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Computational study of adsorption of some gas molecules on the undoped and N-doped fullerenes C_{20} bowl as a gas sensor

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Abstract: Many researchers from around the world are working hard to find solutions to purify the air of pollutants, specifically greenhouse gases like (CO, CO_2 and CH_4) during this project, great efforts have been made for finding the simplest way to get rid of these gas molecules in the air by adsorption using pure and nitrogen doped fullerenes (C_{20}).Density functional theory (DFT) was used at the B3LYP/6-21G level through the Gaussian 09W program package. The results indicate in our work that the gas molecules CO and CO_2) are weak physisorption molecules of pure and N- fullerenes with an adsorption energy (E_{ad}) ranging from (- 0.44 to- 0.3), while (CH_4) is a powerful chemisorption molecule on C_{20} and N- C_{20}. The geometry optimization and electronic properties of fullerene C_{20}were investigated with the presence of gas molecules and their absence, to understand the possibility of fullerene C_{20} and N-fullerene $C_{20}$to be used as a sensor to detect these gases leading to improve the human health.

Keywords: Nitrogen-doped fullerene, DFT, Gas sensor, Adsorption; Green House.

Introduction

Recently, the emission of greenhouse gases, such as CO, CO_2 and CH_4, has been increased so rapidly that has caused a serious environmental problem, as well as led to the elevation of earth temperature. Scientists pay great attention in solving the problem of greenhouse gases by separating them or concentrating them [1-3]. To date, various technologies have been developed for gas separation/purification, like membrane separation, absorption, cryogenic distillation and adsorption. Among the above mentioned separation techniques, adsorption has received intense interest due to its good advantages: high energy efficiency, easily controlled low cost [4-5]. Since the discovery of fullerenes [6],a massive attention has been given to study their physical and chemical properties [7].

Many studies focused on their geometry [8], energetic stability [7, 9-11], spectra [7, 12], and interactions with other molecules. Both theoretical and experimental investigations of fullerene molecules are very challenging [9]. Moreover, some of the recently published studiesreveal about the ability of fullerenes especially C_{20} fullerene semiconductor in sensing, adsorbing and reacting with some chemical species like dipoles [13], dienes [3], hazardous air pollutants [14] and aromatics [15]. The synthesis of macroscopic amounts of fullerene C_{60} and fullerene C_{70}, has stimulated the scientific community who interested in this field to study their chemical and physical properties [16]. the bigger numbered carbon clusters (Cn with n>20) have been suggested in many works to correspond to a spheroidal cage [17-18], while smaller carbon clusters (n<20) correspond to the linear chains or monocyclic rings which are one of the most chemically stable isomers [19-20]. For fullerene C_{20} the

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most chemically stable isomer can have a ring-shaped, a bowl or a cage structure, depending on the computational method. the bowl shaped C_{20} structure is found to be more stable than the cage shaped by Huda and co-workers[21].In the present study, DFT calculations are performed to simulate the adsorption of (CO, $CO_2$and CH_4) gas molecules on the surface of fullerenes C_{20} bowl as well as N-C_{20} and investigated their effect on the electronic propertiesof these surfaces. It doubted that N incorporation alters the structure of fullerene at the same time it will upgrade its quality as a gas sensor [22].

Result and Discussion

In this work calculation starts with a pure fullerene C_{20} bowl, the optimum bond length for C- C is about 1.43Å for pure fullerene as depicted in Figure **1** (a), which is in agreement with previous results [23-25].

