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Authors: Mehmet Dinçer ERBAŞ, Ferhat DEMİRAY
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INVESTIGATION ON THE ADSORPTION OF THE POTASSIUM ATOM ONTO C_{20} FULLERENE SURFACE

Mehmet DinçerERBAŞ[1], Ferhat DEMİRAY[*2]

Abstract

In this study, based on the Density Functional Theory (DFT), we examined the structural and electronic properties of potassium (K) atoms doped fullerene ($C_{20}K$).Structural optimization calculations were performed without any symmetry restrictions for the three distinct formations, namely, "pentagon", "bridge" and "on-top", in which K atom can be adsorbed onto C_{20} fullerene.The "pentagon" structure was obtained as the most stable structure because it has a lower total energy value compared to the other two structures.Adsorption energies were calculated as -1.52 eV in the "pentagon" structure, -1.47 eV in the "bridge" structure and -1.41 eV in the "on-top" structure. According to the computed E_{ads} values, adsorption for all of the three distinct structures is chemisorption. The GapHL value for the “pentagon” structure, which is the most stable structure, was calculated as 0.98 eV and this structure can be considered as a semiconductor material.The results obtained by the adsorption of C_{20} fullerene with K atom are expected to guide future experimental and theoretical studies.

Keywords: Molecular Structures, Density Functional Theory, C_{20} fullerene, Potassium, Nanotechnology.

[1]Bolu Abant İzzet Baysal University, Department of Engineering, Bolu, Turkey, Email:dincer.erbas@ibu.edu.tr, ORCID: https://orcid.org/0000-0003-1762-0428, , ORCID: https://orcid.org/0000-0002-4071-9285

[*]Corresponding Author: ferhatdemiray@ibu.edu.tr

1. INTRODUCTION

Nanotechnology, as a general definition, is a field of research aiming at the macro level production of new and different materials with manipulation activities on 1 - 100 nanometer scale material [1]. Due to the study of matter at this scale, intermolecular interactions in research on nanotechnology can be examined using Density Functional Theory (DFT) [2], [3], which is a computational quantum mechanics modeling method. Thus, it is possible to theoretically scale the structural and electronic properties of the material planned to be produced. Stability and conductivity are the main characteristics that are scaled on the newly produced material. Stable molecules with superconductivity and semiconductivity have a wide range of uses in research and development activities carried out at the nano-scale. New generation semiconductor materials have a wide range of uses, especially in the creation of nano-scale robots and the control of robot swarms consisting of these robots [4]. The main purpose of this research is to examine the structural and electronic properties of the fullerene molecule doped with potassium, which is possible to be produced at nano-scale. Structural optimization of this molecule, which has not been studied in the literature yet, has been carried out at different geometric positions. In addition, the molecule mentioned has been shown to have semi-conductor properties in a stable geometric structure.

The remainder of the article is organized as follows: In section 2, information is given on the research on fullerene. In section 3, the theoretical calculation method used for modeling is introduced. The results of the analysis made on this model and the comments on the results are presented in section 4. Finally in section 5, the research conducted was summarized and further information was given about the subjects that could be seen as a continuation of this research.

2. RELATED WORK

One of the most studied molecular structures in nano-scale manipulation is fullerenes. Fullerene is an allotrope of carbon formed by the combination of many carbon atoms. Fullerenes are defined as C_n in which n represents the number of carbon atoms contained in the molecules. All fullerenes contain even numbers of carbon atoms. The first discovered and most widely studied type of fullerene is the C_{60} molecule with its soccer ball-like geometric structure [5], [6]. Although fullerenes are mostly synthesized in a laboratory environment, they can be also found in nature [7]. Fullerenes are studied extensively in many fields such as chemistry, materials science and nanotechnology [8], [9], [10], [11].

The smallest possible fullerene type is the C_{20}dodechedral molecule [12]. The C_{20} isomers can have many different geometric shapes, such as rings, bowls, or cages. Possible stable structures obtained by functionalization of C_{20} are candidates to have both superconducting and semiconductor properties; for this reason, they have been the subject of many different studies. Due to its reactive structure, C_{20} is more difficult to be formed in the laboratory compared to C_{60} [12]. For this reason, theoretical studies have a very large place in the study of the different isomers of this molecule or the structures of complex molecules consisting of the combination of this molecule with other atoms and molecules.

