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DFT Study of $COCl_2$ Adsorption on Pristine Fullerene and Doped Fullerene

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Abstract: By using Density Functional Theory (DFT), study the electron properties of the fullerene molecules adsorbed with gas ($COCl_2$). The gas with the molecule was placed with two sites at the first position (S1) vertically on one of the carbon atom for C60 molecule, vertically on one of the chlorine atom for (C59Cl and $C58Cl_2$) molecules and vertically on one of the bromine atom for (C59Br and $C58Br_2$) molecules. The second position (S2) is at the center of a ring of six carbon atoms of pristine fullerene (C60), center of a ring of six atom of (C59Cl and $C58Cl_2$) molecules and center of a ring of six atom of (C59Br and $C58Br_2$) molecules using the functional (B3LYP) and the basis set 6-31G (d, p). The results show that, the lowest adsorption energy obtained by gas adsorption with the molecule (C59Br) at the sites (S1) and the value of (-0.627 eV) and ($C58Cl_2$) at the sites (S2) and the value of (-0.654 eV) through this result can be considered this case gas sensor to detect gas ($COCl_2$). The rest of the cases is weak sensors and can be used as a sensor assistant.

Key words: Fullerene, gas adsorption, density functional theory, HOMO, LUMO, weak sensors

INTRODUCTION

The great interest of scientists has recently become in the field of carbon nanotubes. Where many research is done around carbon nanotubes, graphene an fullerenes. The possible applications of these materials and finding them are also important. In this study, the electronic properties of the adsorbed fullerenes with gas (Gabriel *et al*., 2010). Among miscellaneous nanostructures, fullerenes are known as suitable candidates for drug delivery regarding their appropriate properties such as hydrophobic characteristic, unique spherical structure, efficient drug loading and less side effects in biological media (De Jong and Borm, 2008; Conti *et al*., 2006; Singh and Lillard Jr., 2009; Bakry *et al*., 2007; Shi *et al*., 2013; Fan *et al*., 2013). So far, a great deal of experimental and theoretical studies have been carried out on C60 (Conti *et al*., 2006; Singh and Lillard Jr., 2009; Bakry *et al*., 2007; Shi *et al*., 2013; Fan *et al*., 2013) as a first fullerene type discovered by Kroto *et al*. (1985). The mentioned drug nanocarrier is potentially appropriate to promote the therapeutic efficiency of drug, since, it can be engineered to moderate the release and the stability of drug in order to prolong the spread time of drug, protecting it from elimination by phagocytic cells or premature degradation (Conti *et al*., 2006; Shi *et al*., 2013; Kroto *et al*., 1985).

Despite the notable advantages of experimental researches, the application of computational methods has been increasingly extended, since, the empirical methods are expensive and time consuming. In the present research, Density Functional Theory (DFT) method has been used by Guo *et al*. (1991).

MATERIALS AND METHODS

Computational details DFT: In this study, fully optimized geometries has been done at the B3LYP/6-31G* level of theoryas implemented in Gaussian 03 suite of program. Software package using the standard keywords implement therein (Raissi *et al*., 2013). We calculate the chemical potential or Fermi Energy (E_F) of the complexes as given (Table 1 and 2):

Table 1: The adsorption Energy (E_{ads}eV) of studied complexes

Complex (center)	E_{ads}	Complex	E_{ads}
C60/$COCl_2$	15.890	C60/$COCl_2$	15.890
C59Cl/$COCl_2$	-2.310	C59Cl/$COCl_2$	-2.330
C59Br/$COCl_2$	-2.724	C59Br/$COCl_2$	-0.627
$C58Cl_2$/$COCl_2$	-0.654	$C58Cl_2$/$COCl_2$	-2.420
$C58Br_2$/$COCl_2$	-6.857	$C58Br_2$/$COCl_2$	-5.742

Table 2: Electronic properties to the studied molecules (eV)

Complex (center)	E_{Tot}	IP = -HOMO	EA = - LUMO	E_g	E_F
C60/$COCl_2$	-90315.894	6.1799	3.31580	2.8640	-4.7478
C59Cl/$COCl_2$	-101813.241	5.2732	3.19140	2.0810	-4.2323
C59Br/$COCl_2$	-159267.941	4.6937	3.33750	1.3562	-4.0156
$C58Cl_2$/$COCl_2$	-113288.535	4.5225	4.00230	0.5202	-4.2624
$C58Br_2$/$COCl_2$	-228204.501	5.8447	3.27608	2.5687	-4.5603
Complex					
C60/$COCl_2$	-90315.894	6.1848	3.31960	2.8652	-4.7522
C59Cl/$COCl_2$	-101813.256	5.2624	3.17810	2.0843	-4.2202
C59Br/$COCl_2$	-156260.674	4.8667	3.32850	1.5382	-4.0976
$C58Cl_2$/$COCl_2$	-113290.304	4.4842	4.00580	0.4784	-4.2450
$C58Br_2$/$COCl_2$	-228203.386	4.7454	3.11250	1.6329	-3.9289

$$E_F = E_{HOMO} + E_{LUMO}/2 \quad (1)$$

Where:

