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THE ADSORPTION PROPERTIES OF POLYCRYSTALLINE GRAPHENE: QUANTUM-CHEMICAL SIMULATION

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This study presents the results of quantum-chemical simulation of H_2O, NH_3, PH_3, and CH_4 molecules and their fragments adsorption onto graphene nanoclusters with different types of grain boundaries. We describe the molecule adsorption states on graphene and estimate the absorption energy characteristics. It is shown that the presence of grain boundaries changes the geometric and electronic parameters of grapheme, and can lead to a physical adsorption and chemisorption of molecules without dissociation, unlike in orderly graphene. Dissociative chemisorption of molecules on the grain boundaries is accompanied by some significant changes in the geometric, electronic, and energy state of graphene. The features of the energy change differences for the HOMO-LUMO of graphene with the chemisorbed dissociation fragments can be used to identify the gas molecules on graphene by their electronic spectra.

Keywords: Polycrystalline graphene, Dislocation defect, Electronic properties, Adsorption properties.

1. Introduction

The discovery of graphene, the first truly two-dimensional crystal, and the study of the remarkable electronic properties of this promising nanoscale structure has caused a huge increase in the interest of carbon nanomaterials. Mostly, studies have focused on electronic transport phenomena in graphene and its applications in carbon-based electronics. There is also interest in the mechanism of interaction between the adsorbed particles and line defects on the graphene surface in connection with the possible use of polycrystalline graphene as a material for chemical sensors [1]. Dislocations, grain boundaries, and other topological defects in graphene are the subject of recent experimental and theoretical studies [2-5]. However, at present, their structure and properties remain poorly investigated.

2. Calculation Techniques

In this paper, we studied the adsorption of molecules and radicals on a graphene surface containing grain boundaries with different θ misorientation angles and concentration of dangling bonds. The modeling was performed using the MNDO semiempirical techniques included in the MOPAC 2009 software package [6], as well as ab initio Hartree-Fock methods of the PC GAMESS software package [7]. $C_{132}H_{28}$, $C_{143}H_{29}$, $C_{91}H_{23}$, $C_{73}H_{21}$, and $C_{119}H_{29}$ graphenes with a (1.0) intergranular boundary were constructed as a model, and $C_{97}H_{24}$, $C_{104}H_{26}$ containing more complex grain boundaries with misorientation angles θ=16°. The boundaries were formed by polygons located in the 7-5-6-6-7-8-5 and 4-7-5-8-4-10-5 sequence. Figures 1,2 illustrate the fragments of clusters with inter-granular boundaries. The boundaries, consisting of a set of various polygons, lead to a change in the graphene sheet topology:

it bends forming a ridge along the boundary. The α angle between the adjacent grains was about 30-35 and 40-45 degrees for the $C_{97}H_{24}$ and $C_{104}H_{26}$ clusters respectively. A similar graphene sheet curvature was obtained by the authors of [2] to simulate the grain boundaries using molecular dynamics. The misorientation angle θ in [2] was from 0 to 30 degrees, the α angle varied in a wide range of 0–85°, but values of α between 20° and 40° occurred most frequently.

In the adsorption simulation for each molecule, we considered various positions as adsorption centers: carbon atoms at the grain boundary; over the carbon polygons centers on the boundaries; and over the C-C bonds. The interaction of molecules and radicals with dislocation defects, graphene grain boundaries can lead to physical adsorption and chemisorption, and that may cause a change in the electrical, physical, and chemical properties of graphene. The binding energies (E_b) of the adsorbed molecules were calculated as the difference between the sum of the pure graphene total energy (E_g) and isolated molecule energy (E_{mol}), and the total energy of a "graphene - adsorbed molecule" system (E_{syst}):

$$E_b = (E_g + E_{mol}) - E_{syst} \tag{1}$$

3. Results and Discussion

3.1. The adsorption of molecules on graphene containing a (1.0) boundary

Such violations of the graphene crystal lattice as the occurrence of adjacent 5- and 7-gons can lead either to the appearance of point defects like the Stone-Wales -type defects [8], or to the formation of dislocations [5]. The (1.0) dislocation defect is characterized by a Burgers vector:

$$\vec{b} = m\vec{a}_1 + n\vec{a}_2, \quad m = 1, n = 0, \tag{2}$$

and an insert of a graphene material strip (the strip is limited by the dotted lines in Figure 1a). The sequence of (1.0) dislocation defects aligned along one axis describes a defect like a (1.0) grain boundary having a wedge-shaped graphene insert and the angle of:

$$\theta = \theta_1 + \theta_2 = 2\arcsin\frac{\left|\vec{b}_{(1.0)}\right|}{2d_{(1.0)}}, \tag{3}$$

where $\vec{b}_{(1.0)}$ is Burgers vector, $d_{(1.0)}$ is the distance between the (1.0) dislocations cores.

