



Adsorption of small gas molecules on pure and Al-doped graphene sheet: a quantum mechanical study

DHARMVEER SINGH, ASHEESH KUMAR and DEVESH KUMAR*

Department of Applied Physics, School for Physical Sciences, Babasaheb Bhimrao Ambedkar University, Lucknow 226025, India

*Author for correspondence (dkclcre@yahoo.com)

MS received 26 September 2016; accepted 13 February 2017; published online 3 October 2017

Abstract. The interaction of small gas molecules (CCl_4 , CH_4 , NH_3 , CO_2 , N_2 , CO , NO_2 , CCl_2F_2 , SO_2 , CF_4 , H_2) on pure and aluminium-doped graphene were investigated by using the density functional theory to explore their potential applications as sensors. It has been found that all gas molecules show much stronger adsorption on the Al-doped graphene than that of pure graphene (PG). The Al-doped graphene shows the highest adsorption energy with NO_2 , NH_3 and CO_2 molecules, whereas the PG binds strongly with NO_2 . Therefore, the strong interactions between the adsorbed gas molecules and the Al-doped graphene induce dramatic changes to graphene's electronic properties. These results reveal that the sensitivity of graphene-based gas sensor could be drastically improved by introducing the appropriate dopant or defect. It also carried out the highest occupied molecular orbital–lowest unoccupied molecular orbital energy gap of the complex molecular structure that has been explored by M06/6-31++G** method. These results indicate that the energy gap fine tuning of the pure and Al-doped graphene can be affected through the binding of small gas molecules.

Keywords. DFT; small gas molecules; graphene; aluminium-doping; non-covalent interaction; graphene-based gas sensors.

1. Introduction

Carbon is the versatile element on the earth's crust and it is found on the earth's surface in different allotropes as graphite, diamonds, charcoal and coke, respectively. The newer allotropes of carbon were discovered such as graphene, carbon nanotubes (CNTs) and fullerenes [1–3]. Graphene is the youngest known allotrope of carbon, which is a two-dimensional and one-atom thick material consisting of sp^2 hybridized carbon atoms arranged in a honeycomb structure. These allotropes of carbon are extensively used in research, that is, from biomedical to environment applications due to their unique physical and chemical properties [4]. The exceptional properties of carbon nano materials, such as electronic, thermal, optical, mechanical and transport properties make them promising candidates for various potential applications [5–7]. From several experimental and theoretical studies it is observed that the transport and electronic properties are extremely sensitive to change in the local chemical environment [8–10]. Carbon nanostructures (CNSs) exhibit non-covalent interaction such as the $\text{XH}-\pi$, cation– π , anion– π and $\pi-\pi$ interaction towards the small gas molecules, metal ions and bio molecules [11–15]. The $\text{XH}-\pi$ weak interactions were extensively studied in recent years [16–20]. These interactions have been considered to be a unique type of hydrogen bonding interaction in which π electron acts as the proton acceptor [14]. Graphene is a sensitive nano material,

which detects all the individual events when a gas molecule is adsorbed to or de-adsorbed from its surface [21]. However, it is very difficult to prepare a perfect single layer graphene with zero band gap. Doping is one of the most efficient method to improve the electronic properties of the materials. Wang *et al* have found that the sp^2 hybridization is affected and it changes the electronic properties of the system when B, N and B–N are doped with pure graphene (PG) [22]. Lherbier *et al* showed that the charge mobility and conductivity of graphene changes when B/N impurity atom is added to its surface [23]. Recently, there are several experimental studies on Al, Ga and Pd-doped graphene sheet-based gas sensor [24,25]. Interestingly, the nanoparticles such as Al, Ga and Pd incorporated the significant changes in the sensitivity and selectivity towards the gas molecules. The structure and physical properties of CNSs make them potential candidates as sensors to detect different types of gas molecules. Dai and co-workers were the first to report the gas sensors based on CNTs to detect gas molecules such as NO_2 and NH_3 [26]. Recently, Schedin *et al* experimentally reported that graphene-based gas sensors possess very high sensitivity such that the adsorption of individual gas molecules could be detected [21]. CNSs can absorb a number of species such as gas molecule, metal ions, polymers, organic molecules and biomolecules such as proteins, nucleobases and deoxyribonucleic acid (DNA) on their surface and these adsorption properties provide opportunities for potential industrial applications [27–30].

Roman *et al* studied the adsorption of few amino acids on a single-walled CNT by using the DFT method [31]. CNTs have also been found to be suitable candidates for the negative electrode of the Li-ion batteries, where the Li diffuse between the positive and negative in the ionic state [32,33]. Thus, the fundamental understanding of the interaction of metals with CNTs in the ionic state is important. It is also important to know the role of various factors such as solvent and other chemical environments, which influence such cation- π interaction [34–36]. Umadevi *et al* have found that the charge transfer between graphene and the molecules is an important factor in determining the binding strength of the complex molecular systems [37]. Zhang *et al* studied that doped graphene strongly interacts with CO, NO and NO₂ while NH₃ interacts weakly [38]. Zou *et al* found that the SiG has higher chemical reactions towards the gas molecules due to doping of silicon atom and shows the higher adsorption energy with CO, O₂, NO₂ and H₂O [39]. In the current study, the Al-doped graphene was theoretically investigated to improve its gas sensing efficiency and selectivity towards the various gas molecules. The gas molecule CCl₄, CH₄, NH₃, CO₂, CO, NO₂, CCl₂F₂, SO₂, CF₄ and N₂O, are all of great practical interest for industrial, environmental and medical applications. On the other hand, the effect of doping of the graphene sheet on the binding strength has been estimated. The charge transfer that occurred during the complex formation has also been explored. The change in the highest occupied molecular orbital–lowest unoccupied molecular orbital (HOMO–LUMO) energy gap of PG and Al-doped graphene upon the binding of these gas molecules has also been estimated.