E_{HOMO} = The Energy of the Highest Occupied Molecular Orbital

E_{LUMO} = The Energy of the Lowest Unoccupied Molecular Orbital

The Energy Gap in energy levels (E_g) of a system is defined as $E_g = E_{LUMO}-E_{HOMO}$. The adsorption energy (E_{ads}) is evaluated using the following approximate expression:

$$E_{ads} = E_{COMPLEX} - \left(E_{(molecule)} + E_{gas}\right) \quad (2)$$

Where:

$E_{complex}$ = The total energy of the molecule with adsorption with gas

$E_{(molecule)}$ = The total energy of the studied molecule without adsorbed

E_{gas} = The total energy of the molecule gas (Wendt and Weinhold, 2001)

After geometry optimization by calculation of the adsorption energy it was found that two adsorption forms of the $COCl_2$ gas ($C58Cl_2/COCl_2$ and $C59Cl_2/COCl_2$) have the value adsorption energy is (-0.6540 and -0.627), respectively can be used as sensor to detected from $COCl_2$ gas (Table 1). Other electronic properties to the studied molecules like HOMO, LUMO, Total energy (E_{Tot}), Energy gap (E_g), Electron Affinity (EA), Ionization Potential (IP) and Fermi Energy (E_F)it was found that as shown in Table 2.

RESULTS AND DISCUSSION

We studied the adsorption behavior of $COCl_2$ gas molecules on the surface of Fullerene molecules. Initially, each gas molecule has been placed on the Fullerene surface into two forms. First form, the central atom of $COCl_2$ gas is close to theone of carbon atoms of C60or is close to the one of chlorine atom of (C59Cl and $C58Cl_2$) or close to the one of bromine atom of (C59Br and $C58Br_2$). In the second form, the gas molecule is located on the top of hexagonal ring of C60 or hexagonal ring of (C59Cl and $C58Cl_2$) or hexagonal ring of (C59Br and $C58Br_2$) (Fig. 1).

From Fig. 2, we noted in all the cases studied, the gas was placed at 3A° of the moleculesand the bond length 1.76 A° between each chlorine atom and the carbon atom

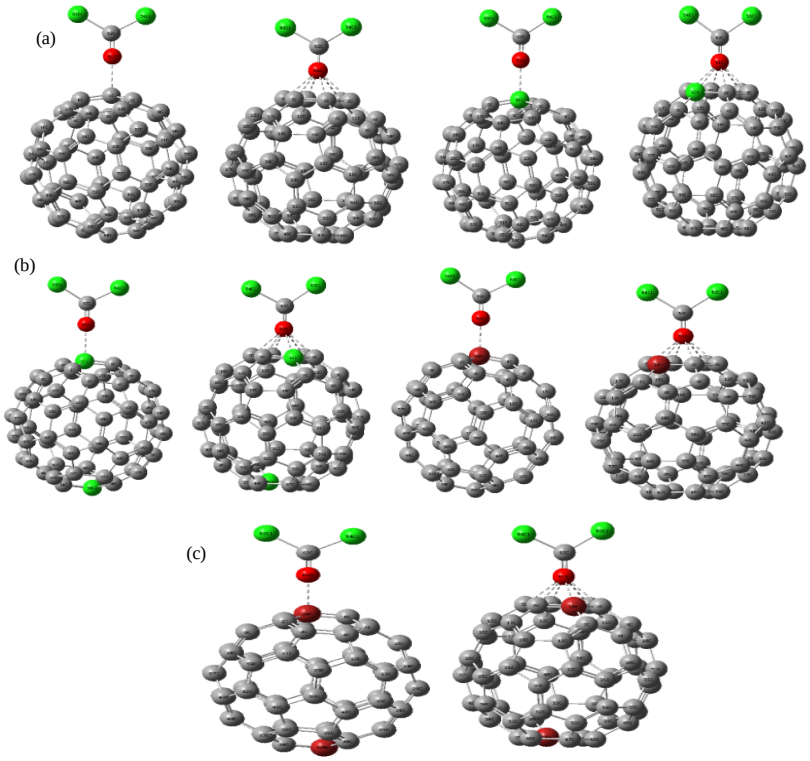

Fig. 1: Initial structures of the studied complexes: a) C60/$COCl_2$ C60/$COCl_2$ (center) C59Cl/$COCl_2$ C59Cl/$COCl_2$ (center); b) $C58Cl_2/COCl_2$/$C58Cl_2/COCl_2$ (center) C59Br/$COCl_2$ C59Br/$COCl_2$ (center) and c) $C58Cl_2/COCl_2$ $C58Cl_2/COCl_2$ (center) C59Br/$COCl_2$ C59Br/$COCl_2$ (center)