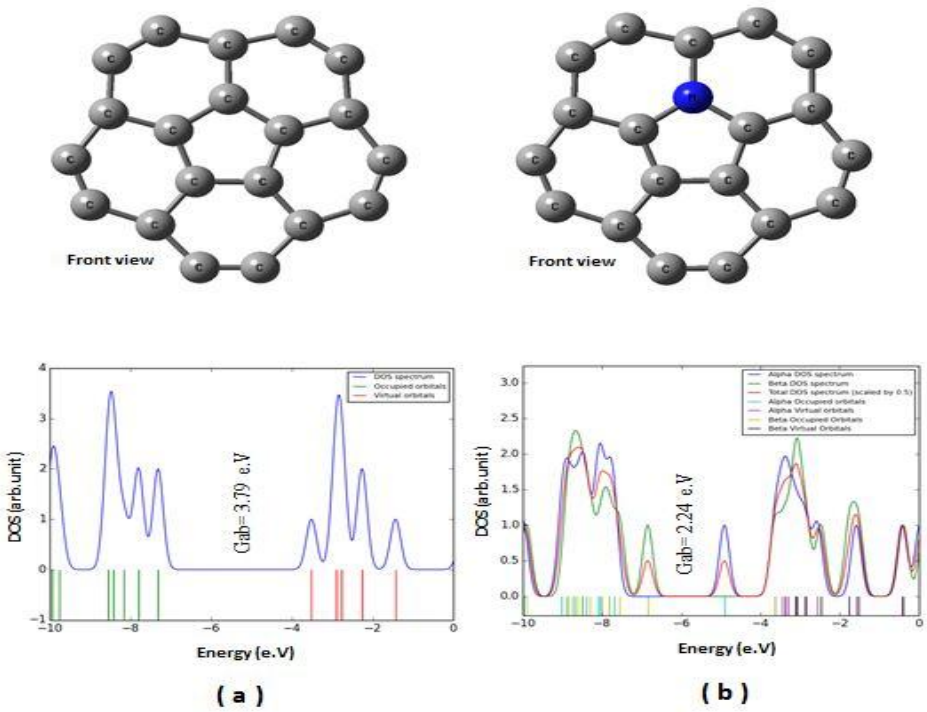

Figure 1: the optimized structure of (a) pure fullerenebowl and (b) N-fullerene andits densityofstates(DOS).

Doping fullerene with nitrogen atoms are efficient ways to improve the electronic and structural characteristics of pure fullerene. The C atom is substituted with N atom. N- Fullerene retains the planar form of fullerene after full relaxation and their corresponding model as shown in Figure **1** (b). The bond length of C- N for N doped fullerene is about 1.39Å, which is smaller than that of C - C bond length 1.41Å in fullerene C_{20}. However, there is no distortion or defect in the fullerene C_{20} bowl. The results of this work are consistent with previous work that confirmed planar structure of N-fullerene [26]. Table **1** explains the electronic properties of pure fullerene and the effect of N - doping to fullerene, where (HOMO) and (LUMO) energies and also the DOS analysis values were used for their.

Table 1: Calculated values of the electronic energies of purefullerene and nitrogen - doped fullerene.

System (e.V)	pure fullerene	N-fullerene
E_{HOMO}	-7.31	-5.87
E_{LUMO}	-3.51	-3.36
E_g	3.79	2.24
E_F	-5.41	-4.75

The computed E_g for N- fullerene are smaller than the pure one. It's well known that the nitrogen atom contains one extra electron than carbon atom; therefore

the system displays electron doping properties. In the electron doping, more states are pulled below Fermi energy level. Thus, it is possible to change the E_g of fullerene by doping N atom, this can affect the electronic characteristics of fullerene, as well, doping causes an slight decrease in the DOS in the conduction and valence levels in comparison with those of pure fullerene C_{20} as shown in Figure **1** (b) where the main peaks can be observed. The DOS for fullerene C_{20} shown in Figure **1** (a) where the conduction and valence bands have the highest number of the degenerated states is (7) for fullerene. It is evident that there are states available for the occupation at the high DOS for a specific energy level and no states can be occupied as a zero- DOS for energy level. We also studded adsorption properties of fullerene C_{20} and N doped C_{20} to CO, CO_2 and CH_4. Figures **2** and **3** and Table **3** show the most stable adsorption structures and corresponding data for one gas molecule adsorption on N-C_{20}. Three molecules were placed initially on sites on fullerene (parallel to fullerenes C_{20}), then after doping it is found that all the gas molecules tend to adsorb near the dopant (N atoms) site due to its high adsorption activity. CO and CO_2 interact with C_{20} and N-C_{20} with physisorption, due to the polyvalent properties of the nitrogen atom.