2. Computational methods

The calculations of the interaction between PG, Al-doped graphene and gas molecule is carried out using the density functional theory. The geometrical calculations of all structures have been done by using one method B3LYP/6-31G* [40,41]. Initially, the individual gas molecule is adsorbed on the surface of PG and Al-doped graphene thereafter. Geometry optimization calculations were accomplished using Gaussian09 suite program [42]. It is important to note that complete geometrical configuration was tested but those shown are the lowest energy species feasible for the interaction of the compounds. Single point energy has been done at the M06/6-31++G** level to fine-tune the energy [43–46].

The adsorption energy (E_{ad}) of the small gas molecule ($X = \text{CCl}_4, \text{CH}_4, \text{NH}_3, \text{CO}_2, \text{N}_2, \text{CO}, \text{NO}_2, \text{CCl}_2\text{F}_2, \text{SO}_2, \text{CF}_4, \text{H}_2$) on the pure and Al-doped graphene is calculated by the following equation (1).

$$E_{\text{ad}} = E_{\text{graphene}_X/\text{graphene@Al}_X} - (E_{\text{graphene/Al@graphene}} + E_X) \quad (1)$$

Here, $E_{\text{graphene}_X/\text{graphene@Al}_X}$ represents the total energy of a complex molecular system. $E_{\text{graphene/Al}}$ and E_X represent the total energies of the graphene and gas molecule, respectively. The individual small gas molecule was placed parallel to the surface of graphene and doped graphene at the 3 Å distance. The variation of the charge on gas molecules as well as on pure and doped graphene when the individual gas molecules are kept at the 3 Å distance from its surface was calculated. The charge transfer has been considered as the sum of all atoms in the pure and Al-doped graphene model system. Positive charge transfer values indicate the transfer of charge from graphene to the molecules, while negative charge values indicate the transfer of charge from the molecules to the pure and Al-doped graphene. The HOMO–LUMO energy gap of pure and Al-doped graphene as well as their complexes at M06/6-31++G** level of theory were also calculated. All calculations were carried out using the Gaussian09 program package.

3. Results and discussion

The optimized structure of pure and Al-doped graphene and their complexes with small molecules are shown in figures 1, 2 and 3. The initial configuration of all small gaseous molecules were assigned so that these are oriented exactly parallel to the pure and Al-doped graphene at 3 Å from its surface. In this paper, pure and Al-doped graphene was considered to study the interaction of small gas molecules with X- π non-covalent interaction towards carbon nano materials. Tables 1 and 2 summarize our results on the adsorption energy, equilibrium graphene–molecule distance (d , defined as the distance of nearest atoms between graphene and molecule), the charge transfer (Q , Mulliken charge) and HOMO–LUMO energy gap for the most stable configurations of pure and Al-doped graphene adsorbed with various gas molecules in our calculations as shown in figures 2, 3 and tables 1, 2. Subsequently, we look at the binding of the pure and Al-doped graphene with various gas molecules and the trend in the charge transfer. The HOMO–LUMO energy gap of pure and Al-doped graphene with adsorption of various gas molecules were also investigated. When one impurity atom as Al is substituted for one C atom in graphene sheet, the optimized configuration of the graphene sheet is dramatically distorted. The Al atom introduces the deformation of the six-membered ring (6MR) near the doping site to relieve stress, as a result the Al atom protrudes out of the graphene sheet. The optimized carbon–dopant atom distance (Al–C) is 1.751 Å at B3YP/6-31G*, which is in agreement with the previous study [47].

3.1 Adsorption energy and charge transfer

The small gas molecules form X- π type complex with the pure and Al-doped graphene that are shown in figures 2 and 3. We observed the adsorption energy of small gas

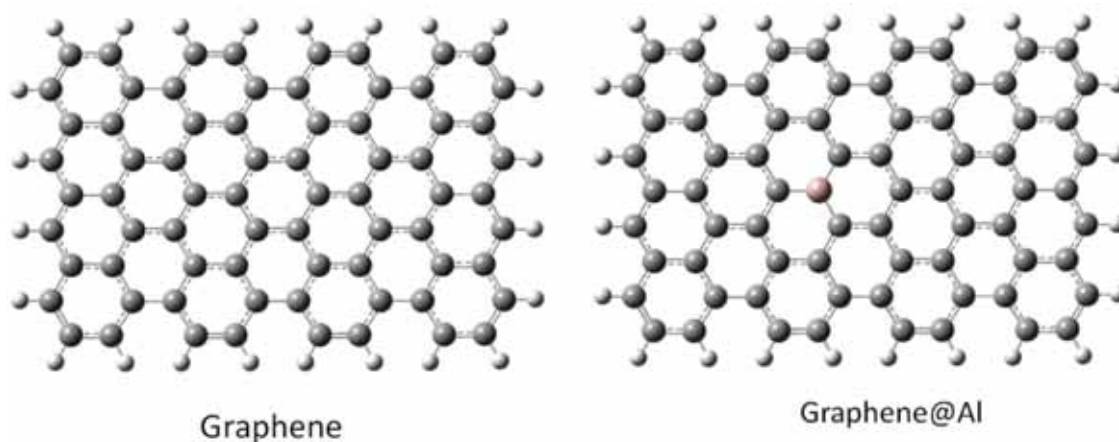


Figure 1. Top view of the optimized structure of pure and Al-doped graphene model system considered in this study.

