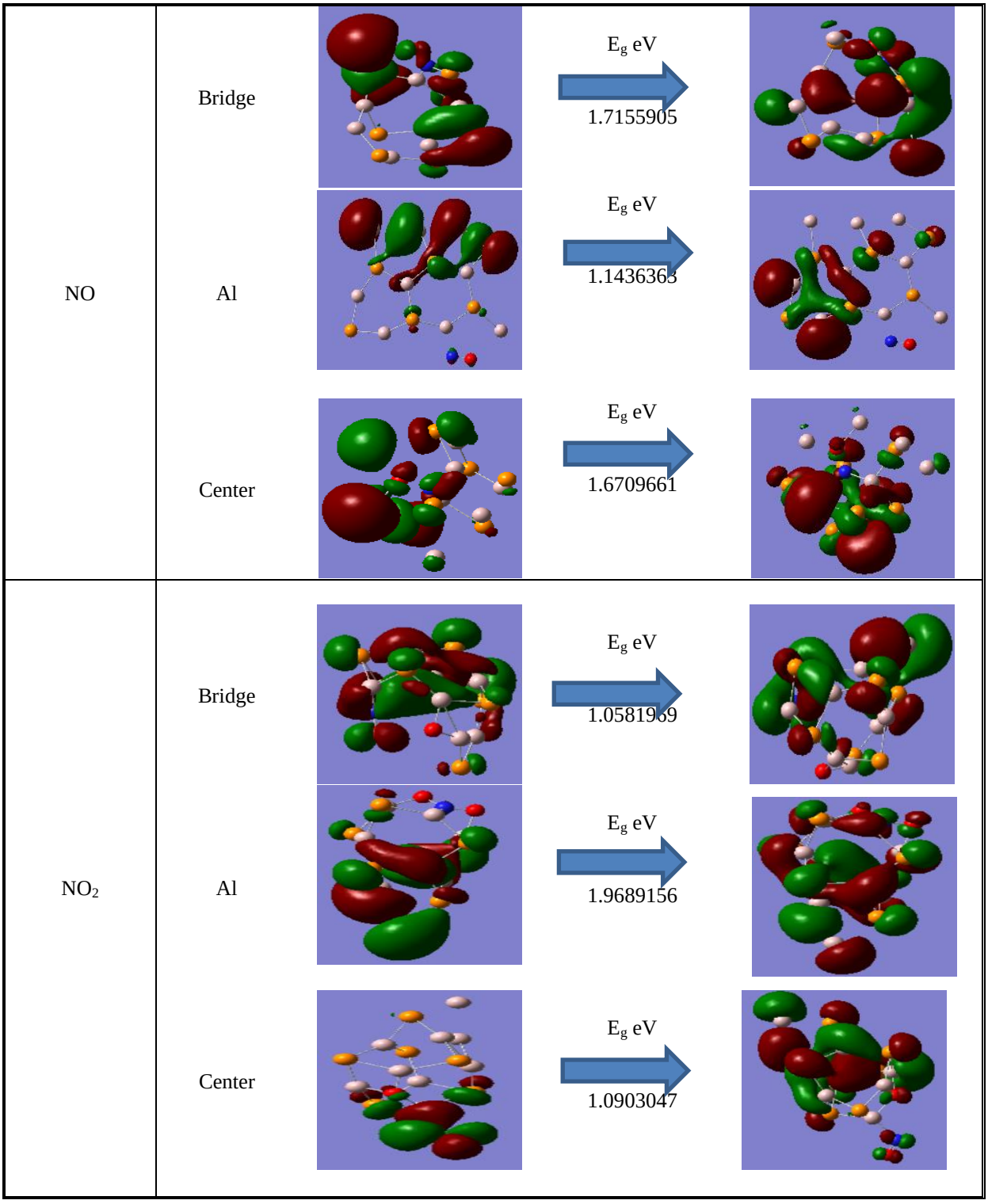


Fig.7: Shows the DFT calculation of HOMO and LUMO shapes for studied AlP monolayer adsorption molecules.