Table 2: Electronic and Structural properties of different gases adsorbed on pure and nitrogen-doped fullerenes

System(eV)	Gas	E_{ad}	E_g	E_{HOMA}	E_{LUMO}	E_F
Pure fullerenes	CO	-0.42	3.81	-7.27	-3.45	-5.36
	CO_2	-0.44	3.8	-7.28	-3.47	-5.37
	CH_4	3.25	2.67	-6.9	-4.23	-5.57
N- fullerenes	CO	-0.3	2.42	-5.98	-3.55	-4.77
	CO_2	-0.32	2.41	-5.96	-3.54	-4.75
	CH_4	29.6	2.32	-6.27	-3.94	-5.11

The chemisorption between molecule CH_4 and the fullerene and N-fullerene surface in the adsorption process causes breakage of CH_4 molecule structure, thus reducing the usability of the fullerene gas sensor, because it impedes the absorption of the gas molecule. The adsorption distance between the gas molecules (CO, CO_2, and CH_4) and the pure fullerene are 2.01 Å , 2.01 Å and 2.0 Å, respectively and the adsorption distance for above gases on N-C_{20} are 2.00 Å, 2.01 Å and 2.00 Å respectively. It can be noticed from Table **2**, the E_g for adsorbed pure C_{20} of molecules (CO and CO_2) is larger than those of C_{20}, this indicates that E_g increases with the adsorbed pure C_{20} except E_g at molecules (CH_4) it decrease, whereas the E_g for adsorbed N- C_{20} of molecules (CO and CO_2) is larger than those of N – C_{20}, this point out that the E_g increase with the adsorbed N–grapheme except E_g at molecules (CH_4). It has been found that the E_{HOMO} and E_{LUMO} for adsorbed N – C_{20} are larger than N- C_{20}, conversely. The E_{HOMO} and E_{LUMO} for fullerene C_{20} at adsorption are larger than the fullerene C_{20}. The results show the high value of E_{HOMO}.

Thus, pure fullerene and nitrogen doped fullerenes can be used in manufacturing sensors for the detection of the molecules (CO, CO_2 and CH_4). The density of states of molecules (CO, CO_2 and CH_4) adsorption on pristine and N- fullerenes illustrated in Figures **2** and **3,** the Figure shows that the DOS of pristine with the adsorption of gas molecules are different from the pure, the highest of peaks becomes higher, i.e., the conduction and valence bands are higher with the highest number of the DOS, the adsorption of gas

molecules on N- fullerenes are conformable with the DOS of N- fullerenes.