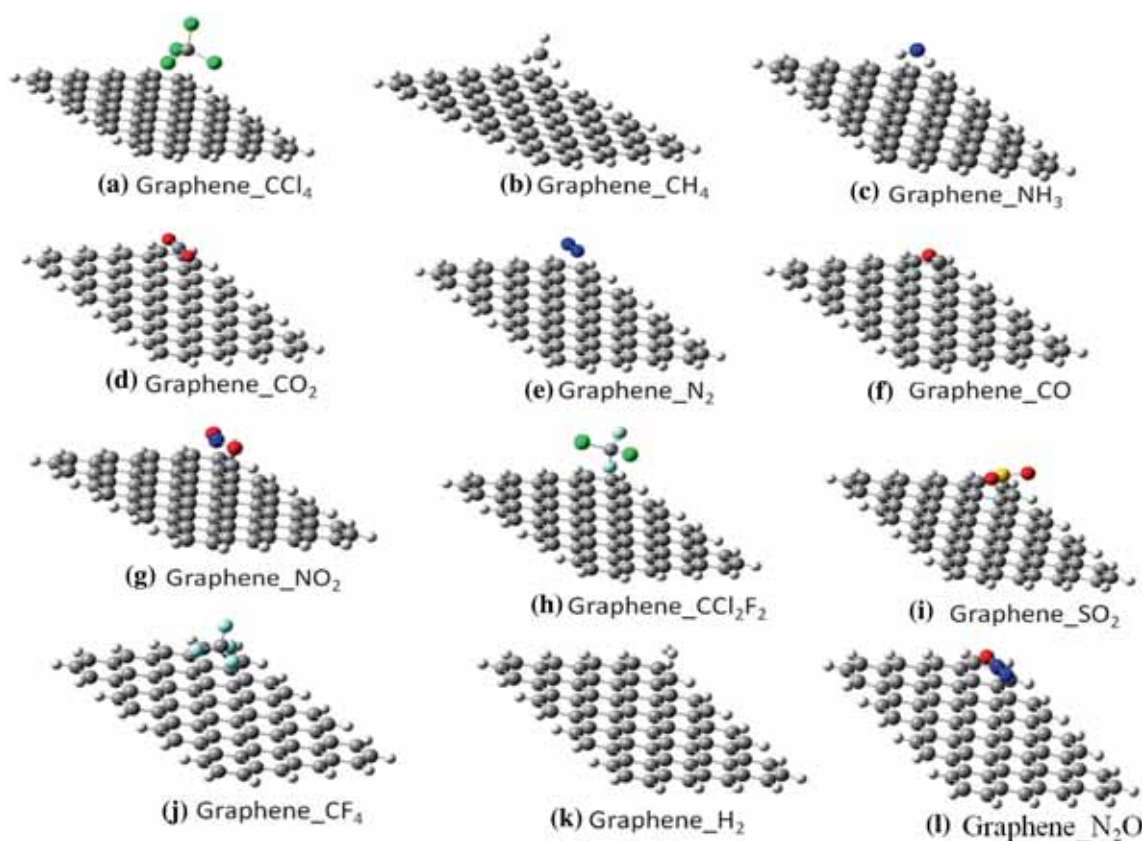


Figure 2. Optimized geometries of pure graphene with small gas molecule adsorbed (a) CCl_4 , (b) CH_4 , (c) NH_3 , (d) CO_2 , (e) N_2 , (f) CO , (g) NO_2 , (h) CCl_2F_2 , (i) SO_2 , (j) CF_4 , (k) H_2 and (l) N_2O by M06/6-31++G** method.

molecule complexes with pure and Al-doped graphene when the gas molecules are kept parallel to the graphene surface at 3 Å distance. Tables 1, 2 and figure 4 display the adsorption energy, charge transfer and molecule sheet distance of the small gas molecule complexes with pure and Al-doped graphene at M06/6-31++g** level of theory.

Interestingly, a different trend in the case of small gas molecule interacting with pure and Al-doped graphene is

observed, the adsorption energy of small gas molecules towards the Al-doped graphene is greater than PG. From table 2 and figure 2, the adsorption energy of all gas molecules is higher for the Al-doped graphene than that of PG.

For CCl_4 and CH_4 adsorbed on PG, the most energetically favourable configuration (Graphene_ CCl_4) is also identical. The adsorption of CCl_4 and CH_4 on PG is non-covalent interaction with the adsorption energy of -0.394 and

