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A DFT Study of Si Doped Graphene: Adsorption of Formaldehyde and Acetaldehyde

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Abstract: In this study, Si doped graphene sensor property for indoor volatile contaminants formaldehyde and acetaldehyde has been examined. The B3LYP hybrid method with 6-31G(d,p) basis set has been used for this purpose. The adsorption energy of formaldehyde and acetaldehyde have been found to be -24.5 and -33.3 kcal/mol, respectively. The characteristic C=O bond frequency has been decreased after adsorption of the molecules and the bond peaks frequencies have been decreased in both aldehydes. There was a charge transfer from adsorbent to formaldehyde oppositely from acetaldehyde to adsorbent.

Keywords: *Adsorption, Formaldehyde, Acetaldehyde, DFT, Graphene, Si doping*

1. Introduction

Graphene is a carbon sheet in a hexagonal lattice [1]. It is preferable due to electrical conductivity, thermal conductivity, structural flexibility, ultrathin thickness, high surface-to-volume ratio and chemical stability [2]. Contrary to these advantages, the lack of functional groups, band gap energy and being not producible in large amount makes graphene inconvenient to be used in the application of gas/vapor adsorption. Some methods such as doping, hybridization and functionalization, etc. have been used to increase the performance of the element in this process. [3]. Doping of graphene with many atoms such as sulfur and boron, etc. have been studied for different applications. [4] Silica (Si) can be preferable as dopant of graphene for gas adsorption since there is a strong interaction [5]. Si doped graphene was investigated for the adsorption of NO [6], N_2O [6], NO_2 [1,6,7], CO [1,2], H_2O [1] and O_2 [1,8] in literature.

There are many pollutants such as formaldehyde, and acetaldehyde, in both indoor and outdoor [9]. These volatile organic compounds are vaporized at room temperature and breathed [10] for that reason damages of these pollutants on human health should be considered [11]. The indoor source and their health effects are summarized in Table 1. Determination of concentration of these compounds in the air is very critical [12].

There have been many studies about formaldehyde adsorption on graphene. In Majidi et al. 's [13] paper, low binding energy, large adsorption distance and small charge transfer in formaldehyde adsorption on graphene were obtained. Hence, researcher focus on doped graphene to increase adsorption efficiency. It was seen that Si, Cr and Au doped graphene adsorbed formaldehyde very strongly while N and B doped graphene structures did not [14]. It is approved that Al [14], Mn [14] and Si [15] doped graphenes are very effective on formaldehyde sensing. Also, in Zhou et al. [16] study, it is noted. The adsorption can be strengthed with formation vacancy in graphene structures.

Formaldehyde was adsorbed on Graphene-like Boron Nitride with pseudo-second-order model [17]. In Wang et al.'s study [18]; it was shown that adsorption efficiency of formaldehyde onto GO/SnO_2 is higher than the bare GO. It was also determined that toluene took precedence over formaldehyde on co-adsorption of toluene and formaldehyde on metal basic zeolite [19].

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Table 1. Formaldehyde and acetaldehyde source and health hazard

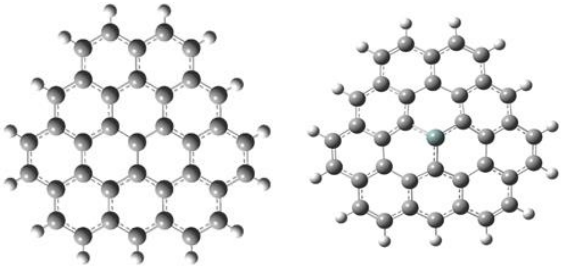
Pollutant	Example Source	Health Hazard
Formaldehyde	Resin, binder, paper, paint [2] wood, cosmetic, textile [3]	poisoning, allergy, asthma, pulmonary damage, cancer [4]
Acetaldehyde	Adhesive, nail polish [5] Alcohol, fermented food, cigarette, exhaled gases [6] deodorant [7]	pulmonary damage, narcosis, cancer [8]

It was reported in the investigation Graphene-Tungsten trioxide for acetaldehyde adsorption that the ratio Graphene/Tungsten was main parameter for gas sensing property [20]. In DFT study of acetaldehyde adsorption on gold, there was no any significant position of acetaldehyde for adsorption on Au [21].

In present work, formaldehyde and acetaldehyde adsorption on Si doped graphene has been studied and sensor property of Si doped graphene for contaminants has been investigated theoretically. DFT-B3LYP method with 6-31G(d,p) basis set have been used for this purpose.