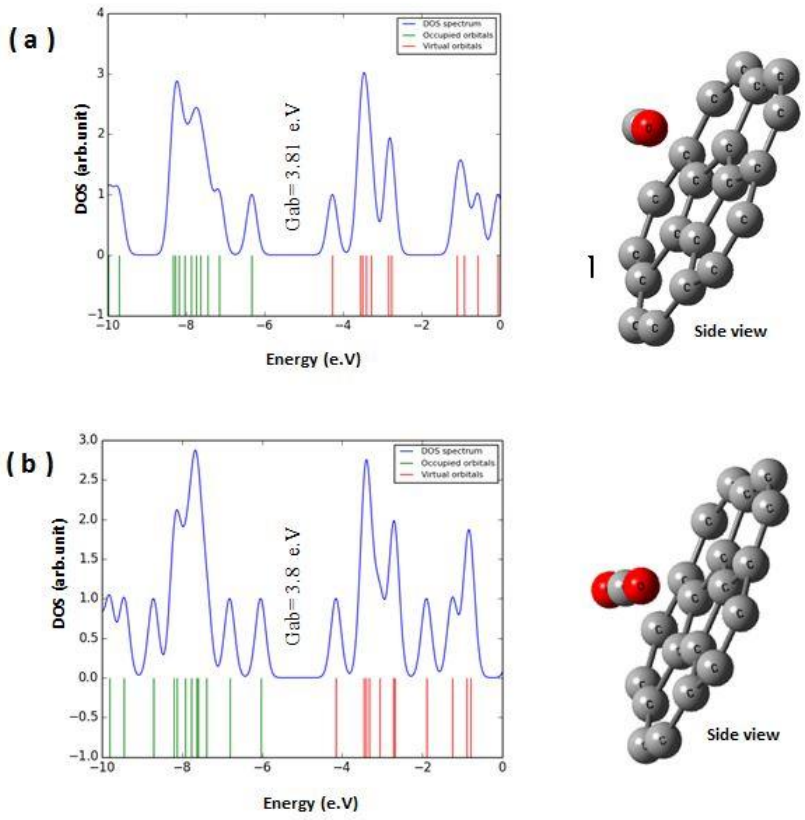

Figure 2: the optimized structure of gas molecules (a) CO, (b) CO_2, (c) CH_4 adsorbed on pure fullerene and its densityofstates (DOS).