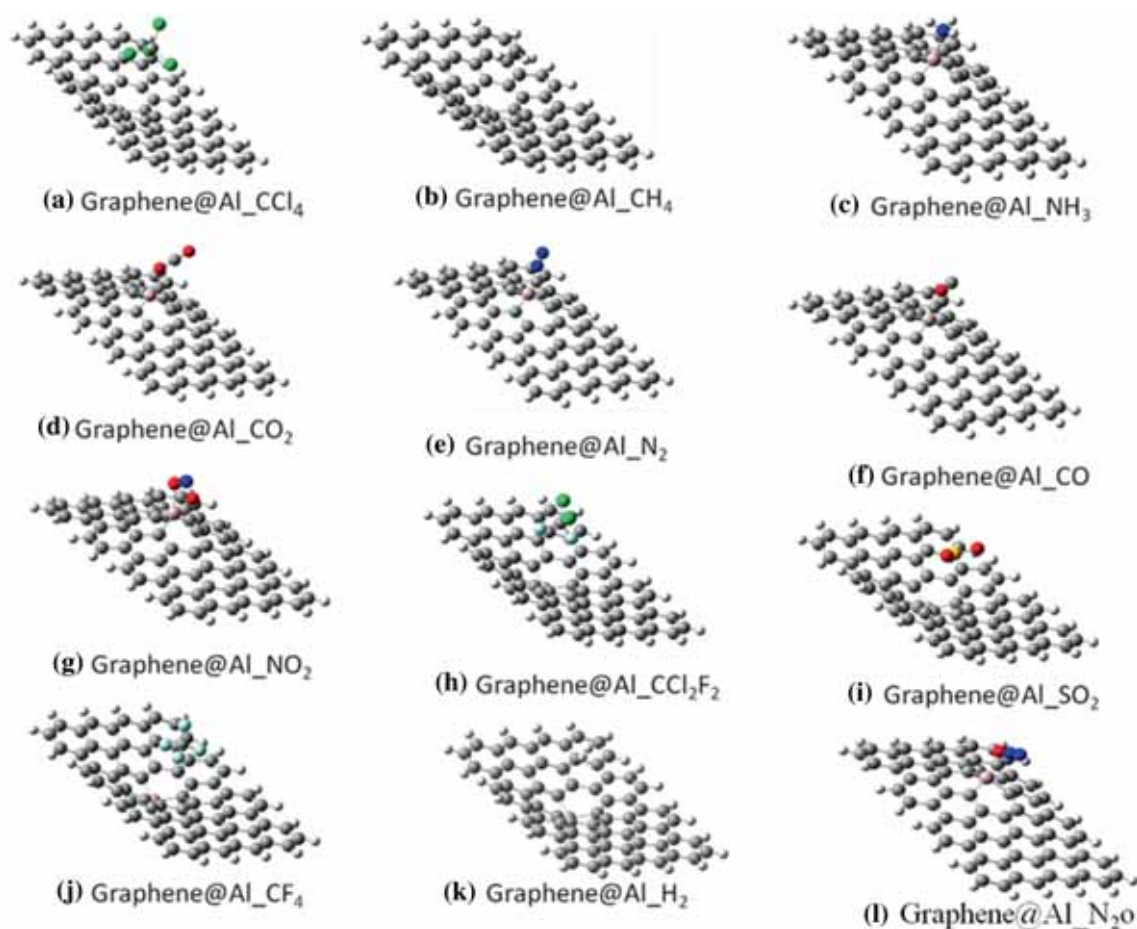


Figure 3. Optimized geometries of aluminium-doped graphene (@Al shown as Al doping in pure graphene) adsorbed with small gas molecules (a) CCl₄, (b) CH₄, (c) NH₃, (d) CO₂, (e) N₂, (f) CO, (g) NO₂, (h) CCl₂F₂, (i) SO₂, (j) CF₄, (k) H₂ and (l) N₂O by M06/6-31++G** method.

Table 1. The adsorption energy (eV), molecule sheet distance (Å), charge transfer (a.u.) and HOMO–LUMO energy gap (eV) at M06/6-31++G** level of theory.

Carbon nanomaterial	Small gas molecule	Adsorption energy (eV)	Molecule sheet distance (Å)	Charge on gas molecule (a.u.)	HOMO–LUMO gap (eV)
Graphene	CCl ₄	−0.394	4.498	−0.0196	0.3339
	CH ₄	−0.067	3.784	−0.0133	0.3336
	NH ₃	−0.145	3.357	0.0334	0.3336
	CO ₂	−0.122	3.626	0.0169	0.3336
	N ₂	−0.083	3.828	0.014	0.3339
	CO	−0.110	3.732	0.0098	0.3336
	NO ₂	−0.996	3.573	0.025	0.8727
	CCl ₂ F ₂	−0.119	3.355	0.0039	0.3336
	SO ₂	−0.279	3.578	0.0254	0.3339
	CF ₄	−0.150	3.404	0.0552	0.3336
	H ₂	−0.013	4.946	0.0006	0.3339
	N ₂ O	−0.123	3.634	0.0180	0.3340

−0.067 eV and the molecule sheet distance of 4.498 and 3.784 Å, respectively. The charge transfer from graphene to CCl₄ and CH₄ molecule is −0.0196 and −0.0133 a.u., which

indicates that the PG acts as a donor, and the gas molecule acts as an acceptor. Therefore, PG is less sensitive to the CCl₄ than CH₄ molecule. The most stable configuration of CCl₄

Table 2. The adsorption energy (eV), molecule sheet distance (Å), charge transfer (a.u.) and HOMO–LUMO energy gap (eV) at M06/6-31++G** level of theory.

Carbon nanomaterial	Small gas molecule	Adsorption energy (eV)	Molecule sheet distance (Å)	Charge on gas molecule (a.u.)	HOMO–LUMO gap (eV)
Graphene@Al	CCl ₄	−1.354	3.920	−0.007	0.661
	CH ₄	−1.242	4.300	0.004	0.616
	NH ₃	−2.948	2.053	0.493	1.080
	CO ₂	−2.019	2.158	0.423	1.574
	N ₂	−1.279	2.210	0.837	0.444
	CO	−1.255	2.344	0.276	0.494
	NO ₂	−3.867	1.894	−0.065	0.330
	CCl ₂ F ₂	−1.361	3.956	0.020	0.579
	SO ₂	−1.608	3.579	0.045	0.599
	CF ₄	−1.354	3.920	0.138	0.662
	H ₂	−1.637	6.306	0.001	1.512
	N ₂ O	−1.409	2.163	0.518	0.453

and CH₄ on graphene@Al is a configuration with the CCl₄ and CH₄ molecule parallel to the graphene sheet and Cl atom of CCl₄ and H atom of CH₄ adsorbed on the top of Al atom, which is shown in figure 3a and b, where the molecular sheet distance is 3.920 and 4.300 Å, respectively. The calculated E_{ad} value is −1.354 and −1.242 eV, which indicates that the graphene@Al has higher adsorption energy than PG with CCl₄ and CH₄.

The NH₃ molecule shows different adsorption configurations on pure and Al-doped graphene, showing a more complicated adsorption mechanism than the other molecules. On the PG, the configuration with the three hydrogen atoms of NH₃ pointing towards the graphene plane is the favourable one (figure 3c), which gives an adsorption energy and molecule distance of −0.145 eV and 3.357 Å, respectively. This result is consistent with previous reports about NH₃ adsorbed on CNTs (−0.14 eV) and NH₃ adsorbed on graphene (0 ~ −0.17 eV) [48,49], which indicates a weak interaction between NH₃ and the PG. On the Al-doped graphene, NH₃ is attached to the Al atom with the N atom pointing at the sheet, which gives an adsorption energy of −2.948 eV and an Al–N distance of 2.053 Å (as shown in figure 3c and table 2). The charge transfer from NH₃ to graphene is 0.493 a.u., which indicates that the graphene behaves as charge acceptor and NH₃ molecule as charge donor. The adsorption energy of NH₃ on Al-graphene (−2.948 eV) is much higher than that on the PG, which attributes to the strong interaction between the electron-deficient Al atom and the electron-donating N atom of NH₃. It is also investigated that the Al-doped graphene undergoes an obvious distortion upon NH₃ adsorption (figure 3c), indicating that the B site is transformed from sp² to sp³ hybridization, which matched the previous study [35]. The molecular distance between Al and N is 2.053 Å. This strong interaction is also evident in the electronic total charge density on Al-doped graphene system, which shows large electron density overlap.