The lengths of the C-C bonds at the (1.0) boundary take the values of 1.39-1.52 Å, which differ significantly from the lengths of C-C bonds for orderly graphene (1.42-1.44 Å). There were changes in the values of the bond angles. Changes in the bond geometry led to the distribution of charge between the carbon atoms, a positive charge is localized on the heptagon carbon atoms, while a negative charge is localized on the pentagon carbon atoms. Although the charge distribution is insignificant, it can affect the adsorption properties of graphene with linear defects. In ordered graphene, the charge on the carbon atoms is missing. For ordered graphene with a (1.0) boundary, the HOMO-LUMO width decreases, while for ordered graphene with the same number of carbon atoms, ΔE_{HL} ~5.49 eV, for the $C_{132}H_{28}$ cluster with a (1.0) boundary ΔE_{HL} =3.70 eV.

Analysis of the H_2O, PH_3, NH_3 and CH_4 adsorption calculation results proved that the physical adsorption states are almost identical to those of ordered graphene, the values of the binding energy of molecules to graphene being 51, 39, 41, and 16 meV. That is, the changes in the electronic state of the graphene with grain boundaries are insufficient for significant changes in the molecules' binding energy during the act of physical adsorption.

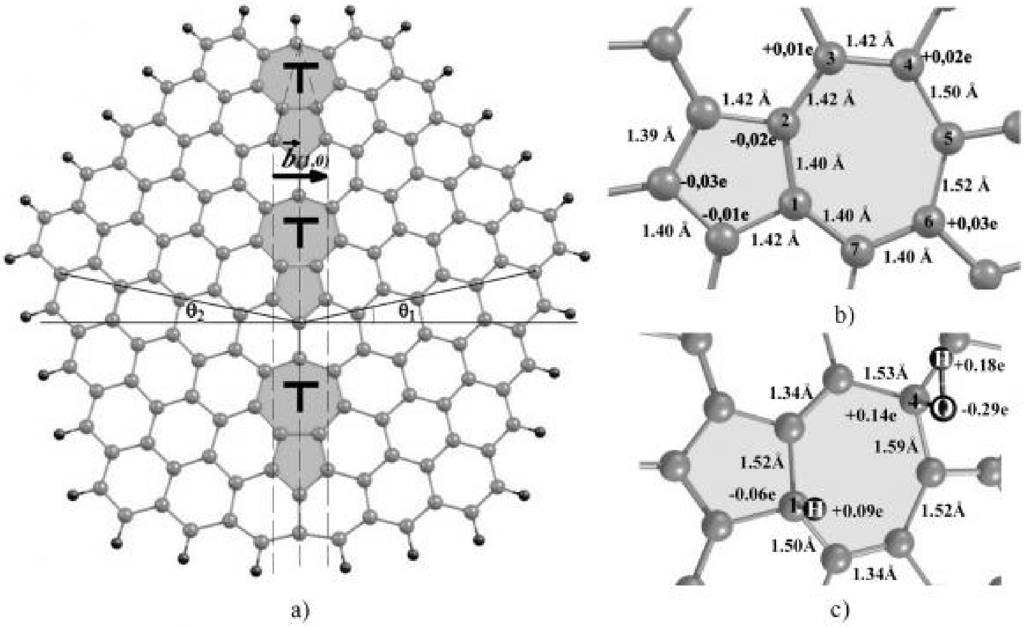

FIG. 1. (a) A $C_{132}H_{28}$ cluster containing (1.0) grain boundary; a fragment of the cluster before (b) and after (c) water molecule adsorption

Chemisorption on the (1.0) graphene grain boundary requires that the H_2O, PH_3, NH_3, and CH_4 molecules dissociate into fragments. The chemisorption induces significant changes in the geometric, electronic, and energy state of graphene. For example, the value of the energy difference between the HOMO-LUMO (ΔE_{HL}) increases, and there is a transfer of charge from graphene to the chemisorbed fragments of the dissociated molecule.