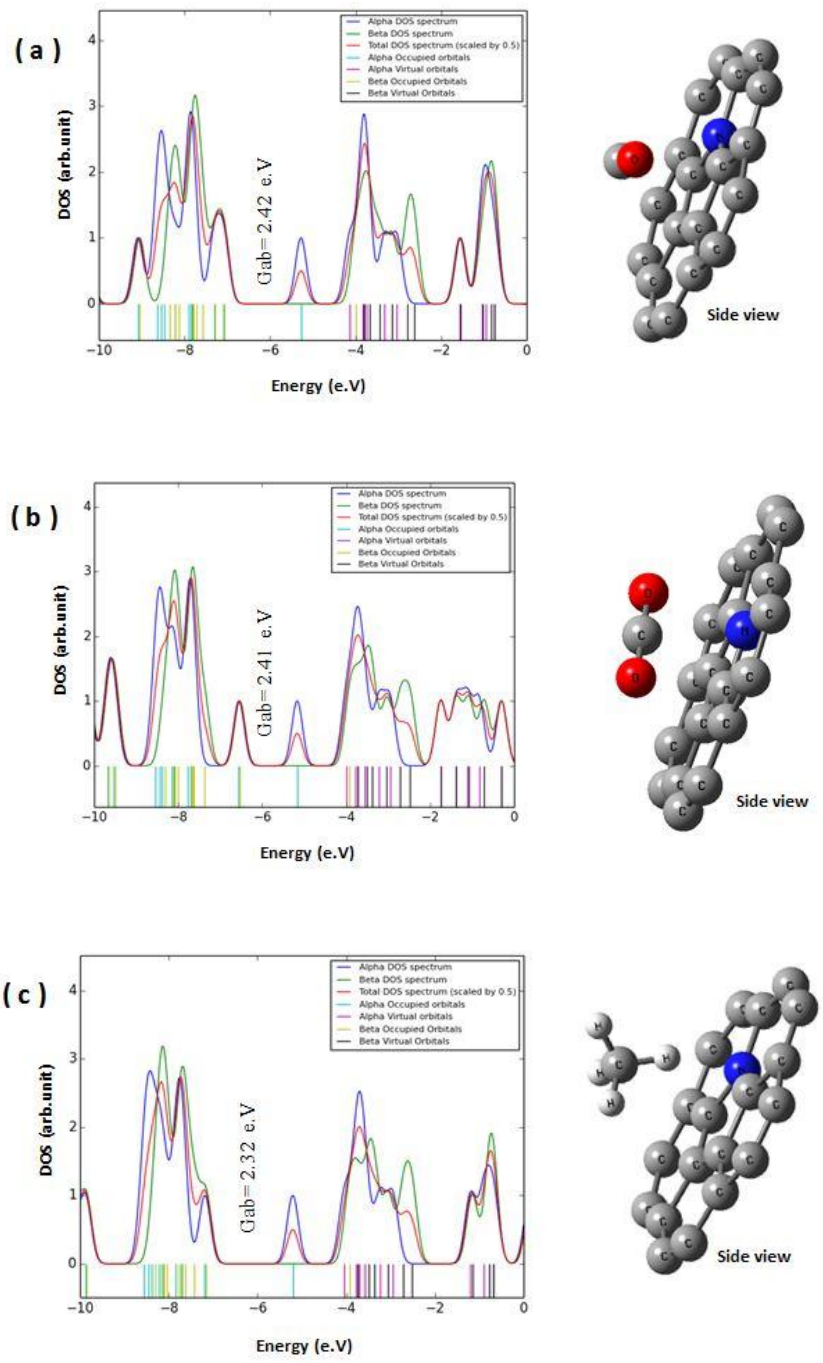

Figure3: the optimized structure of gas molecules (a) CO, (b) CO_2, (c) CH_4 adsorbed on N-doped fullerene and its densityofstates (DOS).

Conclusions

This study has calculated the electronic properties of adsorption CO, $CO_2$and CH_4 molecules on the surface of fullerenes **C_{20} bowl and N-doped the fullerenes**, based on the DFT calculations. The results of our research are summarized that the adsorption of all gas molecules on C_{20} and N-C_{20} undergoes a weak

physisorption interaction with a moderate adsorption energy, except of CH_4 has higher adsorption energy with the adsorption a strong chemisorption. Our results reveal that the electronic properties of fullerene could be modified by nitrogen doping and molecule adsorption, Thus can be used to design nanostructure as chemical sensors, and fullerene and N-fullerene could be used to build sensors for the detection to purify the air of pollutants

Computational details

A fullerene C_{20} bowl was selected as a model for this study, which consists of five hexagons and one pentagon, as seen in Figure **1**. All quantum calculations are performed using DFT , the geometric structures were completely optimized using Gaussian 09 program package [27-28]. The system consist (20) carbon atoms of fullerene as well as N- C_{20} was created, where the doping ratio reached 5 %.The E_{ad} of molecules on the C_{20} ($E_{ad\ (gas+\ C20)}$) and N- C_{20} $E_{ad\ (gas+\ N\text{-}C20)}$ is defined as:

$$E_{ad\ (gas+\ C20)} = E_{(gas+\ C20)} - (E_{C20} + E_{gas}) \quad \ldots\ldots. (1)$$

$$E_{ad\ (gas+\ N\text{-}C20\ )} = E_{(gas+\ N\text{-}C20)} - (E_{N\text{-}C20} + E_{gas}) \quad \ldots\ldots (2)$$

Where: $E_{(gas+C20\ )}$ and $E_{(gas+\ N\text{-}C20)}$ are represent total energies of the gas molecules on the C_{20} and N- C_{20} respectively , E_{C20} and $E_{N\text{-}C20}$ are represent the energies of isolated C_{20} and N- C_{20} and E_{gas} is the energy of isolated gas molecule. The diversity of relative energy of the highest occupied (HOMO)and the lowest unoccupied molecular orbital (LUMO) of free N- fullerene C_{20} and adsorbed molecule on N-fullerene C_{20} demonstrated the mechanism of interaction [29].