The adsorption energy of this complex system is −0.122 eV and molecule–sheet distance is 3.626 Å, which are shown in table 1 and figure 2d. The low adsorption energy and long molecule sheet distance indicate a weak interaction. When the CO₂ molecule is adsorbed on PG, the calculated charge transfer of CO₂ is 0.0169 a.u. In this configuration, the CO₂ molecule acts as a charge donor. When the CO₂ molecule is adsorbed on Al-doped graphene, one oxygen atom of CO₂ shows most stable configuration towards the Al atom of graphene@Al sheet. In this configuration, the adsorption energy and molecule sheet distance (O–Al) is −2.019 eV and 2.158 Å, respectively. This result indicates that the interaction of CO₂ with graphene@Al is much stronger than that of PG due to large transfer of charge. In this configuration, the charge transfer from CO₂ to the graphene@Al is 0.423 a.u., which means that the CO₂ molecule acts as a charge donor and graphene@Al acts as a charge acceptor.

In case of graphene_N₂ configuration, the N–N axis gets aligned parallel to the graphene plane along the axis of two opposite C atoms of the 6MR, which was found to be the most stable configuration. The adsorption energy and the molecule sheet distance of this complex system is −0.083 eV and 3.828 Å, respectively as shown in figure 4a, c and table 1. The charge transfer between N₂ and graphene was calculated from Mulliken population analysis, which is shown in table 1. This result indicates that the interaction is weak in nature due to very small adsorption energy and charge transfer. When adsorbed on Al-doped graphene (graphene@Al), N₂ adopts perpendicular orientation with Al atom of the graphene sheet. In this configuration, the one N atom of N₂ and Al atom of graphene@Al is very close as shown in figure 3e. The adsorption energy and the molecule sheet distance is −1.279 eV and 2.210 Å, respectively (as shown in figures 4a and c). The charge transfer from N₂ to graphene@Al is 0.837 a.u., which indicates that N₂ acts as a charge donor. In this configuration, the adsorption energy of the complex system is higher than

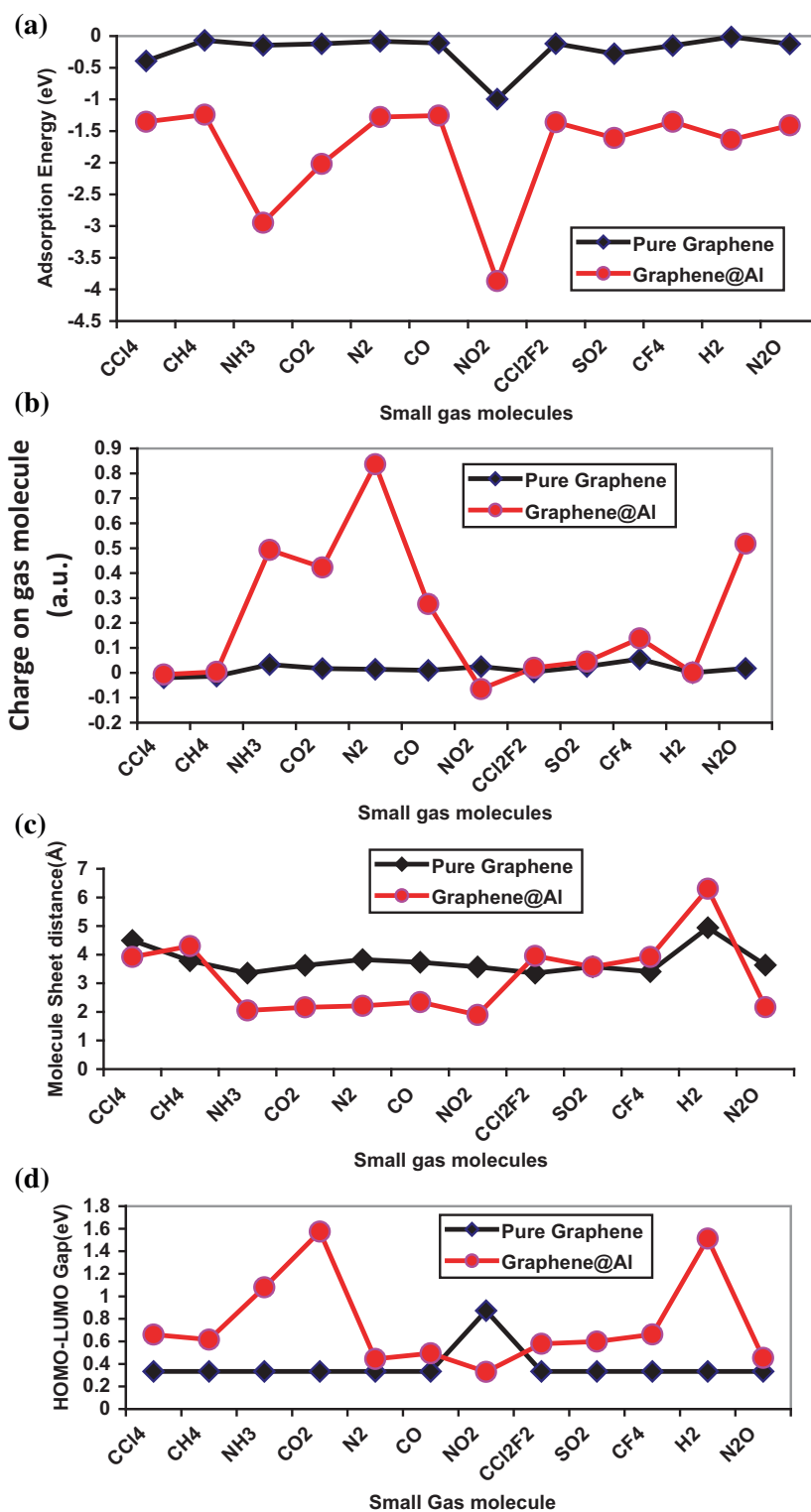


Figure 4. (a) The adsorption energy E_{ad} , (b) charge transfer, (c) molecule sheet distance and (d) HOMO–LUMO energy gap of small gas molecules with pure and Al-doped graphene complexes at the M06/-31++G** level of theory. The red line with solid red circles represents the variation for the aluminium-doped graphene whereas the black line with black solid squares represent the variation for pure graphene. The HOMO–LUMO gap for pure graphene is 0.33 eV and for Al-doped graphene is 0.22 eV without any gas molecules.

the graphene_N₂ due to large transfer of charge, which are responsible for strong interaction.

