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Investigation of the Effect of Poly-Methyl Subgroups on the Electronic and Spectroscopic Properties of Fullerene C60 Molecule

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Abstract

This study focuses on employing the B3LYP hybrid functional method with 6-31G basis sets to study the effects of the addition of poly-methyl subgroups on the electronic and spectroscopic properties of fullerene C60 cage molecule. Koopman's method was used to calculate some important electronic variables, such as, the ionization energy, electron affinity and electronegativity. We showed that the location and the subgroups number of methyl in fullerene molecule effect on the calculated energies. The addition of the methyl reduces the energy gap, means we construct new molecular electronic structures which can be used in many applications.

Keywords: B3LYP, Koopman^s theorem, Energy Gap and Polarizability.

Introduction

Carbon has been believed to be found only as graphite and diamond sp^3 –hybridization, but these discoveries revealed that it is possible of forming novel structures with nano size and that lead to huge experimental and theoretical studies which has made this field of research one of the most exciting areas in materials science[1]. A cylindrical fullerene is called either carbon nanotube or bucky tube while a spherical fullerene is known as a bucky ball[2-4]. Fullerene C60 consists of 60 carbon atoms arranged in twenty hexagons and twelve pentagons that form a perfectly symmetrical cage structure of a soccer ball with 1 nm size[5]. C60 molecule follows Euler's theorem where each fullerene consists of twelve pentagons and M hexagons containing 2(10+M) carbon atoms[6, 7]. Each carbon atom is bonded to three other carbon atoms to form sp2 hybridization and, consequently, entire C60 molecule is surrounded by electron clouds[8]. C60 has two different types of bonds; 6:6 bond which located in between two hexagon rings and 6:5 bond which located in between a hexagon ring and a pentagon ring and 6:6 bonds are considered as double bonds having shorter bonding length than 6:5 bonds [8]. C60 molecule was first found in 1985 by Kroto et al.[5] from the ablation of a graphite with energetic pulsed laser. However, mass production of these carbon based nanoparticles was not possible until Kratchmer et al.[9-12] succeeded in synthesizing C60 by resistive heating method. Fullerene can be used as organic photovoltaic device[13-17]. Currently, the record efficiency for a bulk hetero-junction polymer solar cell is a fullerene-polymer blend. The fullerene acts as the n-type semiconductor (electron acceptor). The n-type is used in conjunction with a p-type polymer (electron donor)[18-21].

Theory

The calculations in present work are performed with the GAUSSIAN 09 suite of programs. Full geometry optimizations of fullerene C60 and hydroxyl fullerene C60 molecules group were performed with Berny optimization algorithm (calculating the energy derivatives with respect to nuclear coordinates analytically, in redundant internal coordinates)[22,23]. The gradient corrected density functional methodology was employed Becke's exchange functional (B) and Becke's three-parameters adiabatic connection (B3) hybrid exchange functional were used in combination with the Lee–Yang–Parr correlation functional B3LYP. While the BLYP methodology is a 'pure DFT' one (it includes no HF exchange), the B3LYP contains an admixture of HF exchange. The B3 functional contains a linear combination of exact HF exchange, Slater exchange and Becke gradient-corrected exchange[24]. The standard 6-31G basis set was used for orbital expansion to solve the Kohn– Sham equations in all cases. The computed stationary points for which the structures and force fields are presented correspond to real minima on the molecular potential energy hyper surfaces. The DFT (LUMO-HOMO) energy for the poly hydroxyl fullerene C60 molecules group studied in this research was calculated at the same level of theory[25-27].

Results and Discussion

The molecules under study in this work are relaxed at DFT-B3YLP/6-31G (d, p), and they are illustrated in figure 1. Fullerene C60 is the reference molecule 1, The others six methyl fullerene C60 molecules are labeled (Molecules 2-7).

The Computed Energies

Table 1 represents the calculated values of the total energy ET in a. u, and some computed energies in eV calculated according to Koopman's theorem of methyl fullerene molecules group, included the ionization energy IE, electron affinity EA, electrochemical hardness H and electronegativity X. The calculations are carried out by performing the three parameters Lee-Yang-Parr B3LYP at 6-31G level of density functional theory.

