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**A COMPARATIVE DENSITY FUNCTIONAL STUDY OF CARBON DIOXIDE AND**  
**METHANE ADSORPTION ON DOPED GRAPHENE MODELS**

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**ABSTRACT**

The present work highlights the theoretical study that confirms the doping effect which can be used to make efficient gas sensors for the two most highly toxic gases carbon dioxide and methane. In this work the three doped models of graphene were considered: Boron doped graphene, Nitrogen doped graphene, and Silicon doped graphene. Density functional theory calculations were performed to evaluate the binding energy for the so formed complex systems. The present study also shows that there is no significant variation in the HOMO LUMO gap however it is well known that with doping, the band gap can be tuned.

**Keywords:** *Density functional theory, gas sensors, doped graphene.*

**I. INTRODUCTION**

In order to detect the toxic gases that are a great threat for the organic life, gas sensors play a very crucial role.[1] Global climates, ozone layer and the human health are very much influenced by the excessive release of the gaseous pollutants that come from the automobiles and industries at a large degree that spreads into the environment. Hence to control such situation, the gas sensors are looked upon with a lot of hope that enable us to know the detection level of such harmful gases in air. Owing to its outstanding stability and surface reactivity in ambient conditions, gas sensors based on the semiconductor are exceptionally demanding in the present era. The main aim of such semiconductor based gas sensors is to not only detect these toxic gases but also to identify the trace amount of these gases because of its higher sensitivity and selectivity. These metal oxide based semiconductor gas sensors are efficient[2-5] but they are not ecofriendly.[6] Hence it can be concluded that the two dimensional semiconducting material show outstanding properties like surface, optical and electrical could be the most reliable gas sensing material.

With the largest surface area (3000 m<sup>2</sup> per gram), graphene is known as the thinnest and mechanically the strongest material [7-9]. This wonder material owing to its astounding properties like mechanical, electrical, and optical properties[10-12], high surface area, high electrical and thermal conductivities, and low Johnson noise[13-15] has become a word of mouth among the researchers. There is a wide range of applications for which graphene can be used like, hydrogen-storage materials, electrodes, solid-state gas sensors, biosensors, and catalysis etc.

It was way back in 1947, that the single layer of graphene and its important properties were proposed theoretically.[16,17] But 40 years later, it was synthesized and showed the identical electronic properties as proposed earlier.[18,19] This clearly portrays the relevance of the theoretical studies in the prediction of new structures and the properties associated with it. Many researchers had a common belief that graphene due to its extra ordinary properties could behave as a suitable candidate for sensor application. Shedin et al. [20] confirmed that with the help of graphene the detection of all the individual events can be recorded when gas molecules are adsorbed or desorbed from its surface. The local carrier concentration gets changed when the small gas molecule are adsorbed thereby leading to a change in the resistance. Graphene is a low noise material that can be used to sense charge fluctuations and it is for this reason that this wonder material becomes a perfect candidate for chemical detection.[21,22] Graphene is also used for the DNA sequencing [23] where the DNA interacts via pi-pi stacking interaction, that reduces the ballistic conductance of graphene based materials[24-26]. The zero band gap and the absence of the dangling bonds in the graphene restricted its application in device-based applications. Different methodologies have been adopted to fabricate high performance graphene based devices that can be used to improve