The most stable configuration of CO molecule is similar to the CO₂ and N₂, which are aligned parallel to the PG plane along the axis of two opposite C atoms of the 6MR in the complex molecular structure. The adsorption energy and molecule sheet distance is -0.110 eV and 3.732 Å, respectively (as shown in table 1). When the CO molecule is adsorbed on PG, the charge calculated on the C and O atoms of the CO molecule are 0.100 and -0.090 a.u., respectively, while there is no charge on the carbon atoms of the PG. Therefore, we can say that a very small charge is transferred from CO to the PG. The low adsorption energy and very small charge transfer indicates weak physisorption. When the CO molecule is adsorbed on Al-doped graphene, CO molecule adopts a tilted orientation with respect to the plane of the Al-containing 6MR, with the O atom close to graphene@Al. In this complex structure, the adsorbed energy and molecule sheet distance are found to be -1.255 eV and 2.344 Å, respectively. The charge transfer from CO molecule to graphene@Al is 0.275 a.u. In this configuration, the adsorption energy of graphene@Al_CO is higher than graphene_CO complex (as shown in table 2 and figure 4a).

The adsorption energy and shortest distance from PG to the nearest O atom of NO₂ are -0.996 eV and 3.573 Å, respectively, which indicates a weak interaction between the NO₂ and PG. However, the adsorption energy of NO₂ on PG can remarkably change the electronic properties of PG and the charge transferred from NO₂ to PG is about 0.02504 a.u. It is clear that PG behaves as charge acceptor. In other words, PG is more sensitive to the NO₂ molecule than any other gas molecule. For NO₂ adsorbed on AlG (Al-doped graphene), the most stable configuration (Graphene@Al_NO₂) is similar to that of graphene_NO₂. However, the oxygen atom of NO₂ is bonded to the AlG as shown in figure 2g. The O-Al bond length is 1.894 Å and the adsorption energy for Graphene@Al_NO₂ is -3.867 eV, which indicates that NO₂ is chemisorbed on the graphene@Al. In this configuration, the adsorption energy is greater than graphene_NO₂ due to large charge transferred from graphene@Al to NO₂, about -0.064582 a.u., which is shown in table 2 and figure 4b. It is clear that the graphene@Al behave as charge donor while interacting with the NO₂.

For CCl₂F₂ adsorption on PG, the most energetically favourable configuration is similar to the graphene_CCl₄ and graphene_CH₄. In this configuration, the CCl₂F₂ is adsorbed to PG with one F atom of CCl₂F₂ pointing downwards as shown in figure 2h and table 1. The adsorption of CCl₂F₂ on PG shows interaction with the adsorption energy of -0.119 eV with molecule sheet distance of 3.355 Å, indicating the weak physisorption nature. The calculated charge transfer from CCl₂F₂ is only 0.004 a.u. Therefore, the PG is not sensitive to the CCl₂F₂. When the CCl₂F₂ is adsorbed on Al-doped graphene, both fluorine atoms of CCl₂F₂ get close to the graphene@Al. In this configuration, the adsorption energy, molecule sheet distance and charge transfer is -1.361 eV,

3.956 Å and 0.02 a.u., respectively, which indicates that interaction is weak in nature due to very small charge transfer (as shown in figure 4b and table 2).

In the graphene_SO₂ complex structure, the S atom of SO₂ is close to the C atom of PG. The adsorption energy E_{ad} and shortest distance from PG to the S atom of SO₂ are -0.279 eV and 3.578 Å, respectively, suggesting a weak interaction between the SO₂ and PG (as shown in figure 4c, d and table 1). However, there is no change in the electronic properties of PG due to the low charge transfer, about 0.025 a.u. from SO₂ to the PG. Therefore, PG is not sensitive to the SO₂ molecule. As shown in figure 3i, the SO₂ is adsorbed on Al-doped graphene, the S atom of SO₂ gets close to the graphene@Al because the Al atom is negatively charged and S atom is positively charged. The charge on Al, S, O(98) and O(99) are -0.283 , 0.796 , -0.373 and -0.378 a.u., respectively, indicating that Al atom repels both oxygen atoms but attracts the S atom because S atom becomes more positively charged. In this complex structure, the adsorption energy and molecule sheet distance between S and Al is -1.608 eV and 3.579 Å as shown in figure 3i and table 2. However, the charge transfer is very low from SO₂ to graphene@Al, which is about 0.045 a.u.

For CF₄ adsorption on PG, the most energetically favourable configuration is similar to the graphene_CCl₄ and graphene_CH₄. In this configuration, the CF₄ is adsorbed to PG with one F atom of CF₄ pointing downward as shown in figure 2j and table 1. The adsorption of CF₄ on PG is the non-covalent interaction with the adsorption energy of -0.150 eV and the molecule sheet distance of 3.404 Å, indicating the weak physisorption. The calculated charge transfer from CF₄ is only 0.055 a.u. Therefore, PG is not sensitive to CF₄. When CF₄ is adsorbed on Al-doped graphene, one fluorine atom of CF₄ gets close to graphene@Al. In this configuration, the adsorption energy, molecule sheet distance and charge transfer is -1.354 eV, 3.404 Å and 0.135 a.u., respectively. Therefore, we can say that graphene@Al is more sensitive than PG towards the CF₄ molecule (figure 3j and table 2). In this complex, graphene@Al acts as a charge acceptor.