Figure 2 shows the relation between the total energy ET and the number of methyl groups added to the fullerene C60 molecule. As shown in this figure, the total energy of methyl fullerene molecules group is less than the total energy of the reference fullerene C60. The total energy decreased with increase of CH2 groups number added to fullerene C60 molecule. From the linear relation in figure 2, we can found a simple equation associates the ET of the methyl fullerene molecules group and the number (n) of methyl groups as:

$$ET = ET(fullerene\ C60) + nET(CH2).$$

Figures 3 and 4 illustrate the behavior of ionization energy IE and electron affinity EA as functions of the number of CH2 groups, respectively. All methyl fullerene molecules group have low values of IE and EA in comparison with the fullerene molecule. Adding the CH2 group reduces the IE and EA of the fullerene. Molecule 7 has the smallest value of IE and EA, that means this molecule needs a small energy to become cation in comparison with the others. These results are global properties and they are not coming from the frontier molecular electronic states. The molecules under study can easily donating an electron, but they cannot easily accepting electrons in comparison with the reference fullerene C60 cage molecule. .

Figures 5 and 6 illustrate the effect of CH2 groups number added to fullerene molecule on the electrochemical hardness H and electronegativity X, respectively. As seen, all the methyl fullerene molecules group have electrochemical hardness less than that for fullerene C60 molecule except molecule 7, it has H larger than that of fullerene C60, that means the molecules 2-6 are more soft than the reference molecule. The decreasing of electrochemical hardness in is the main future and as a sign to that band gap goes to be rather soft and lowering the resistance of these structures to lose an electron . On the other hand, the electronegativity of the molecule is linearly decreasing with increase the number of methyl groups. Molecules 2-7 have a small escaping tendency comes from the presence of CH2 groups in the molecule.

2 Electronic States and Energy Gap

Table 2 shows the calculated values of the high occupied molecular orbital energy E_{HOMO}, lower unoccupied molecular orbital energy E_{LUMO} and the energy gap E_g of methyl fullerene molecules group. Figures 7 and 8 show the influence of CH2 groups on the energies of HOMO and LUMO. As seen, both HOMO and LUMO energies are effected by addition of methyl groups, but its effect on HOMO energy is more than on LUMO energy. Figure 9 showed that the energy gap of fullerene C60 decreases with the addition of CH2 groups except molecule 7 . The mode of variation of the energy gap refers to that the energy gap of fullerene will be soft depends on the number of methyl groups in the molecule..

IR-Spectra

Figure 8 shows the IR-spectra of fullerene C60 and poly-methyl fullerene molecules studied in this work, as we see, the number of modes of frequencies are increased with increasing the number of ethyl sub groups added to fullerene and observed new intensities due to the streaching of C-O bonds in the new structures.

Conclusions

The total energy is linearly decreased with increasing the number of methyl subgroups added to the fullerene molecule. The new methyl- fullerene molecules group have low ionization energy and electron affinity. Adding the methyl subgroups to the fullerene molecule leads to change both the HOMO and LUMO energies, and therefore, reduced the energy gap of the molecule except hexa-methyl fullerene molecule in which it has the largest value of energy gap, this result indicates to build new structures have new electronic properties as molecular electronic applications. The location and the subgroups number of methyl in fullerene molecule effect on the calculated energies. So, the new constructing molecules have high reactivity to interact with the surrounding media.