CONCLUSION

In summary, the results measured using DFT theory show that when exposed to normal and polluting gas molecules, the AlP monolayer displays various behaviors. The AlP monolayer has a higher affinity for CO_2, CO, NO, and NO_2 molecules. The chemical adsorption character of CO, CO_2, NO, and NO_2 adsorptions can be seen clearly with broad E_{ad}, charge transfer, and short adsorption distance. This suggests that AlP sheet are ideal for use as CO, CO_2, NO, and NO_2 gas sensors.

References:

1. Aghaei, S. M., Monshi, M. M., Torres, I., & Calizo, I. (2017). Adsorption and Dissociation of Toxic Gas Molecules on Graphene-like BC3: A Search for Highly Sensitive Molecular Sensors and Catalysts. *arXiv preprint arXiv*:1706.00774.
2. Leenaerts, O., Partoens, B., & Peeters, F. M. (2009). Adsorption of small molecules on graphene. *Microelectronics Journal*, 40(4-5), 860-862.
3. Schedin, F., Geim, A. K., Morozov, S. V., Hill, E. W., Blake, P., Katsnelson, M. I., & Novoselov, K. S. (2007). Detection of individual gas molecules adsorbed on graphene. *Nature materials*, 6(9), 652-655.
4. Sánchez, M., & Rincón, M. (2011). Ammonia Sensors Based on Composites of Carbon Nanotubes and Titanium Dioxide. *Carbon Nanotubes: Growth and Applications*, 457.
5. Novoselov, K. S., & Fal, V. I. (2012). ko, L. Colombo, PR Gellet, MG Schwab and K. Kim. *Nature*, 940, 192-200.
6. Klinovaja, J., & Loss, D. (2013). Spintronics in MoS 2 monolayer quantum wires. *Physical Review B*, 88(7), 075404.
7. Ganguly, S., & Ghosh, J. J. (1979). Steroid hormone induced alterations in endometrium: Part I--Changes in lipid content, swelling pattern & lipid peroxidation of mitochondria. *Indian journal of biochemistry & biophysics*, 16(2), 61-65.
8. Novoselov, K. S., Geim, A. K., Morozov, S. V., Jiang, D., Katsnelson, M. I., Grigorieva, I., ... & Firsov, A. A. (2005). Two-dimensional gas of massless Dirac fermions in graphene. *nature*, 438(7065), 197-200.
9. Schedin, F., Geim, A. K., Morozov, S. V., Hill, E. W., Blake, P., Katsnelson, M. I., & Novoselov, K. S. (1971). Acute toxic effects of drug abuse: Diagnosis and treatment. *J. Fla. Med. Assoc*, 58(4), 41-42.
10. Gaussian09, R. A. (2009). 1, mj frisch, gw trucks, hb schlegel, ge scuseria, ma robb, jr cheeseman, g. Scalmani, v. Barone, b. Mennucci, ga petersson et al., gaussian. Inc., *Wallingford CT*, 121, 150-166.
11. Politzer, P., & Seminario, J. M. (Eds.). (1995). *Modern density functional theory: a tool for chemistry*. Elsevier.
12. Beheshtian, J., Kamfiroozi, M., Bagheri, Z., & Ahmadi, A. (2011). Computational study of CO and NO adsorption on magnesium oxide nanotubes. Physica E: *Low-dimensional Systems and Nanostructures*, 44(3), 546-549.
13. Aghaei, S. M., Monshi, M. M., Torres, I., & Calizo, I. (2017). Adsorption and Dissociation of Toxic Gas Molecules on Graphene-like BC3: A Search for Highly Sensitive Molecular Sensors and Catalysts. *arXiv preprint arXiv*:1706.00774.
14. Zhang, Y. H., Chen, Y. B., Zhou, K. G., Liu, C. H., Zeng, J., Zhang, H. L., & Peng, Y. (2009). Improving gas sensing properties of graphene by introducing dopants and defects: a first-principles study. *Nanotechnology*, 20(18), 185504.