The adsorption sites selected for the water dissociation fragments affects the system parameters. The minimum energy is in the system where the -H and -OH groups are chemisorbed respectively on the carbon atoms of the pentagon and the heptagon on the boundary (Figure 1c). There is the second water molecule physically adsorbed on the (1.0) boundary. The second molecule is held at the surface, forming a hydrogen bond with the oxygen atom of the -OH fragment chemisorbed on the (1.0) boundary. The binding energy is 0.47 eV.

The charge transfer in the case of -OH and -NH_2 radical chemisorption is -0.115 and -0.085 e, these particles act as acceptors, while -PH_2 and -CH_3 fragment chemisorption does not result in the "particle-graphene" charge redistribution (Table 1). For all the chemisorbed molecules, the binding energy value for the fragments calculated using formula (1) is about 1 eV, which is significantly less than the sum of the heats of adsorption for -H and the -OH group on graphene. Thus, following the results obtained in [9], the heat of adsorption of hydrogen on the ordered graphene is $\sim$5 eV. Obviously, the total energy of the "graphene-adsorbed fragments" system increases due to the formation of dangling bonds of some carbon atoms and the tension in the graphene lattice. It is noticed that the ΔE_{HL} value for the chemisorption of different fragments of the molecule dissociation take different values. This feature can be used to identify the molecules of gases on graphene in the electronic spectra.

TABLE 1. Geometric, electronic, and energy parameters of the $C_{132}H_{28}$ graphene cluster (Figure 1) containing the (1.0) boundary with adsorbed fragments of dissociation of water, phosphine, ammonia, and methane

Molecule, XH_n	Graphene atom bonded to (XH_{n-1})	Graphene atom bonded to (H)	^{1}R(C-X), Å	$Q(XH_{n-1})$, e	Q(C), e	$\Delta(\Delta E_{HL})$, eV	E_b, eV
H_2O	C4	C1	1.46	-0.115	+0.139	+1.51	0.81
PH_3	C6	C4	1.98	+0.030	-0.013	+1.75	0.73
NH_3	C2	C1	1.51	-0.085	+0.101	+1.47	0.94
CH_4	C2	C5	1.58	+0.026	+0.023	+1.58	1.14

^{1}R(C-X) is C-X interatomic distance, X is O,P,N,C; $Q(X_{n-1})$ is charge on radicals, Q(C) - charge on graphene atom bonded to (XH_{n-1}), $\Delta(\Delta E_{HL}) = \Delta E_{HL(ads)} - \Delta E_{HL(clean)}$ is the difference between the energy values $\Delta E_{HL(ads)}$ for the cluster with an adsorbed molecule and $\Delta E_{HL(clean)}$ for the clean cluster.

3.2. Adsorption of molecules on graphene containing a boundary with a misorientation angle of $\theta = 16°$

The ideal grain boundaries formed by pentagon-heptagon pairs have been observed in experiments [2]. However, the boundaries between the grains with random orientation are most common. These boundaries can be rough, corrugated or protruding, and have some dangling bonds and other active adsorption sites. Due to this, it is interesting to research the structure and properties of grain boundaries with an arbitrary crystallographic orientation via quantum chemistry techniques. The structure of grain boundaries has been studied in [3,4] using a transmission electron microscopy technique. Statistical analysis showed that the most frequent misorientation angles included were near 0 and 30°, and in the intermediate values of 13–17 degrees. In this study, we investigated the adsorption properties of the grain boundary separating the areas with a misorientation angle θ=16°. The corresponding crystallographic directions in different grains were positioned symmetrically relative to the boundary.