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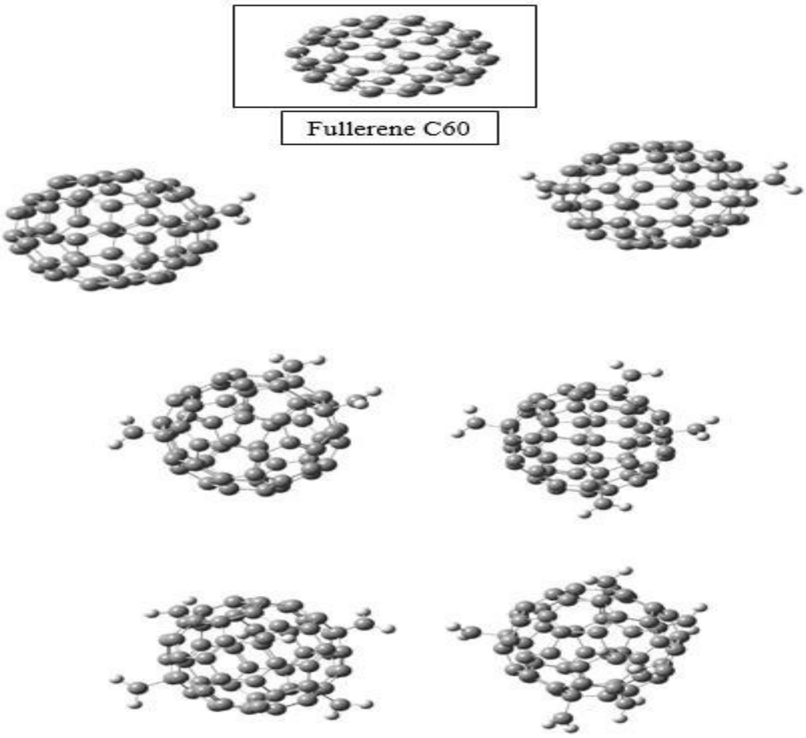


Figure 1: The optimized structures of methyl fullerene molecules group using DFT- B3LYP/6-31G(d, p).

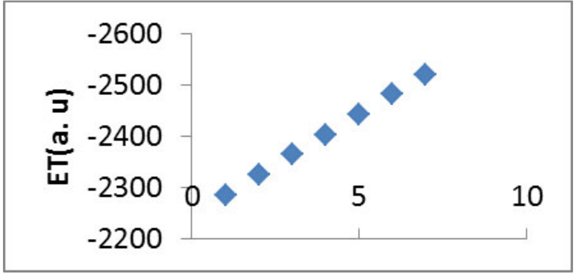


Figure 2 : The relation between the total energy and CH2 groups number.

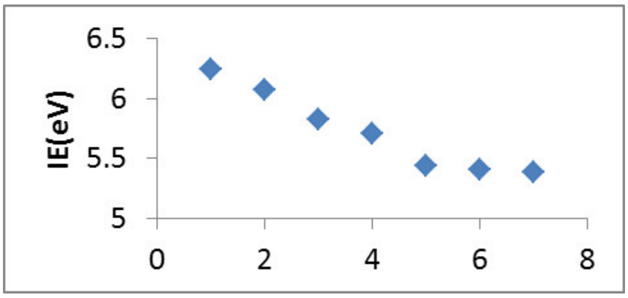


Figure 3 : The relation between the IE and CH2 groups number

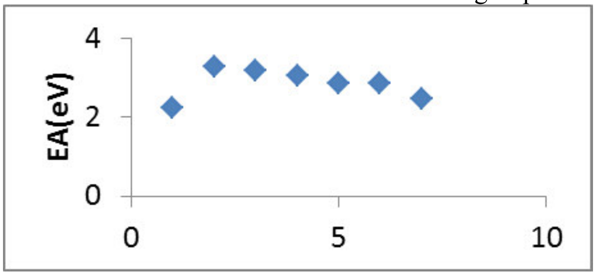


Figure 4 : The relation between the EA and CH2 groups number

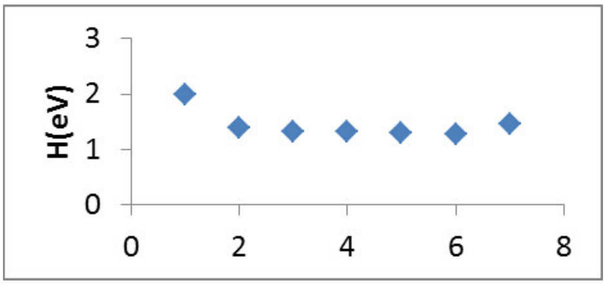


Figure 5 : The relation between H and CH2 groups number.