2. Computational Method

Structure of Si doped graphene will be determined with based on DFT (Density Functional Theory) [22,23] which is one of the quantum chemical calculation methods according to scope of the study. The Gaussian 09 software [24] was run for the B3LYP method from DFT calculations. This method will be run in the quantum chemical calculations to be conducted within the scope of the project. The B3LYP method is actual hybrid DFT method using Becke's triple parameter [25]. The functional hybrid B3LYP has become prominent with its the cost of calculation, the coverage and the accuracy of the results. It is very common method for organic chemistry researches. [26,27]. The basis set to be used for the elements are 6-31G (d, p), which is mostly used in quantum chemical calculations in the literature [28-30]. Also, Van der Waals corrections can also be used to provide the most commonly used ab-initio molecular dynamics (AIMD) In addition, depending on the changing thermodynamic conditions and the variety of reactions occurring, Van der Waals corrections can also be used to provide usually, used ab-initio molecular dynamics (AIMD) [31]. Hence, graphene can be synthesized in practice as a monolayer, graphene structures will be protecting as monolayer with quantum chemical calculations on it. The doping process will be performing on the carbon vacancy that is formed conveniently on the graphene surface. **Figure 1a** shows the monolayer graphene structure used in this study.



(a) **(b)**

Figure 1. a) Pure Graphene Structure b) Si-doped Graphene Structure

The theoretical calculations used by DFT method for both cluster model and periodic structures generally give very close trends for the structural parameters and reactivity [32,33]. Ricca et al. [34] have been studied on B and N co-doped graphene structure by both periodic and cluster approaches. It has been confirmed similar structural properties for both approaches. Additionally, the cluster models were used to form a quality image at molecular level for furfural adsorption on Pt doped graphene [35]. The complexes adsorbed on clusters gave very similar adsorption energy (within the 1.2% range for electronic energy) and geometrical properties (as example: 1.952 Å and 1.951 Å for Pt-C atoms respectively) on both small cluster ($PtC_{72}H_{21}$) and large cluster ($PtC_{180}H_{33}$) [32]. Also, in a theoretical work [36] which is a comparative study of cluster and supercell approaches for the reaction N and H to NH on Ru(0001) surface it has been reported that a periodic supercell approach adopted plane waves and density functional methods reveals similar barriers for reaction. Thus, in this study Si-doped graphene structure has been simulated by the cluster modeling approach.

A monolayer graphene structure includes 37 carbon atoms and 12 honeycomb rings to be employed within the scope of the research is seen. It has been reported in experimental and theoretical studies that elements have been mostly doped into hexagonal (honeycomb ring) structure of the

graphene and accomplished results have been get [37-39]. Therefore, the structure where the element doping takes place was desired a hexagonal (honeycomb) ring. As shown in the **Figure 1**, instead of the carbon in the honeycomb ring in the center, the atom Si is substituted. The free bonds of the last carbon atoms are saturated with hydrogen atoms (15 in total). In cluster modeling, saturation with hydrogen is fulfilled so that the atoms remaining at the end are not charged. Due to the graphene studies, which are doped with basic elements, this model seems to be proper, since the cluster approach is preferable to the periodic approach and the selected cluster size is adequate for the accuracy of the studies [40,41].

After the optimized geometry of the designed structure, formaldehyde adsorption was then performed. In addition, acetaldehyde adsorption on Si-doped graphene structure having the same dimension and acetaldehyde adsorption on Si-doped graphene structure will be made and compared.

The geometry optimized by doping Si atom to graphene structure and adsorption of formaldehyde and acetaldehyde on it will be brought to the most suitable geometry with (EG) Equilibrium Geometry calculation. EG calculations were used to optimize the geometries of the structures and to obtain the adsorption energies. In this study, energy difference values contain ZPE (Zero Point Energy) corrections. These energies were obtained using frequency expression in SPE (Single Point Energy) calculations after determine optimized structure. Besides, thermal enthalpy, vibration frequency, Gibbs free energy and energy values were obtained by SPE calculations under standard conditions in Gaussian software [42]. The indicated energy values were obtained for formaldehyde and acetaldehyde adsorption to the Si-doped graphene structure having the next formulas.

