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SIMULATION OF INTERACTION PROCESSES OF C_{20} FULLERENE WITH GRAPHENE

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Graphene, a carbon sheet one atom thick, with carbon atoms arranged in a two-dimensional honeycomb configuration, has a number of intriguing properties. Fullerenes are a promising material for creating electro-active elements in solar cells and active layers in thin-film organic transistors. A computer model of the C_{20} fullerene molecule was constructed using the energy minimization method with the second-generation Brenner potential (REBO). A computer model of "infinite" defect-free graphene was built, designed to consider the process of adsorption of a C_{20} fullerene molecule on its surface. To study adsorption process computer models of fullerene and "infinite" graphene were approached to the required distance with a different set of geometric arrangement of fullerene with respect to the graphene surface. It has been established that the adsorption of fullerene C_{20} on the surface of graphene can be carried out in three different ways, differing in the number of interacting fullerene and graphene atoms. The binding energies and adsorption lengths for C_{20} fullerene molecules adsorbed on the graphene surface in different ways are calculated. The way of adsorption corresponding to the highest binding energy and the shortest adsorption length was revealed.
Keywords: *Fullerene molecule; Graphene; Adsorption; Simulation; Brenner potential*
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INTRODUCTION

Graphene, a carbon sheet one atom thick, with carbon atoms arranged in a two-dimensional (2D) honeycomb configuration, has a number of intriguing properties. Graphene has been extensively studied and is expected to find applications in many areas, especially in nanoelectronic devices [1-4]. Fullerenes are a promising material for creating electro-active elements in solar cells and active layers in a thin-film organic transistor [5, 6]. Many researchers have focused their attention on the interaction of fullerene molecules with solid surfaces. From the seminal article by Li et al. in [7] and later, the study of the interaction of fullerenes with a surface turned out to be an exciting area of research. In particular, while some researchers in this field have obtained results showing that the fullerene molecule experiences physical adsorption [8-10], others, on the contrary, have shown that the fullerene molecule is chemisorbed [11-16].

The study of C_{20} molecules and solids from C_{20} molecules can help expand the possibilities of using C_{20} molecules and solids from these molecules. In addition to the above applications, a known application of the C_{20} fullerene molecule is in the high temperature superconductivity (T_c) region due to its stronger electron-phonon coupling than C_{60} fullerene [17,18]. This is due to the fact that the vibronic coupling increases as the cluster size decreases [19]. As a result, it was suggested that the condensed form of the smallest fullerene C_{20} [20–22] may be the best potential candidate for high-temperature superconductors [23]. However, the use of this promising molecule, for example, in fullerene-based heterostructures, requires understanding the nature of C_{20} adsorption on various two-dimensional materials, since their interface interaction and binding properties play an important role in the molecular functionality of heterostructural nanomaterials.

The purpose of this research is to determine the energy and bond length for various methods of adsorption of a C_{20} fullerene molecule on a graphene surface, as well as changes in the geometry of molecular fullerene after adsorption. The geometry of adsorbed fullerenes can significantly influence their chemical properties, so analysis of the molecular system C_{20} + graphene may be of some interest.

At present, objects based on fullerenes C_{60}, C_{70} and others, the synthesis methods of which are quite developed, are mainly being studied. Low-atomic fullerenes (C_{20}, etc.) are studied to a less extent. The goals of the proposed work are aimed at some clarification of the mechanisms of interaction of C_{20} fullerene with graphene, which may be of interest for optimizing methods for their synthesis.

In connection with the above, in this work, research results related to the interaction of the C_{20} molecule with graphene were highlighted, and the interaction process was considered using molecular dynamics (MD) simulation.

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METHODS AND INVESTIGATED MATERIALS

Using the energy minimization method with the second-generation Brenner potential (REBO), which describes carbon structures well [24], a computer model of the C_{20} fullerene molecule was constructed, the atomic coordinates of which were taken from [25]. As a result, it was found that the cohesive energy E_f of each carbon atom in fullerene is 6.123 eV. Then a computer model of "infinite" defect-free graphene was built, designed to consider the issues of interaction and adsorption of the C_{20} fullerene molecule on its surface. For this, a rectangular section of graphene was chosen, consisting of 112 carbon atoms (Figure 1). The construction and substantiation of the model is described in more detail in [26].

Defect-free graphene is a flat carbon structure consisting only of hexagons, similar to C_{60} fullerene hexagons, with each carbon atom in the fullerene molecule surrounded by three neighbors, with each of which it is connected by a simple covalent bond. In the smallest fullerene C_{20}, C-C bonds form only regular pentagons, in other fullerenes, in addition to pentagons, there are hexagons, and, for example, in the most common fullerene C_{60}, C-C bonds form 20 hexagons and 12 pentagons (Figure 2). Each carbon atom in a fullerene molecule is surrounded by three neighbors, with two of which it is connected by a single covalent bond and with the third by a double bond.