Studies on potassium-doped Carbon nanotube can be found in the literature [13], [14]. These studies have shown that superconductivity is achieved by doping potassium into the fullerene C_{60} and C_{70} molecules, which are carbon allotropes [15], [16]. As far as we know, there is no study on the adsorption of potassium atom on the outer surface of C_{20} fullerene. In this theoretical study, changes in the structural properties of fullerene C_{20} upon the adsorption of K atom on the outer surface of the molecule have been investigated. The electronic properties of the most stable C_{20}K molecular structure that is obtained are also presented. Our primary goal in this study is to provide a foresight for future experimental and theoretical studies on this material.

3. THEORETICAL CALCULATION METHOD

In calculations for the adsorption of potassium atom onto C_{20} fullerene, geometry optimizations and total energy calculations were performed using the generalized gradient approximation (GGA) with the help of SIESTA code [17]. In the generalized gradient approximation (GGA), for the exchange-correlation energy functional, the Perdew – Burke – Ehrenzhof (PBE) parameterization was utilized [18]; furthermore, polarized orbitals and expanded double-ζ orbitals were utilized as the base set. No symmetry constraints were used for optimized geometries and all force components on each atom were performed using the conjugate gradient algorithm until all force components were less than 0.01 eV / Å. To determine the electronic structure, the difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) was computed and the energy range for the optimized structures, HOMO - LUMO gap (GapHL), was calculated.

4. RESULTS AND DISCUSSION

As shown in Figure 1, there are three possible positions for determining the adsorption of potassium (K) atom on C_{20} fullerene. As shown in Figure 1. a, the adsorbed K atom can be placed in the center of the pentagon and this structure is called the "pentagon". Similarly, as shown in Figure 1 b and c, the K atom can be adsorbed on the C - C bond or on the C atom, and these structures are named as the "bridge" and the "on-top", respectively. Structural optimization calculations were made for all three possible adsorption positions without using any symmetry constraints. Adsorption energies of the optimized molecular structures were calculated as follows:

$$E_{ads} = E(C_{20}K) - E(C_{20}) - E(K) \quad (1)$$

In this formula; E ($C_{20}K$) is the total energy of the new molecular structure obtained $C_{20}K$, E(C_{20}) is the total energy of pure fullerene, and finally E(K) is the total energy of the potassium atom.

As it has the lowest energy in the total energy calculations we have made, we determined the "pentagon" structure as the most stable among all structures. The pentagon structure has 0.05 and 0.11 eV lower energy than the bridge and on-top structures, respectively. The C - K bond length is calculated as 2.804 Å for the "on-top" structure. In the bridge structure, C - K bond lengths show a slight asymmetry and they are obtained as 2.804 and 2.947 Å. For the "bridge" structure shown in Figure 1b, the bond angle between C - K - C atoms was obtained as 31.52° degrees. The bond lengths between carbon and potassium atoms were calculated as 3.027 Å for the "pentagon" structure. The C - K bond lengths obtained are in agreement with the previous studies [19], [20].

The C - C bond lengths for the undoped fullerene C_{20} structure vary between 1.44 - 1.51 Å. The bond lengths of the C atom, to which the potassium atom will be doped, with other carbon atoms increase slightly for the "on-top" structure and it has been obtained as 1.52 Å. The bond lengths between other C - C atoms do not change and are the same as those in pure fullerene. The C - C bond length between the C atoms bonding with the K atom in the "bridge" structure increases and it is calculated as 1.57 Å. Other bond lengths between C - C are the same as the bond lengths in pure fullerene and range between 1.44 to 1.51 Å. The C - C bond lengths obtained for the "pentagon" structure are also obtained at the same values as the C - C bond lengths in pure fullerene.

The adsorption energies for the optimized structures shown in Fig. 1 were obtained as -1.52, -1.47 and -1.41 eV for the "pentagon", "bridge" and "on-top" structures, respectively. The range of adsorption energy ranges from 0 to -0.829 eV for physisorption and -0.829 to -4.1457 eV for chemisorption [21], [22]. Considering the adsorption energies calculated for the structure shown in figure 1, the adsorption is determined as chemisorption for all of the three structures.