$$E = E_{electronic} + ZPE + E_{vibrational} + E_{rotational} + E_{tanslational} \quad (1)$$

$$H = E + RT \quad (2)$$

$$G = H + TS \quad (3)$$

E is the sum of electronic energies, thermal energies and ZPE. H is the sum of enthalpy and thermal energies, G is the sum of electronic free energy and thermal enthalpy, T is the temperature, S is entropy and R is the ideal gas constant value applied for the vibration frequency calculations. The scaling factor [40] was used as 0.9613 for each vibration frequencies for continuous renewal of the experimental foundations. The HOMO and LUMO energy values were obtained up to all optimized geometries. Some values were used to get information about optimized structures using HOMO LUMO values. The following equations were derived to comment on the activity of the graphene structure, electrophilicity, electronegativity, chemical hardness and chemical potential, values were obtained. ϵHOMO is the highest occupied molecular orbital energy and ϵLUMO is the lowest un-occupied molecular orbital energy. The basis of these equations is Koopman's approach [43-45] are as next.

$$Chemical\ hardness\ (\eta) = \frac{I-A}{2} \quad (4)$$

$$Chemical\ potential\ (\mu) = -\frac{I+A}{2} \quad (5)$$

$$Electronegativity\ (\lambda) = -\mu \quad (6)$$

$$Electrophilicity\ (\omega) = \frac{\mu^2}{2\eta} \quad (7)$$

where $I \cong -\epsilon_{HOMO}\ and\ A \cong -\epsilon_{LUMO}$

The SM (spin multiplicity) of the cluster and of the adsorbing molecule was obtained as a theoretical approach using SPE calculations. The SPE values of the systems were set using different SM values. In accordance with the results obtained, the SM value giving the lowest energy was accepted as the SM required for the system since the lowest energy state of the systems was considered the most stable state. The Si-doped graphene structure and adsorptive molecule were then optimized by EG calculations. Relative energy values were calculated by the following equations.

$$\Delta(E/H/G) = (E/H/G)_{Adsorp-Cluster} - [(E/H/G)_{Adsorp} + (E/H/G)_{Cluster}] \quad (8)$$

Here $E_{Adsorptive\text{-}Cluster}$ finds the thermal energy of the adsorbent on the doped graphene, the thermal energy of the $E_{Adsorptive}$ adsorbing molecule, e.g.. The adsorptive molecule and the $E_{Cluster}$ calculate the thermal energy of the first group. In addition, enthalpy (ΔH) and Gibbs free energy (ΔG) for acetaldehyde adsorption on Si-doped graphene are calculated.

3. Results and discussion

The optimized molecules and Si doped graphene cluster are shown in **Figure 2**. The optimized adsorptive molecules angle and bond length before and after adsorption are shown in **Table 2.** In this study, the O=H and C-H bonds of formaldehyde were 1.206 Å and 1.110 Å, respectively. The most closed values of 1.1 Å and 1.2 Å respectively were reported with B3LYP/LanL2DZ method [46]. The bond angles for H-C-H and H-C=O were computed to be 115.2 º and 122.4º, respectively. The O=H and C-H bonds and H-C-H angle were calculated as 1.1 Å, 1.1 Å and 115ºC respectively which were close to

experimental results [47]. For acetaldehyde molecule C=O, C-C, and C-H bond lengths were found as 1.2 Å, 1.5 Å, and 1.11 Å respectively which are well agreement with the literature [48].

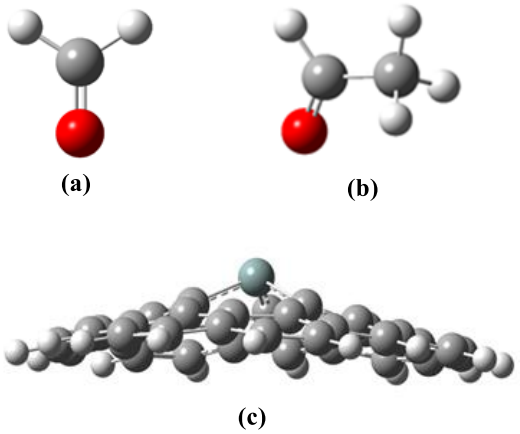


Figure 2. Optimized structures a) Formaldehyde b) Acetaldehyde c) Top view of Si doped Graphene c) Side view of Si doped graphene

Table 2. Bond Lengths (Values are in units of Å)