the semiconducting properties.[27] It is a well known fact among the researchers that the pure graphene shows a zero band gap semiconductor properties due to the overlapping of the conduction and valence band in the Brillouin zone.[28,29] This property restricts its usage in many other fields. Doping is an efficient and easy way to improve the electronic properties of graphene. In graphene, substitutional doping with various atoms (eg. B, N, B-N) changes the sp<sup>2</sup> hybridization of carbon atoms.[30] Since the N and B atoms are comparable to the carbon atoms keeping in view their atomic masses these are used to replace C-atoms in graphene. Lherbie et al. [31] reported that the conductivity and charge mobility of the system can be tuned by doping it with different concentration of B and N impurities. Fan et al.[32] proposed theoretically that the band gap opening is possible via small nitride domain which was later confirmed experimentally by Bepete et al.[33] Since then the importance of the theoretical prediction in search of novel materials came into light. Cervantes-Sodi et al.[34] confirmed theoretically that with the help of B and N doping, the band gap opening can be achieved. Also there are other experimental studies that validates the band gap opening by various dopants.[35-37] Panchakarla et al.[35] synthesized doped graphene and showed the shifting of the Fermi-energy as proposed theoretically. There are many theoretical and experimental studies showing the interaction of the gaseous molecules with pure and doped graphene surfaces.[38-42] Singh et al.[43] confirmed theoretically that the doped graphene is more efficient than the pristine graphene to detect the green house gases. So the theoretical predictions are quite important in predicting the new material and the associated properties. In the present work, a detailed analysis of the interaction of the two most toxic gases with the doped graphenes will be performed using the density functional theory as implemented in the Gaussian09[44] software package.

## II. COMPUTATIONAL METHODOLOGY

All the geometries in the present work were optimized without any constraints. The calculations pertaining to the interaction of the methane and carbon dioxide gas molecules with the three different doped models of graphene were performed using the density functional theory. Initially, the geometries of the graphene doped with Boron, Nitrogen and Silicon atoms were optimized using the method M062X[45] with basis set 6-31+G\*\*, along with the geometries of the gas molecules thereafter these structures were subjected to the single point energy calculations using the B3LYP/6-311+G\*\* (BS1)[46,47] and M062X/6-311+G\*\* (BS2). For both of the gases considered in this study different positions were assigned so as to check the most interacting configuration for each of the two gases considered in the present study. The methane gas is made to interact in two modes. In the first mode single H-atom is pointing downward (CH<sub>4</sub>\_01) while in the second mode the single H-atom is pointing upward (CH<sub>4</sub>\_02). Since the carbon dioxide gas molecule owes a linear geometry, this gas too is made to interact in two modes i.e placing the molecule in parallel (CO<sub>2</sub>\_01) and perpendicular position (CO<sub>2</sub>\_02). The gas molecules were placed at a distance of approximately 3 Å from the doped graphene surface.

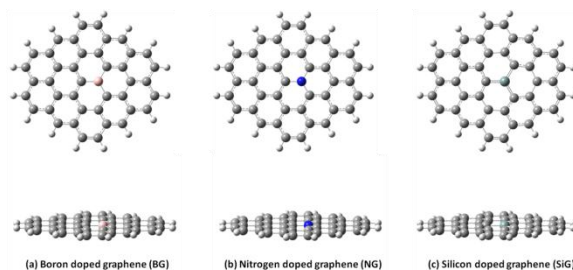


Figure 1: Optimized geometry various doped graphene models i.e (a) BG, (b) NG, and (c) SiG

The binding energy (B.E) was calculated using the given formula:

$$\text{Binding Energy} = [(E_A + E_B) - E_{AB}] \dots (1)$$

Where,  $E_{AB}$  is the energy of the complex system comprised of the doped graphene and gas molecule (CH<sub>4</sub>/CO<sub>2</sub>),  $E_A$  is the energy of the doped graphene while  $E_B$  is the energy of the gas molecule (CH<sub>4</sub>/CO<sub>2</sub>).

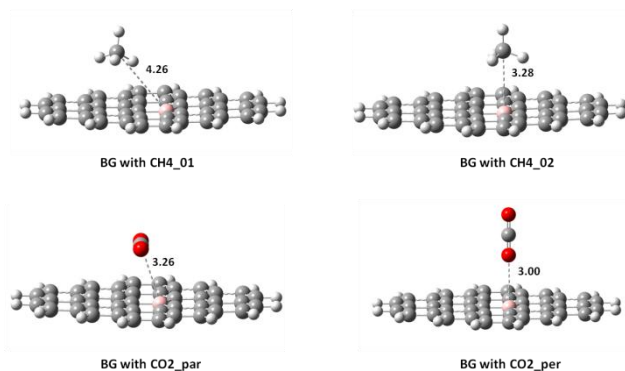


Figure 2: Optimized geometries of carbon dioxide and methane with Boron doped graphene. The numerical value shown is the distance between doped graphene sheet and the gaseous molecule in eV.