The H₂ molecule was initially placed parallel to the graphene. After full relaxation, a configuration with the adsorbed H₂ axis gets aligned almost parallel to the graphene surface along the axis of two opposite C atoms of the 6MR and was found to be the most stable one for the PG. The adsorption energy of this system is -0.013 eV and the molecule sheet distance is 3.946 Å as shown in figure 3k and table 1, which are suggesting weak interaction between H₂ and graphene. The charge transfer between H₂ and graphene is 0.0007 a.u. In this configuration, PG is not sensitive towards the H₂ molecule. When adsorbed on graphene@Al, H₂ is oriented perpendicular to the Al-doped graphene plane, with one H(97) atom close to the graphene@Al. In this complex structure, the adsorption energy, molecule sheet distance and charge transfer are -1.637 eV, 6.306 Å and 0.001 a.u., respectively. Interestingly, the graphene@Al has more adsorption energy than PG.

As shown in figure 2l, the most stable configuration of N_2O adsorbed on PG (graphene_ N_2O) is similar to graphene_ CO_2 , where the gas molecule axis is aligned parallel to the graphene plane along the axis of two opposite C atoms of the 6MR. However, the N_2O in graphene_ N_2O is located above the centre of the 6MR. The calculated adsorption energy and molecule sheet distance are 0.123 eV and 3.634 Å, respectively. The low adsorption energy and long molecule sheet distance are suggesting weak physisorption. However, it is found that the interaction is significantly improved when a C atom in the PG is replaced by an Al atom. Figure 3l shows the most stable configuration of N_2O adsorbed on graphene@Al, where the oxygen atom of N_2O is close to the Al atom of graphene@Al. The adsorption energy E_{ad} for graphene@Al_ N_2O is -1.409 eV, which is clearly higher than that for graphene_ N_2O . The interaction distance between the N_2O molecule and the graphene@Al decreases to 2.163 Å, which indicates strong interaction. The charge transfer from N_2O to the graphene is 0.518 a.u. The large transferred charge suggests that the local electronic properties of graphene@Al is remarkably changed due to the adsorption of N_2O on graphene@Al.

The above mentioned results suggest that PG has weak interaction towards all gas molecules. Introducing dopants like Al atom into the graphene significantly increases the molecule-graphene interaction. The order of adsorption energy for small gas molecule complexes is $NO_2 > CCl_4 > SO_2 > CF_4 > NH_3 > N_2O > CO_2 > CCl_2F_2 > CO > N_2 > CH_4 > H_2$ with PG and $NO_2 > NH_3 > CO_2 > H_2 > SO_2 > N_2O > CCl_2F_2 > CF_4 > CCl_4 > N_2 > CO > CH_4$ with Al-doped graphene. Interestingly, our results predicted that Al-doped graphene are more suitable for gas sensing applications, since they have stronger interactions with all small gas molecules than PG. The Al-doped graphene particularly shows the highest sensitivity towards NO_2 , NH_3 and CO_2 .

3.2 HOMO–LUMO energy gap

The primary requisite for a material to perform as a sensor is to undergo a change in its physical property on interacting with an analyte. Such changes can be monitored and recorded to determine the presence of the analyte. The HOMO–LUMO energy gap is defined as the difference between lowest unoccupied molecular orbital and highest occupied molecular orbital. It is the electronic property of any molecular system, which is helpful to design new materials. In order to notice such a depiction in the case of carbon materials, we have calculated the HOMO–LUMO energy gap of the PG and Al-doped graphene in the free state and in the small gas molecule complexes. In general, in the case of X– π complexes, the HOMO–LUMO energy gap of single-walled carbon nanotube (SWCNT) varies with orientation of small gas molecules on the PG and Al-doped graphene. It has been shown that the energy gap of PG is not significant but when the gas molecules is adsorbed on graphene@Al then significant changes in HOMO–LUMO energy gap is observed

(as shown in table 2). Therefore, we can say that the variation in HOMO–LUMO energy gap of the graphene upon binding with the various small gas molecules is significant.

4. Conclusion

The adsorption energy of various small gas molecules such as CCl_4 , CH_4 , NH_3 , CO_2 , CO , NO_2 , CCl_2F_2 , SO_2 , CF_4 and N_2O with the pure and Al-doped graphene (graphene@Al) has been comprehensively analysed. These calculations reveal that the adsorption energy has preferences of small gas molecules with the doping in graphene as well as molecule sheet distance. It can be seen from the results that the adsorption energy of these gas molecules is higher for the Al-doped graphene than for the PG. PG shows weak sensitivity to all gas molecules. Compared with PG, graphene@Al has a higher chemical reactivity towards all gas molecules due to the doping of Al atom and shows higher adsorption energy with NO_2 , NH_3 and CO_2 . The strong interactions between graphene@Al and the adsorbed molecules induce dramatic changes in the electronic properties of graphene@Al and make graphene@Al a promising candidate as gas sensing materials for NO_2 , NH_3 and CO_2 . The Mulliken charge analysis reveals that the gas molecule acts as charge donor and acceptor in different configurations towards the pure and Al-doped graphene and influence the physical properties of carbon materials, which leads to the sensitivity. It has also been found that HOMO–LUMO energy gap of the CNT is always affected by the binding of the small gas molecules. Significant changes occur in the HOMO–LUMO energy gap on PG and graphene@Al on interacting with gas molecules, which provides a handle to tune the electronic and conductivity properties of graphene through gas molecule complexation. These studies can also be applied to develop new carbon-based materials and sensing applications, focusing particularly on the binding mechanism of various gas molecules with graphene. Developing chemical and gas sensors based on carbon materials has become an area of significant research interest since the physical and electronic properties of these materials are vulnerable to external environment. It is to hope that our results would be helpful to develop novel carbon material-based gas sensors.

Acknowledgements

Dharmveer Singh and Asheesh Kumar acknowledge their financial support from the University Grants Commission (UGC), New Delhi.