Bond		Formaldehyde		Acetaldehyde	
		Before Adsorption	After Adsorption	Before Adsorption	After Adsorption
Adsorptive Molecules	C=O	1.20676	1.36499	1.21072	1.37139
	C-H1	1.11056	1.08318	1.11349	1.08645
	C-C	-	-	1.51449	1.48964
	C-H2	1.11057	1.08565	1.09513	1.09430
	C-H3	-	-	1.09241	1.09757
	C-H4	-	-	1.09513	1.10350
Si Doped Graphene	Si-C1	1.77751	1.79779	1.77751	1.80106
	Si-C2	1.77762	1.79728	1.77762	1.79678
	Si-C3	1.77766	1.79462	1.77766	1.80207
	h	1.61217	1.79604	1.61217	1.70484
	Si-O	-	1.68025		1.67319

Table 3. Adsorption Energies, Enthalpy, and Gibbs free energy (Values are in units of kcal/mol)

	Adsorption Energy ΔE	Adsorption Enthalpy ΔH	Gibbs Free Energy ΔG
Formaldehyde	-24.50	-25.09	-14.13
Acetaldehyde	-33.32	-33.91	-24.00

Geometrical parameters of the optimized Si doped graphene structure before and after adsorption were tabulated in **Table 2.** Si-C bonds were 1.777 A. Corresponding literature values were reported as 1.765 [6], 1.76 [49], 1.85 [50], 1.772 Å [15] and 1.73 A [51,52]. While C=O bond lengths increase C-H bond lengths with same C atoms decrease. Previously it was reported the bond length of Si and O atoms of formaldehyde was 1.772 Å which very close our result 1.680 A [15]. The distance between acetaldehyde and doped Si was calculated as 1.673 Å. The characteristic IR peak of aldehydes is for C=O bond. In the spectrum C=O peak of formaldehyde and acetaldehyde are 1845 cm^{-1} and 1835 cm^{-1}, respectively. The peaks shifted to 1262 cm^{-1} and 1284 cm^{-1} after adsorption, respectively.

The adsorption energy, enthalpy and Gibbs free energy values were shown in **Table 3.** It could be deduced that the adsorptions occur spontaneously at room temperature. Acetaldehyde adsorption energy is lower than that of formaldehyde as expected [53]. The adsorption energy of acetaldehyde on Si-doped graphene structure was computed to be -33.32 kcal/mol. This value is somewhat higher than literature values. Previously, the formaldehyde adsorption energy on Si doped graphene was reported as -17.7 kcal/mol [15]. In the other study with aluminum nitride nanotubes the adsorption energy was reported as -29 kcal/mol [54]. Acetaldehyde adsorption on Au(111) surface was -1.15 kcal/mol [21]. The adsorption energy of formaldehyde on Si-doped graphene structure was computed to be -24.50 kcal/mol. Adsorption energy

of formaldehyde on Si-doped BC3 sheet was −26.49 kcal/mol [16]. Gibbs free energy change for acetaldehyde and formaldehyde adsorptions on Si-doped graphene were calculated to be -24.00 kcal/mol and -14.13 kcal/mol respectively, these values indicating that acetaldehyde and formaldehyde adsorptions occurs simultaneously on Si-doped graphene.

The Mulliken atomic charges both adoptive and adsorbed molecules are shown in **Figure 3** and some of them were tabulated in **Table 4**. The total charge of formaldehyde and acetaldehyde were computed to be -0.081e and 0.430e, respectively. Meanwhile, the charge of graphene doped metal and abounded C atoms after formaldehyde adsorption increased. Oppositely, the graphene charge decreased after acetaldehyde adsorption. It was inferred from the information the charge transfer for acetaldehyde adsorption was from adsorptive to adsorbent but the charge transfer for formaldehyde adsorption was opposite direction. In addition, there is a small charge transfer with formaldehyde as previously reported [13].

The chemical hardness (η), the chemical potential (μ), the electronegativity (χ), the electrophilicity (ω) and the energy gap between HOMO and LUMO (HLG) of the Si-doped graphene structure before and after acetaldehyde and formaldehyde adsorptions; HOMO and LUMO energy values were determined. The results obtained are shown in Table 5.