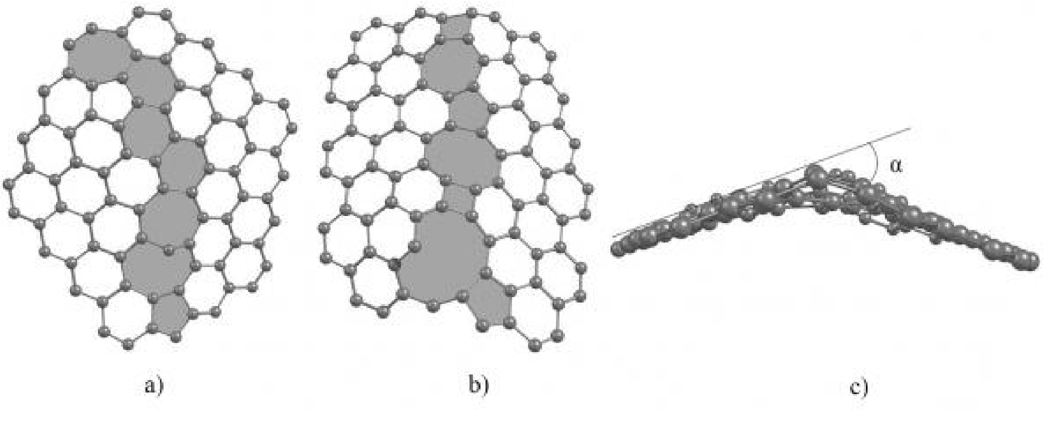

FIG. 2. Fragments of clusters containing grain boundaries for θ=16°: $C_{97}H_{24}$, a top view (a), $C_{104}H_{26}$, a top view (b) and a side view (c)

The calculations in this study showed that the C-C bond lengths at the boundary with θ=16° vary from 1.34–1.58 Å, wider than at the (1.0) boundary. The charges on the atoms are distributed in a complex manner from of -0.07 to +0.10 e, and for each of the clusters, the maximum positive charge is localized on the atoms with only two nearest neighbors. The authors of [2] discovered that the addition of hydrogen atoms to similar atoms leads to the maximized heat adsorption. In [10], to simulate water adsorption onto the diamond surface with a vacancy defect, the authors found a metastable state in which the molecule, without losing its integrity, is chemisorbed onto the surface. The oxygen atom thus forms a bond with the carbon atom initially having two nearest neighbors and a dangling bond. In this regard, it is of interest to find these bound states that do not require pre-dissociation at the grain boundaries of polycrystalline graphene.

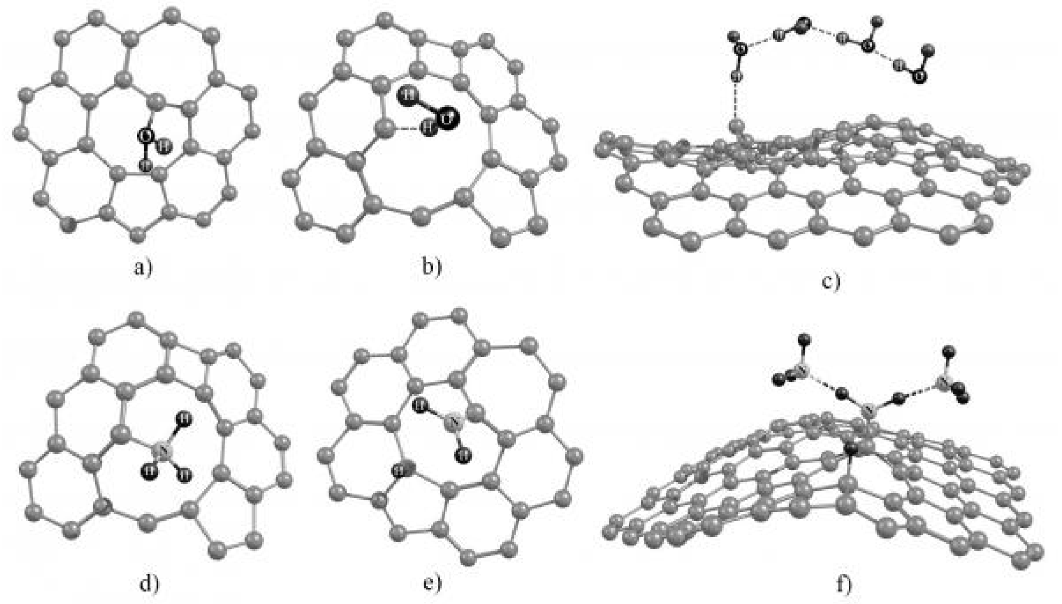

FIG. 3. Boundary molecules adsorption results: a water molecule is chemisorbed to form a covalent (a) and a hydrogen (b) surface-molecule bond; (c) - chain formation of four bound water molecules; the ammonia molecule adsorption result on the boundary to form a covalent bond (d), a dissociation on the surface of the $C_{97}H_{24}$ cluster (e); attaching three molecules (f)

In this study we found a bound state of a water molecule, which forms a C-O chemical bond (Figure 3a). However, the molecule can also join the cluster surface with the formation of a weak hydrogen bond (Figure 3b). Subsequent water molecules can be attached to the first molecule, thus forming chains along the graphene sheet surface (Figure 3c). The binding energy per molecule for such a chain is bigger than for the first molecule. The bound state was also found for an ammonia molecule (Figure 3d). We also observed a dissociation of the molecule as it approached the surface atoms, where a positive charge of +0.094 e was initially localized on the ($C_{97}H_{24}$ cluster) and +0.023 e on the ($C_{104}H_{26}$ cluster). The dissociation results are plotted in Figure 3e. Two molecules can join the adsorbed radical NH_2 to form the hydrogen bonds (Figure 3f). These calculation results are shown in Table 2.