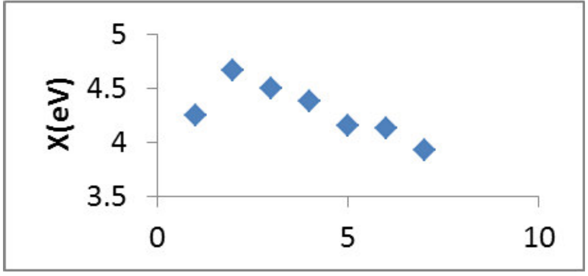


Figure 6 : The relation between X and CH2 groups number.

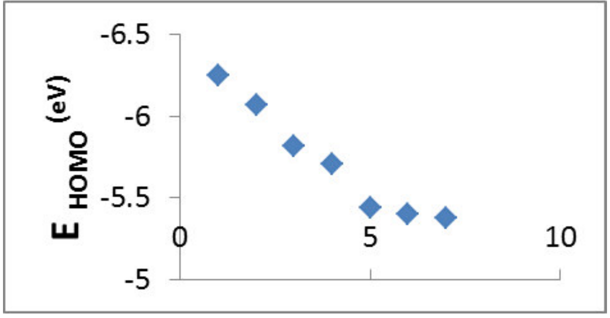


Figure 7: The relation between the HOMO energy CH2 groups number.