Table 1: Calculated binding energy (in kcal/mol) of doped graphene models (BG) and gaseous molecules at BS1 (B3LYPD/6-311+G\*\* // M062X/6-31+G\*\*) and BS2 (M062X/6-311+G\*\*// M062X/6-31+G\*\*).

Model System	Gaseous molecules	Binding Energy (BS1, B3LYPD/6-311+G** )	Binding Energy (BS2, M062X/6-311+G**)
(BG)	CH4_01	-3.238	-2.961
	CH4_02	-3.419	-3.379
	CO2_01	-4.635	-4.461
	CO2_02	-1.832	-1.862

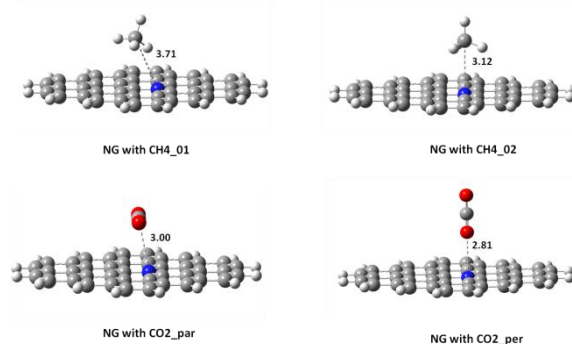


Figure 3: Optimized geometries carbon dioxide and methane with Nitrogen doped graphene. The numerical value shown is the distance between doped graphene sheet and the gaseous molecule in eV.

Table 2: Calculated binding energy (in kcal/mol) of doped graphene models (NG) and gaseous molecules at BS1 (B3LYPD/6-311+G\*\* // M062X/6-31+G\*\*) and BS2 (M062X/6-311+G\*\*// M062X/6-31+G\*\*).

Model System	Gaseous molecules	Binding Energy (BS1, B3LYPD/6-311+G** )	Binding Energy (BS2, M062X/6-311+G**)
(NG)	CH4_01	-3.534	-3.223
	CH4_02	-4.279	-4.171
	CO2_01	-4.0420	-4.302
	CO2_02	-3.236	-3.196

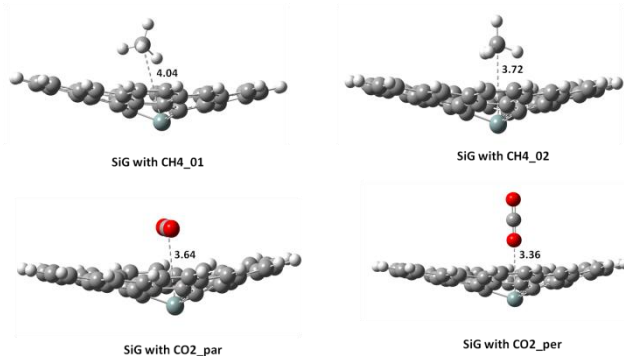


Figure 4: Optimized geometries carbon dioxide and methane with Silicon doped graphene. The numerical value shown is the distance between doped graphene sheet and the gaseous molecule in eV.

Table 3: Calculated binding energy (in kcal/mol) of doped graphene models (SiG) and gaseous molecules at BS1 (B3LYP/6-311+G\*\* // M062X/6-31+G\*\*) and BS2 (M062X/6-311+G\*\*// M062X/6-31+G\*\*).

Model System	Gaseous molecules	Binding Energy (BS1, B3LYPD/6-311+G** )	Binding Energy (BS2, M062X/6-311+G**)
(SiG)	CH4_01	-18.470	-16.764
	CH4_02	-19.027	-17.4560
	CO2_01	-19.422	-18.145
	CO2_02	-17.313	-15.798

#### IV. BINDING ENERGY AND HOMO-LUMO GAP

Usually, the magnitude of physisorption energy is defined as lower than ~5 kcal/mol, whereas for chemisorption energy it is higher than ~12 kcal/mol. Our calculations show that for the three different doped models of graphene, the adsorption energy is well within the range of physisorption and chemisorption.