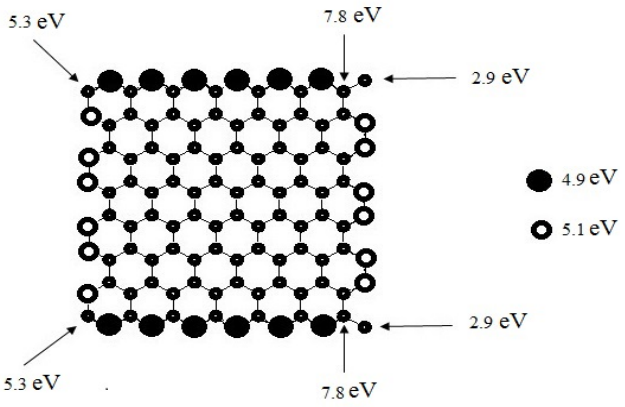


Figure 1. Atomic structure of a defect-free 112-atom rectangular section of graphene

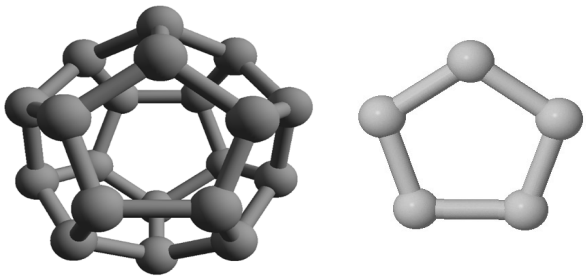


Figure 2. Spatial configuration of atoms and the C_{20} fullerene face

After computer models of single defect-free objects were obtained: fullerene C_{20}, "infinite" graphene, the process of adsorption of fullerene on the surface of graphene was studied. To study the process of fullerene adsorption on graphene, computer models of fullerene and "infinite" graphene were approached to the required distance with a different set of geometric arrangement of fullerene with respect to the graphene surface, followed by the application of the energy minimization method within the framework of the Brenner potential and periodic boundary conditions on the edge atoms of graphene.

The C_{20} fullerene molecule with a graphene layer is studied by the energy minimization method, where we use the conjugate gradient algorithm. Since the energy is a function of different degrees of freedom, i.e. bond lengths, bond angles, and dihedrals, this method finds the energetically preferred conformation of the system, which is equivalent to locating all minima of its energy function. This article explores the lowest energy state and the other most important local minimum states. On the other hand, empirical or parametric methods give the interaction potential in an analytical form and are based on the corresponding parameters determined by comparison with experimental data. Due to the analytical form of the potential, it is convenient for further calculations of other properties of the material. Here we use a version of the Brenner potential specifically parameterized for carbon and hydrocarbon systems. The expression of this potential and its parameters used in our calculation can be found in [27]. This potential describes the carbon-carbon interaction very well. Here we further demonstrate its suitability for characterizing hydrocarbon systems. In Table 1, the binding energy and bond length calculated using the modified Brenner potential are in very good agreement with available other theoretical data. This confirms our model for the interaction of graphene with the C_{20} fullerene molecule.

Table 1. Values of bond energy and bond length for carbon-carbons obtained in the current approach (bold), DFT B3LYP [28] and TD-DFT [29] methods

carbon	Binding energy (eV/atom)	Bond length (Å)
C_{20} 	**6.123** 6.086 [28] -	**1.46** 1.445 [28] 1.44-1.51 [29]

RESULTS AND DISCUSSION

It was found that the adsorption of fullerene C_{20} on the surface of graphene can be carried out in different ways. The paper lists only 3 selected methods of such adsorption. Horizontal edges of nanographene are zigzag edges, vertical edges are armchair edges. Atoms whose cohesion energy differs from 7.4 eV are marked with large sizes or arrows indicating their cohesion energies.

The following are the ways of C_{20} fullerene adsorption on the graphene surface:

I) through the interaction of one atom of fullerene and one atom of graphene (C-ATP),

II) through the interaction of two neighboring fullerene atoms and two neighboring graphene atoms (BRI),

III) through the interaction of two nearest non-neighboring fullerene atoms and two nearest non-neighboring graphene atoms.

Table 2 shows the geometric characteristics of adsorbed fullerene obtained by analyzing the results of computer simulation of three selected adsorption methods. Since the radius of the free C_{20} fullerene is 1.99 Å, and its spherical symmetry leads to the fact that the values of its maximum and minimum radii are equal to each other and their ratio is equal to 1, then, according to Table 2, as a result of adsorption, the spherical symmetry of the C_{20} fullerene is violated and this is a violation of the symmetry depends on the way the molecule is adsorbed on the graphene surface.