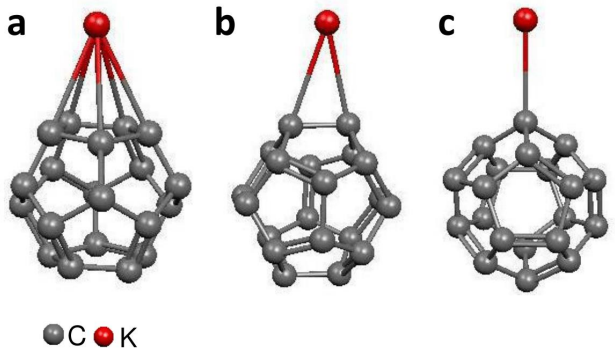

Figure 1. Adsorption positions of the K atom on C_{20}. a) "pentagon", b) "bridge", and c) "on-top" structures.

The density of states for the "pentagon" structure, which has the most stable optimized molecular structure obtained by doping potassium atom to C_{20} fullerene, is shown in Figure 2. Here, the energies are in accordance with the Fermi energy level (E_F) represented by the dashed line. In order to determine the electronic structure, the difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) was taken and the energy range HOMO - LUMO gap (GapHL) of the "pentagon" structure was calculated.

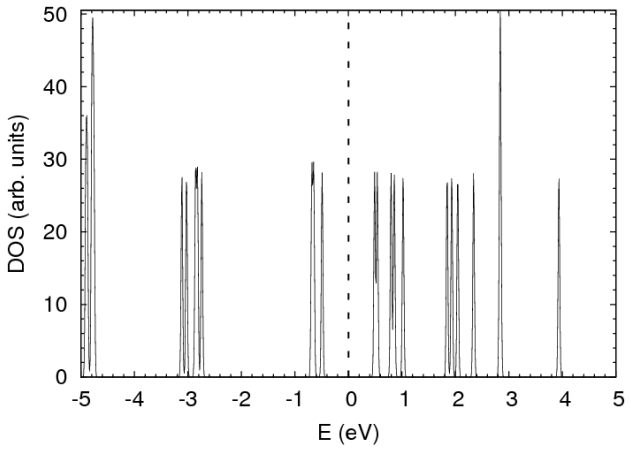

Figure 2. Density of states (DOS) for the optimized "pentagon" structure. Energies are according to the Fermi energy level (E_F), shown by the dashed line.

The GapHL value of the pure fullerene C_{20} was obtained as 0.61 eV. As seen in Figure 2, the pentagon formed by the addition of K atoms to the fullerene molecule increases the value of GapHL to 0.98 eV in the $C_{20}K$ structure and so it is a semiconductor material. No experimental or theoretical data, that we can compare the GapHL value we obtained, can be found in the literature.

5. CONCLUSION

By using Density Functional Theory (DFT), the structural and electronic properties of the new molecular structure obtained by doping potassium atom to C_{20} fullerene were investigated. Structural optimization calculations were made without any symmetry restrictions for the "pentagon", "bridge" and "on-top" positions, which are the three cases where the K atom can be doped to the fullerene C_{20}. According to the calculated total energy values, the "pentagon" structure has the lowest energy value and was obtained as the most stable structure. The adsorption energies for the "pentagon", "bridge" and "on-top" positions are computed as -1.52, -1.47 and -1.41 eV, respectively. Considering the adsorption energies obtained, adsorption is chemisorption for all three structures. GapHL for the "pentagon" structure, which was obtained as the most stable structure, was 0.98eV and so this material can be considered as a semiconductor. The results obtained in our study are expected to guide future experimental and theoretical studies.

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The Declaration of Conflict of Interest/ Common Interest

No conflict of interest or common interest has been declared by the authors.

Authors' Contribution

MDE: Investigation, conceptualization, visualization, editing and finalizing the manuscript.

FD:Investigation, conceptualization, visualization, editing and finalizing the manuscript

The Declaration of Ethics Committee Approval

The authors declare that this document does not require an ethics committee approval or any special permission.

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The authors of the paper declare that they comply with the scientific, ethical and quotation rules of SAUJS in all processes of the paper and that they do not make any falsification on the data collected. In addition, they declare that Sakarya University Journal of Science and its editorial board have no responsibility for any ethical violations that may be encountered, and that this study has not been evaluated in any academic publication environment other than Sakarya University Journal of Science.

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