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References

[1] Chen, Z.; Deng, S.; Wei, H.; Wang, B.; Huang, J.; Yu, G. *Front. Env. Sci. Eng.* **2013**, *7*, 326.
[2] Xu, X.; Song, C.; Andresen, J. M.; Miller, B. G.; Scaroni, A. W. *Micro. Meso.Mater.* **2003**, *62*, 29.
[3] Siadati, A. *Lett. Org. Chem.* **2016**, *13*, 2.
[4] Cavenati, S.; Grande, C. A.; Rodrigues, A. E. *Energy Fuels* **2006**, *20*, 2648.
[5] Peng, X.; Wang, W.; Xue, R.; Shen, Z. *AIChE J.* **2006**, *52*, 994.
[6] Kroto, H. W.; Heath, J. R.; O'Brien, S. C.; Curl, R. F.; Smalley, R. E. *Nature* **1985**, *318*, 162.
[7] Małolepsza, E.; Witek, H. A.; Irle, S. *J. Phys. Chem. A.* **2007**, *111*, 6649.
[8] Manolopoulos, D.; Fowler, P. Oxford University Press Oxford, **1995**.
[9] Kroto, H. *Nature* **1987**, *329*, 529.
[10] Martin, J. M.; El-Yazal, J.; François, J.-P. *Chem. Phys. Lett.* **1996**, *255*, 7.
[11] Lu, X.; Chen, Z. *Chem. Rev.* **2005**, *105*, 3643.
[12] Witek, H. A;. Irle, S.; Zheng, G.; de Jong, W. A.; Morokuma, K. *J. Chem. Phys.* **2006**, *125*, 214706.
[13] Siadati, S. A.; Mirabi, A. *Iran. J. Org. Chem.* **2013**, *5*, 1099.
[14] Siadati, S. A.; Amini-Fazl, M. S.; Babanezhad, E. *Sen. Actu. B: Chem.l* **2016**, *237*, 591.
[15] Siadati, S. A.; Nami, N. *Physica E:* **2016**, *84*, 55.
[16] Zhang, Q.-L.; O'brien, S.; Heath, J.; Liu, Y.; Curl, R.; Kroto, H.; Smalley, R. *J. Phys. Chem.* **1986**, *90*, 525.
[17] Kroto, H.; McKay, K. *Nature* **1988**, *331*, 328.
[18] O'brien, S.; Heath, J.; Curl, R.; Smalley, R. *J. Chem. Phys.* **1988**, *88*, 220.
[19] Weltner Jr, W.; Van Zee, R. J. *Chem. Rev.* **1989**, *89*, 1713.
[20] Grossman, J. C.; Côté, M.; Louie, S. G.; Cohen, M. L. *Chem. Phys. Lett.* **1998**, *284*, 344.
[21] Ray, A. K.; Huda, M. *J. Comp. Theor. Nanosci.* **2006**, *3*, 315.
[22] Siadati, S. A.; Vessally, E.; Hosseinian, A.; Edjlali, L. *Synt. Met.* **2016**, *220*, 606.
[23] An, W.; Gao, Y.; Bulusu, S.; Zeng, X. C. *J. Chem. Phys.* **2005**, *122*, 204109.
[24] Zhang, C.; Sun, W.; Cao, Z. *J. Chem. Phys.* **2007**, *126*, 144306.
[25] Pashangpour, M.; Peyghan, A. A. *J. Mol. Mod.* **2015**, *21*, 116.
[26] Muhammad, R.; Shuai, Y.; Tan, H.-P.*Physica E: Low-dimensional Systems and Nanostructures* **2017**, *88*, 115.
[27] Frisch, M.; Trucks, G.; Schlegel, H.; Scuseria, G.; Robb, M.; Cheeseman, J.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. *Gaussian, Wallingford* **2009**.
[28] Frisch, M.; Trucks, G.; Schlegel, H.; Scuseria, G.; Robb, M.; Cheeseman, J.; Scalmani, G.; Barone, V.;

Mennucci, B.; Petersson, G. J. Chem. Phys, **2009**, *25*. 1258.
[29] Jappor, H. R. Khudair, S. A. M. *Sen. Lett.* **2017**, *15*, 432-439.