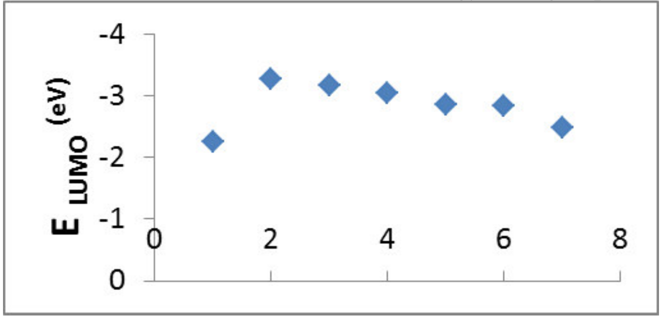


Figure 8: The relation between the LUMO energy and OH groups number

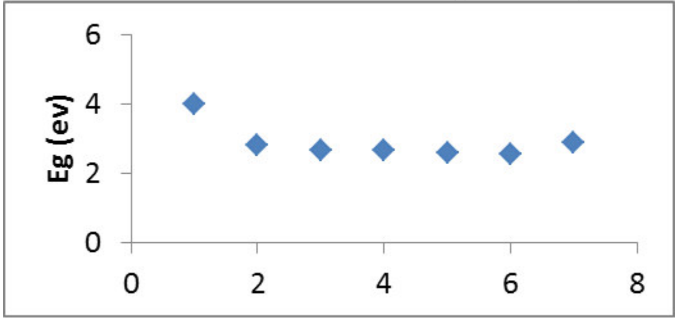
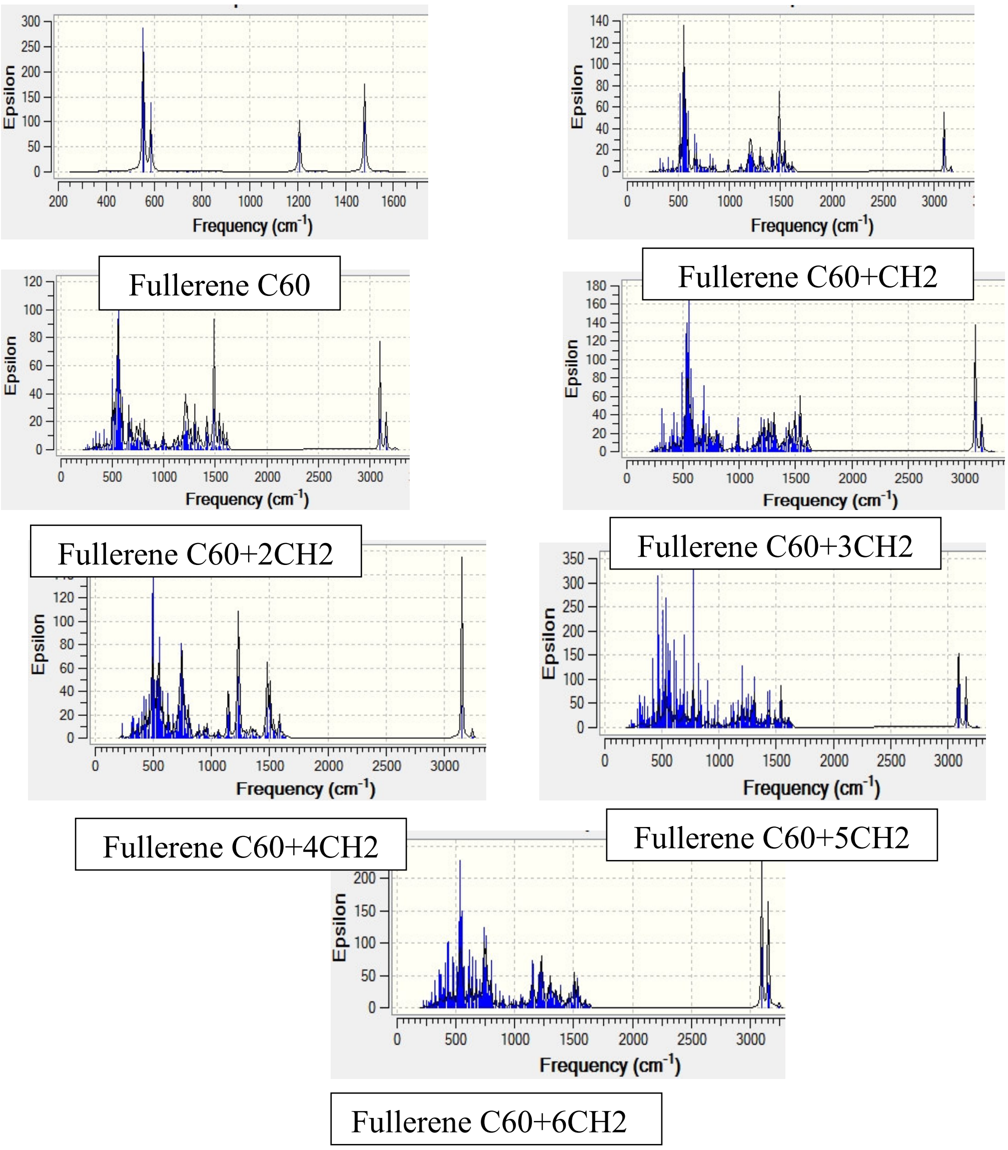


Figure 9 : The relation between the E_g and CH2 groups number



Fullerene C60

Fullerene C60+CH2

Fullerene C60+2CH2

Fullerene C60+3CH2

Fullerene C60+4CH2

Fullerene C60+5CH2

Fullerene C60+6CH2

Figure 10 : The IR-spectra of the studied molecules.

Table 1 : The calculated energies of methyl fullerene molecules group

Molecule	ET(a.u)	IE(eV)	EA(eV)	H(eV)	eV)(X
1	-2285.5	6.2484	3.3752	1.4366	4.8118
2	-2324.87	6.0691	3.2753	1.3969	4.6722
3	-2364.15	5.8209	3.1755	1.3227	4.4982
4	-2403.43	5.7045	3.0481	1.3282	4.3763
5	-2442.69	5.4422	2.8576	1.2923	4.1499
6	-2481.98	5.4038	2.8489	1.2774	4.1263
7	-2521.26	5.3809	2.4808	1.4500	3.9308

Table 2 : The E_{HOMO}, E_{LUMO} and E_g of methyl fullerene molecules group.

Molecule	**E_{HOMO}(eV)**	**E_{LUMO}(eV)**	**Eg(eV)**
1	-6.2484	-3.3752	2.8732
2	-6.0691	-3.2753	2.7938
3	-5.8209	-3.1755	2.6454
4	-5.7045	-3.0481	2.6564
5	-5.4422	-2.8576	2.5846
6	-5.4038	-2.8489	2.5549
7	-5.3809	-2.4808	2.9001