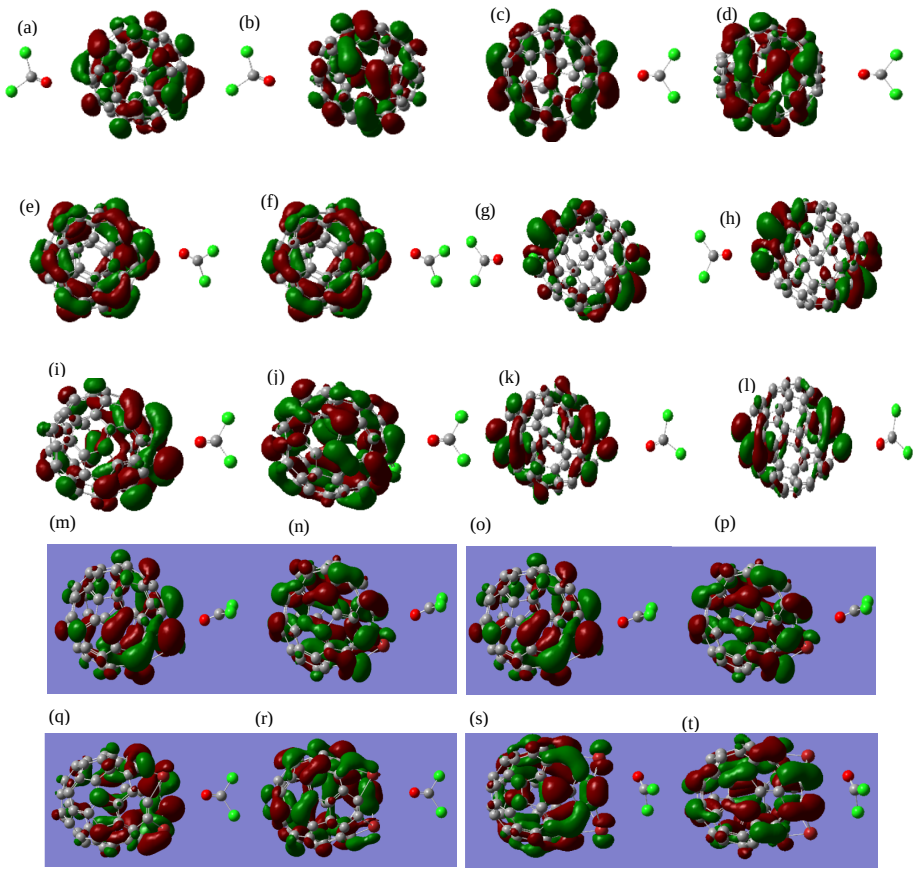

Fig. 2: HOMO and LUMO shapes for the studied molecules: a) HOMO; b) C60/$COCl_2$ LUMO; c) HOMO; d) C60/$COCl_2$ (center) LUMO; e) HOMO; f) C59Cl/$COCl_2$ LUMO; g) HOMO; h) C59Cl/$COCl_2$ (center) LUMO; i) HOMO; j) $C58Cl_2$/$COCl_2$LUMO; k) HOMO; l) $C58Cl_2$/$COCl_2$ LUMO; m) HOMO; n) $C58Br_2$/$COCl_2$ (Center) LUMO; o) HOMO; p) C59Br/$COCl_2$ (Center) LUMO; q) HOMO; r) $C58Br_2$/$COCl_2$ (center) LUMO; s) HOMO and t) C59Br/$COCl_2$ (center) LUMO

of the gas, the bond length of the atom between the carbon atom and the oxygen atom is 1.18 A° of the gas. The angle between the atoms for the gas is 111.8°.

We notes in all cases the lobes concentrated almost around all atoms except in case $C58Cl_2$/$COCl_2$ (center) the lobes concentrated for two chlorine atoms and the atoms adjacent to the chlorine atoms. For this reason, the adsorption energy that can be used as a sensor to detect this gas has been obtained.

CONCLUSION

We explore the adsorption of $COCL_2$ on the surface of fullerene C60 and doped fullerenesby DFT calculation at B3LYP/6-31G(d,p) level of theory.In general, the adsorption energies in the results indicates that C60 and doped fullerenes is strongly reactive to $COCL_2$ in all sites except $C58Cl_2$ at site (center)and C59Br because the gases slow desorption from pristine fullerene and doped fullerene, the pristine fullerene and doped fullereneis not suitable as the sensor of $COCL_2$. However, the pristine fullerene anddoped fullerene could catalyst or activate this adsorbate due to the strong interaction, the pristine fullerene anddoped fullereneas a metal-free catalyst. For $C58Cl_2$ at site (center) and C59Br can be used a sensor to detect $COCL_2$ gas. The adsorption energy of $C58CL_2$ at site (center) is (-0.465 eV) andthe adsorption energy C59Br is (-0.672 eV).

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