References

- [1] Hirsch A 2010 *Nat. Mater.* **9** 868
- [2] Rao C N R, Sood A K, Subrahmanyam K S and Govindaraj A 2009 *Angew. Chem. Int. Ed.* **48** 7752

- [3] Iijima S 1991 *Nature* **354** 56
- [4] Liu J, Cui L and Losic D 2013 *Acta Biomater.* **9** 9243
- [5] Dinadayalane T C and Leszczynski J 2010 *Struct. Chem.* **21** 1155
- [6] Liang F and Chen B 2010 *Curr. Med. Chem.* **17** 10
- [7] Zhu Y, Murali S, Cai W, Li X, Suk J W, Potts J R *et al* 2010 *Adv. Mater.* **22** 3906
- [8] Goldoni A, Larciprete R, Petaccia L and Lizzit S 2003 *J. Am. Chem. Soc.* **125** 11329
- [9] Guo Z, Feng Y, He S, Qu M, Chen H, Liu H *et al* 2012 *Adv. Mater.* **25** 584
- [10] Zhong J, Chiou J, Dong C, Glans P A, Pong W F, Chang C *et al* 2012 *Appl. Phys. Lett.* **100** 201605
- [11] Umadevi D, Panigrahi S and Sastry G N 2014 *Acc. Chem. Res.* **47** 2574
- [12] Vijay D and Sastry G N 2010 *Chem. Phys. Lett.* **485** 235
- [13] Shi G, Ding Y and Fang H 2012 *J. Comput. Chem.* **33** 1328
- [14] Grabowski S J and Lipkowski P 2011 *J. Phys. Chem. A* **115** 4765
- [15] Mahadevi A S and Sastry G N 2016 *Chem. Rev.* **116** 2775
- [16] Charlier J C 2002 *Acc. Chem. Res.* **35** 1063
- [17] Huang P, Zhu H, Jing L, Zhao Y and Cao X 2011 *ACS Nano* **5** 7945
- [18] Dougherty D A 1996 *Science* **271** 163
- [19] Kim S K, Hu S, Tarakeshwar P and Lee J Y 2000 *Chem. Rev.* **100** 4145
- [20] Ready A S and Sastry G N 2005 *J. Phys. Chem. A* **109** 8893
- [21] Schedin F, Geim A K, Morozov S V, Hill E W, Blake P, Katsnelson M I *et al* 2007 *Nat. Mater.* **6** 652
- [22] Wang X, Sun G, Routh P, Kim D H, Huang W and Chen P 2014 *Chem. Soc. Rev.* **43** 7067
- [23] Lherbier A, Blase R X, Niquet Y, Triozon F and Roche S 2008 *Phys. Rev. Lett.* **101** 036808
- [24] Lv Y-A, G-I Zhuang G-I, Wang J-g, Jia Y-B and Xie Q 2011 *Phys. Chem. Chem. Phys.* **13** 12472
- [25] Cho B, Yoon J, Hahn M G, Kim D H, Kim A R, Kahng Y H *et al* 2014 *J. Mater. Chem.* **2** 5280
- [26] Kong J, Franklin N, Zhou C, Chapline M, Peng S, Cho K *et al* 2000 *Science* **287** 622
- [27] Umadevi D and Sastry G N 2011 *J. Phys. Chem. C* **115** 9656
- [28] Umadevi D and Sastry G N 2011 *J. Phys. Chem. Lett.* **2** 1572
- [29] Chen W, Duan L and Zhu D 2007 *Environ. Sci. Technol.* **41** 8295
- [30] Panigrahi S, Bhattacharya S, Banerjee S and Bhattacharyya D 2012 *J. Phys. Chem. C* **116** 4374
- [31] Roman T, Dino W A, Nakanishi H and Kasai H 2006 *Eur. Phys. J. D.* **38** 117
- [32] Kumar A, Reddy A L M, Mukherjee A, Dubey M, Zhan X, Singh N *et al* 2011 *ACS Nano* **5** 4345
- [33] Reddy A L M, Srivastav A, Gowda S R, Gullapalli H, Dubey M and Ajayan P M 2010 *ACS Nano* **4** 6337
- [34] Rao J S, Zipse H and Sastry G N 2009 *J. Phys. Chem. B* **113** 7225
- [35] Sharma B, Rao J S and Sastry G N 2011 *J. Phys. Chem. A* **115** 1971
- [36] Mahadevi A S and Sastry G N 2011 *J. Phys. Chem. B* **115** 703
- [37] Umadevi D and Sastry G N 2015 *Phys. Chem. Chem. Phys.* **17** 30260
- [38] Zhang Y H, Chen Y B, Zhou K C, Liu C H, Zeng J, Zhang H L *et al* 2009 *Nanotechnology* **20** 185504
- [39] Zou Y, Li F, Zhu Z H, Zhao M W, Xu X G and Su X Y 2011 *Eur. Phys. B* **81** 475
- [40] Becke A D 1993 *J. Chem. Phys.* **98** 5648
- [41] Ditchfield R, Hehre W J and Pople J A 1971 *J. Chem. Phys.* **54** 724
- [42] Frisch M J, Trucks G W, Schlegel H B, Scuseria G E, Robb M A, Cheeseman J R *et al* 2010 Gaussian Inc., Wallingford, CT
- [43] Zhao Y and Truhlar D G 2008 *Theor. Chem. Acc.* **120** 215
- [44] Petersson G A, Bennett A, Tensfeldt T G, Al-Laham M A, Shirley W A and Mantzaris J 1988 *J. Chem. Phys.* **89** 2193
- [45] Petersson G A and Al-Laham M A 1991 *J. Chem. Phys.* **94** 6081
- [46] Frisch M J, Pople J A and Binkley J S 1984 *J. Chem. Phys.* **80** 3265
- [47] Dai J Y and Yuan J M 2010 *Phys. Rev. B* **81** 165414
- [48] Bai L and Zhou Z 2007 *Carbon* **45** 2105
- [49] Charles W, Bauschlicher J and Ricca A 2004 *Phys. Rev. B* **70** 115409