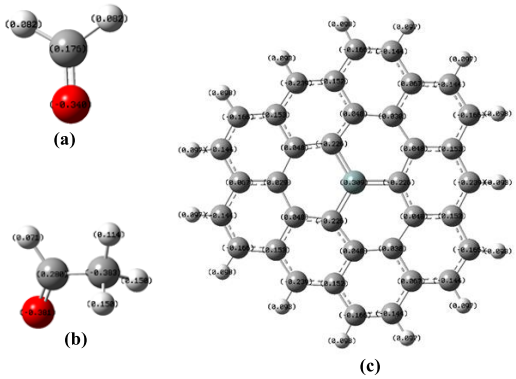


Figure 3. Atomic charges a) Formaldehyde b) Acetaldehyde c) Si doped graphene

Table 4. Atomic charges of Si doped graphene clusters (Values are in units of e)

Atom	Before Adsorption	After Formaldehyde Adsorption	After Acetaldehyde Adsorption
20Si	0.226	0.272	0.571
C1	-0.118	-0.153	-0.208
C2	-0.118	-0.176	-0.201
C3	-0.118	-0.158	-0.212

Table 5. Adsorption properties of formaldehyde and acetaldehyde adsorption on Si doped graphene (Values are in units of kcal/mol)

	Si doped Graphene		Formaldehyde adsorbed on Si doped Graphene		Acetaldehyde adsorbed on Si doped Graphene	
Properties	α MOs	β MOs	α MOs	β MOs	α MOs	β MOs
HOMO Energy	-98.9	-128.6	-104.1	-121.7	-97.4	-121.0
LUMO Energy	-46.5	-68.4	-59.9	-60.0	-59.3	-59.2
HLG	52.4	60.2	44.3	61.8	38.1	61.9
Chemical Hardness	26.2	30.1	22.1	30.9	19.1	30.9
Chemical Potential((μ)	72.7	98.5	82.0	90.9	78.3	90.1
Electronegativity (χ)	-72.7	-98.5	-82.0	-90.9	-78.3	-90.1
Electrophilicity (ω)	101.0	161.0	151.9	133.7	160.9	131.3

The HOMO LUMO Spectrum and images are shown in **Figures 4 and 5.** For both acetaldehyde and formaldehyde adsorptions on Si-doped graphene structure the HOMO-LUMO gap of αMOs decreased after adsorptions while a small increase in the HLG of βMOs has been observed. In previous studies formaldehyde adsorption on boron nitride nanotubes and Si-doped BC3 sheet, it was reported energy gap change 3.9% [47] and 28.2% [16] with mixed orbitals. Additionally, it can be deduced from the following equation that the electrical conductivity of the Si-doped graphene

cluster increased because of the decrease of the HLG value after adsorption of the acetaldehyde and formaldehyde molecules [54-56].

$$\sigma = AT^{3\prime 2}\exp\left(\frac{-E_g}{2kT}\right) \quad (9)$$

where σ is electrical conductivity, A is a constant (electrons / $m^3K^{3/2}$), for example a cavity of HOMO-LUMO Gap (HLG), T is room temperature and k is a Boltzmann constant. According to this equation, for a standard temperature, a smaller HLG is a greater electrical conductivity. So far, it has been reported that this relationship agrees well with the experimental results [57]. As a result, adsorption of the acetaldehyde and formaldehyde molecules increase the electrical conductivity of the Si-doped graphene cluster, suggesting that Si-doped graphene may be a potential sensor for the acetaldehyde and formaldehyde molecules.

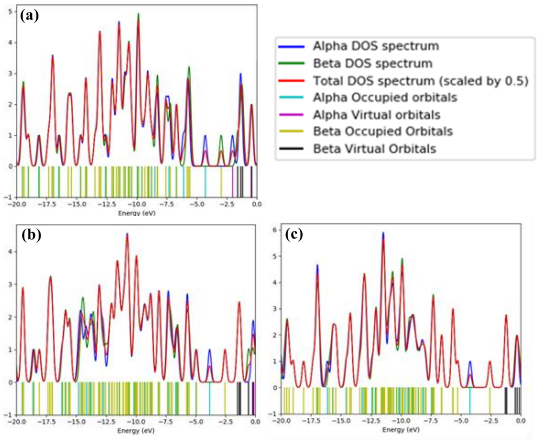


Figure 4. DOS plots a) Si Doped Graphene b) Formaldehyde adsorbed on Si doped Graphene c) Acetaldehyde adsorbed on Si doped graphene