The frontier orbitals viz. the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) were analyzed in order to further explain their chemical reactivity. The frontier molecular orbitals of molecules play significant role understanding the chemical reactivity of molecules. These orbitals participate in chemical interactions with other moieties and their energy difference (termed as gap) helps to know the chemical

reactivity of the molecule. The HOMO, in general, behave as an electron donor while the LUMO acts as an electron acceptor. Thus, HOMO-LUMO energy gap is an important measure for understanding the stability of the system.

**Table 4: Comparison of the Homo-Lumo gap (in eV) of various doped graphene models using two basis sets viz. BS1 (B3LYPD/6-311+G\*\* // M062X/6-31+G\*\*) and BS2 (M062X/6-311+G\*\*// M062X/6-31+G\*\*)**

Model system	Gaseous molecule	Homo-Lumo gap (BS1)	Homo-Lumo gap (BS2)
<b>Boron doped Graphene</b>	CH <sub>4</sub> _01	1.12	2.45
	CH <sub>4</sub> _02	1.13	2.47
	CO <sub>2</sub> _01	1.11	2.43
	CO <sub>2</sub> _02	1.13	2.49
<b>Nitrogen doped Graphene</b>	CH <sub>4</sub> _01	1.13	2.40
	CH <sub>4</sub> _02	1.12	2.40
	CO <sub>2</sub> _01	1.14	2.41
	CO <sub>2</sub> _02	1.12	2.39
<b>Silicon doped Graphene</b>	CH <sub>4</sub> _01	2.28	3.69
	CH <sub>4</sub> _02	2.29	3.69
	CO <sub>2</sub> _01	2.28	3.68
	CO <sub>2</sub> _02	2.29	3.69

The optimized geometries of various doped graphene models and their complexes with gaseous molecules are shown in Figure 1, 2 3, and 4. The initial configuration of all gaseous molecule were placed initially above the graphene surface in parallel configuration such that the  $\pi$ - $\pi$  stacking interaction may be observed. The gaseous molecule were placed at a distance of approximately 3Å .

On the basis of the complex system considered in this study, following significant conclusions can be drawn:

In the case of graphene doped with Boron atom, where the gas molecules interact with the graphene in parallel mode, there is no significant change in the Homo-Lumo gap. The Homo-Lumo gap ranges from 1.11 to 1.13 for BS1. For BS2, the Homo-Lumo gap is 2.43 for carbon dioxide in parallel position and ranges to 2.49 for BS2.

In the case of graphene doped with Nitrogen atom, where the gas molecules interact with the graphene in parallel mode, the Homo-Lumo gap ranges from 1.12 to 1.14 for BS1. For BS2, the Homo-Lumo gap is 2.39 for carbon dioxide in parallel position and ranges to 2.41 for BS2.

Similarly, .for graphene doped with silicon atom, where the gas molecules interact with the graphene in parallel mode, the Homo-Lumo gap ranges from 2.28 to 2.29 for BS1. For BS2, the Homo-Lumo gap is 3.68 for carbon dioxide in perpendicular position and ranges to 3.69 for BS2.

Hence, it can be concluded that the band gap opening is viable through doping and these gas molecules can be detected using theses doped graphene models.

## V. CONCLUSION

In the present study, the binding energy is calculated using the density functional theory of the complexes formed between the three graphene models i.e Boron doped graphene, Nitrogen doped graphene and Silicon doped graphene and the gaseous molecules. The two most toxic gases were considered in the present work i.e. methane and carbon dioxide. These two gases were subjected to interact with these three doped graphene at a distance of 3 Å. For each of these two gases, two different configurations were chosen and the binding energy along with the HOMO LUMO gap was calculated. The present study can be used to develop new carbon-based materials for sensing applications, focusing particularly on the binding mechanism of various gas molecules with doped graphene

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