A CH_2 radical is chemisorbed on the surface to form a double bond with one carbon atom (Figure 4a) and single bonds with two carbon atoms (Figure 4b). In the state shown in Figure 4b, a significant positive charge of Q=+0.12 e is localized on the attached radical, and the ΔE_{HL} value significantly decreases (by 0.46 eV).

Table 2. Calculation results of the geometric, electronic, and energy parameters for graphenes interacting with H_2O, NH_3 molecules and CH_2 radical (to Figure 3,4)

Molecule, XH_n	$^1P_{C-X}$	R(C-X), Å	$Q(XH_{n-1})$, e	Q(C), e	Δ (ΔE_{HL}),eV	E_b per molecule, eV
H_2O, covalent bond C-O	1.49	1.49	+0.335	-0.041	-0.37	0.41
H_2O, hydrogen bond C-H	0.05	2.04	-0.043	+0.006	-0.04	0.26
H_2O, four bound molecules	0.09	1.89	-0.064	-0.01	-0.12	0.36
NH_3, covalent bond C-N	0.83	1.50	+0.506	+0.011	-0.45	1.35
NH_3, a dissociation on the $C_{97}H_{24}$ cluster	1.24	1.37	+0.068	+0.219	+0.24	2.50
NH_3, a dissociation on the $C_{104}H_{26}$ cluster	0.95	1.49	-0.074	+0.111	+0.48	4.27
NH_3, three bound molecules	1.77	1.29	+0.328	+0.243	-0.16	1.44
CH_2, a double bond	1.92	1.31	-0.003	+0.014	+0.10	7.87
CH_2, two single bonds	0.99	1.48	+0.120	+0.194, -0.011	-0.46	3.63

$^1P_{C-X}$ is bond order between the C and X atoms.

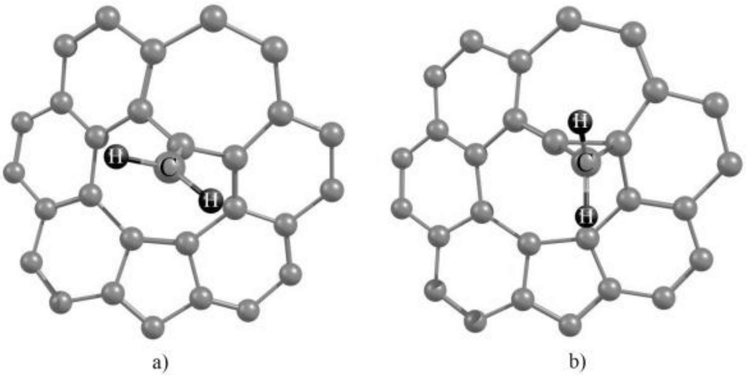

Fig. 4. CH_2 radical adsorption result, forming a double bond (a) and two single bonds (b)

4. Conclusion

These calculations enable one to conclude that H_2O, PH_3, NH_3 and CH_4 molecules are chemisorbed on the (1.0) grain boundary in graphene only in case of dissociation into fragments. The dissociation fragments' chemisorption increases the HOMO-LUMO energy difference values for (ΔE_{HL}) graphene. The ΔE_{HL} dependence on the type of adsorbed molecules can be used to create gas sensors.

For more complex grain boundaries, separating the areas with a misorientation angle of $\theta = 16^\circ$, with dangling bonds and other active adsorption sites, physical and chemical adsorption of molecules is possible without their dissociation into fragments. The activation energy of molecular and dissociative adsorption and the molecule-surface binding energy depend on the type of molecule, on the position of the adsorbing center, the number of adsorbed particles in the immediate vicinity, and the distance to the neighboring adsorbed particle. The simulation studies showed that molecules such as H_2O and NH_3 can form a chemical bond on the graphene surface containing a grain boundary with $\theta=16^\circ$ misorientation angles, without prior dissociation. In chemisorption states on graphene, the H_2O molecules show the acceptor properties, while the NH_3 molecules possess the donor properties. The CH_2 radical is chemisorbed on the surface to form some strong chemical bonds, wherein there can be a charge transfer of up to +0.12 e.

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