Table 2. Geometric characteristics of fullerene C_{20}, adsorbed on the surface of graphene

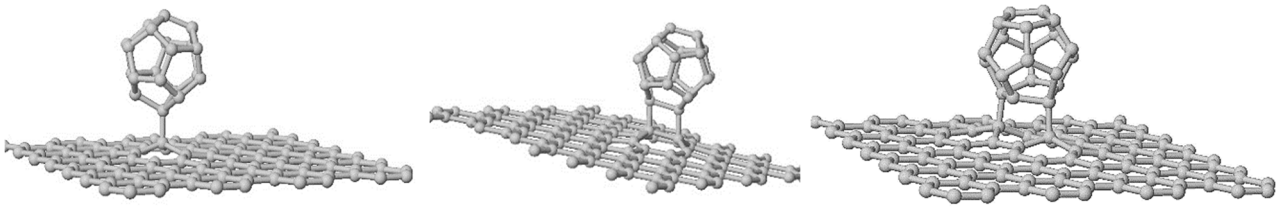
	Adsorption ways		
	I C-ATP	II BRI	III
radius averaged, Å	1.99	1.99	1.99
maximum radius, Å	2.19	2.19	2.21
minimum radius, Å	2.07	2.06	2.05
ratio of maximum radius to minimum	1.05	1.06	1.07

Three variants of fullerene adsorption on the graphene surface are considered: a) through the interaction of one fullerene atom and one graphene atom, b) through the interaction of two neighboring fullerene atoms and two neighboring graphene atoms, c) through the interaction of two nearest non-neighboring fullerene atoms and two nearest non-neighboring graphene atoms (Figure 3).

The binding energy E_{ads} for C_{20} molecule adsorbed on the surface of the graphene substrate is the difference between the total potential energy of the substrate and the adsorbed molecule $E_{ads/sub}^{tot}$ from the potential energy of the substrate in the state where they do not interact E_{ads}^{tot} and the potential energy of the adsorbed molecule E_{sub}^{tot} equals to [30]:

$$E_{ads} = E_{ads/sub}^{tot} - (E_{sub}^{tot} + E_{ads}^{tot}).$$

The following binding energies and adsorption lengths for C_{20} fullerenes adsorbed on graphene were obtained: a) 1.63 eV; 1.52Å, b) 1.07 eV; 1.58Å and c) 0.83 eV; 1.57Å. Thus, the first of the three adsorption variants a) corresponds to the highest binding energy of fullerene molecules with graphene and the shortest adsorption length.



(a) (b) (c)

Figure 3. Adsorption processes of the C_{20} fullerene molecule on the surface of graphene. (a) interaction of one atom of fullerene and one atom of graphene (C-ATP), (b) interaction of two neighboring fullerene atoms and two neighboring graphene atoms (BRI), (c) interaction of two nearest non-neighboring fullerene atoms and two nearest non-neighboring graphene atoms

CONCLUSIONS

A model experiment of the interaction of C_{20} fullerene molecules with the surface of graphene has been carried out. The geometric characteristics of fullerene molecules adsorbed on the surface of graphene are determined. It is shown that as a result of adsorption, the spherical symmetry of fullerene molecules is violated. It has been established that the degree

of symmetry breaking depends on the method of fullerene molecule adsorption on the graphene surface. Binding energies and adsorption lengths are calculated for C_{20} fullerene molecules adsorbed on the graphene surface in three different ways. The variant of adsorption with the highest binding energy and the shortest adsorption distance was determined.

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МОДЕЛЮВАННЯ ПРОЦЕСІВ ВЗАЄМОДІЇ ФУЛЕРЕНУ С20 З ГРАФЕНОМ

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Графен, вуглецевий лист товщиною в один атом, з атомами вуглецю, розташованими у двовимірній стільниковій конфігурації, має ряд цікавих властивостей. Фулерени є перспективним матеріалом для створення електроактивних елементів в сонячних елементах і активних шарів в тонкоплівкових органічних транзисторах. Методом мінімізації енергії з потенціалом Бреннера другого покоління (REBO) побудовано комп'ютерну модель молекули фулерену C_{20}. Побудовано комп'ютерну модель «нескінченного» бездефектного графену, призначену для розгляду процесу адсорбції молекули фулерену C_{20} на його поверхні. Для дослідження процесу адсорбції комп'ютерні моделі фулерену та «нескінченного» графену були наближені до необхідної відстані з іншим набором геометричного розташування фулерену відносно поверхні графену. Встановлено, що адсорбція фулерену C_{20} на поверхні графену може здійснюватися трьома різними способами, які відрізняються кількістю взаємодіючих атомів фулерену і графену. Розраховано енергію зв'язку та довжину адсорбції для молекул фулерену C_{20}, адсорбованих на поверхні графену різними способами. Виявлено шлях адсорбції, що відповідає найбільшій енергії зв'язку і найменшій довжині адсорбції.

Ключові слова: *молекула фулерену; графен; адсорбція; моделювання; потенціал Бреннера*