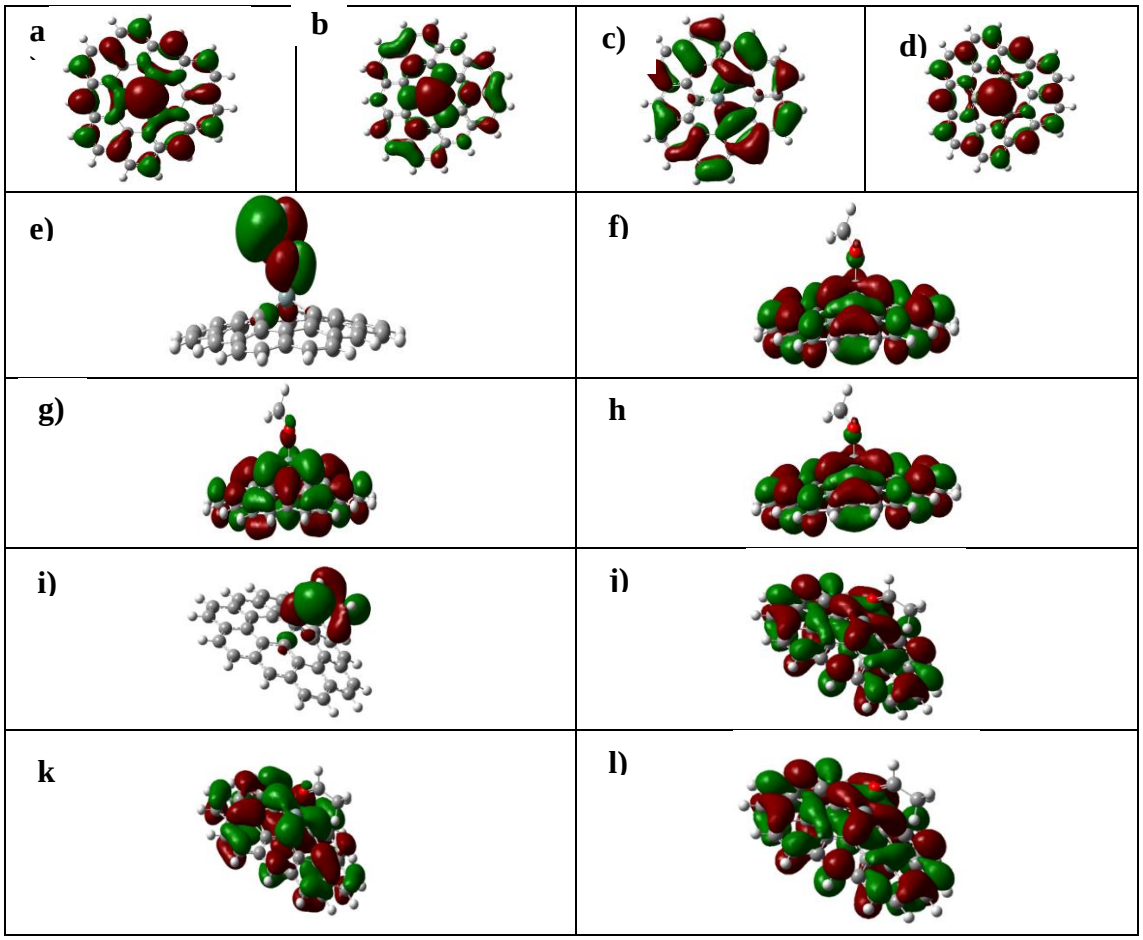


Figure 5. a) Si doped Graphene αHOMO b) Si doped Graphene αLUMO c) Si Doped Graphene βHOMO d) Si Doped Graphene βHOMO e) Formaldehyde adsorbed Si doped Graphene αHOMO f) Formaldehyde adsorbed Si doped Graphene αLUMO g) Formaldehyde adsorbed Si doped Graphene βHOMO h) Formaldehyde adsorbed Si doped Graphene βLUMO i) Acetaldehyde adsorbed Si doped Graphene αHOMO j) Acetaldehyde adsorbed Si doped Graphene αLUMO k) Acetaldehyde adsorbed Si doped Graphene βHOMO l) Acetaldehyde adsorbed Si doped Graphene βLUMO.

4. Conclusion

In this study DFT calculation with hybrid B3LYP method with 6-31G(d,p) basis set is performed for sensor property of Si doped graphene for common indoor contaminants, formaldehyde and acetaldehyde. The charge transfer of formaldehyde is very weak. The charge transfers occur after adsorptions from acetaldehyde molecule to cluster and from cluster to formaldehyde molecule. The HOMO-LUMO gap value has decreased for αMOs, which indicates that it has gained conductivity. The chemical hardness decreased and the chemical potential increased for αMOs after adsorption. Subsequently, these properties prove that the Si element doped graphene structure might be a sensor for the detection of acetaldehyde and formaldehyde molecules.

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