



---

---

## Theoretical study of the effect the hydroxyl subgroups on the electronic properties of iso-indene molecule

Abbas Ibrahim Obayes<sup>1</sup>, Nahida B. Hasan<sup>2</sup>, Hamed Ibrahim Aboud<sup>3</sup>,  
Mohammed Ahmed Mohammed<sup>4,\*</sup>

<sup>1-3</sup>Physics Department-College of Science, Babylon University, Iraq

<sup>4</sup>Department of Soil Science and Water Resources, College of Agriculture,  
University of Al-Qadisiyah, Iraq

\*E-mail address: [iraq\\_moh\\_iraq@yahoo.com](mailto:iraq_moh_iraq@yahoo.com)

### ABSTRACT

In this work, six molecules model are optimized at B3LYP/6-31G\*\* density functional theory. Electronic properties of iso-indene molecules were investigated depending on the three parameters (B3LYP) by density functional theory method. The best geometry for all molecules were investigated at (6-31G\*\*) basis sets. The total energies, energy gaps, ionization potentials, electron affinities and softness were calculated for the studied molecules. Adding the (OH) ion and Nitrogen, Sulfur atoms to the iso-indene molecules leads to decrease the energy gap and the hardness of the studied molecules. The IR-spectra shows the effect of adding the (OH) ion and Nitrogen, Sulfur atoms in the ring on the vibrations of the reference molecule, the electronic properties and IR spectrum for all molecules were investigated by Gaussian 03 program.

**Keywords:** DFT; energy gap; ionization potential; hardness and IR-spectrum

## **1. INTRODUCTION**

Any problem in the electronic structure for any system treated by quantum mechanics; it is based on the Schrödinger equation. Some of the largest important applications of quantum mechanics is semiconductor physics and technology [1]. Engineers have incorporated the quantum mechanical into the design of new electronic devices [2].

The hydrogen atom was Schrödinger's immediate goal when he develops his equation and the solution obtained in 1926 persuaded him [3].

Physicists derived the physical laws and mathematical structure that constitute the basis of quantum mechanics, but subsequent applications became interest not just to the physicists but also chemists, biologists, medical scientists, engineers, and philosophers, where sophisticated computer programs are routinely used for predicting the structures and geometries of large molecules [2].

The organic semiconductor materials, such as, conjugated organic molecules have been widely used as active materials for optoelectronic devices such as light emitting diodes [4-6], field effect transistor [6-8], and photovoltaic and solar cells[9,10]. The organic thin film transistors are one type of the so called organic devices, in which they fabricated by using the organic semiconductors [11].

These materials have advantages of easy fabrication, mechanical flexibility and low cost. There are many organic materials show useful field effect transistor performance, which can be characterized by their carrier mobility and on/off current ratios [12,13].

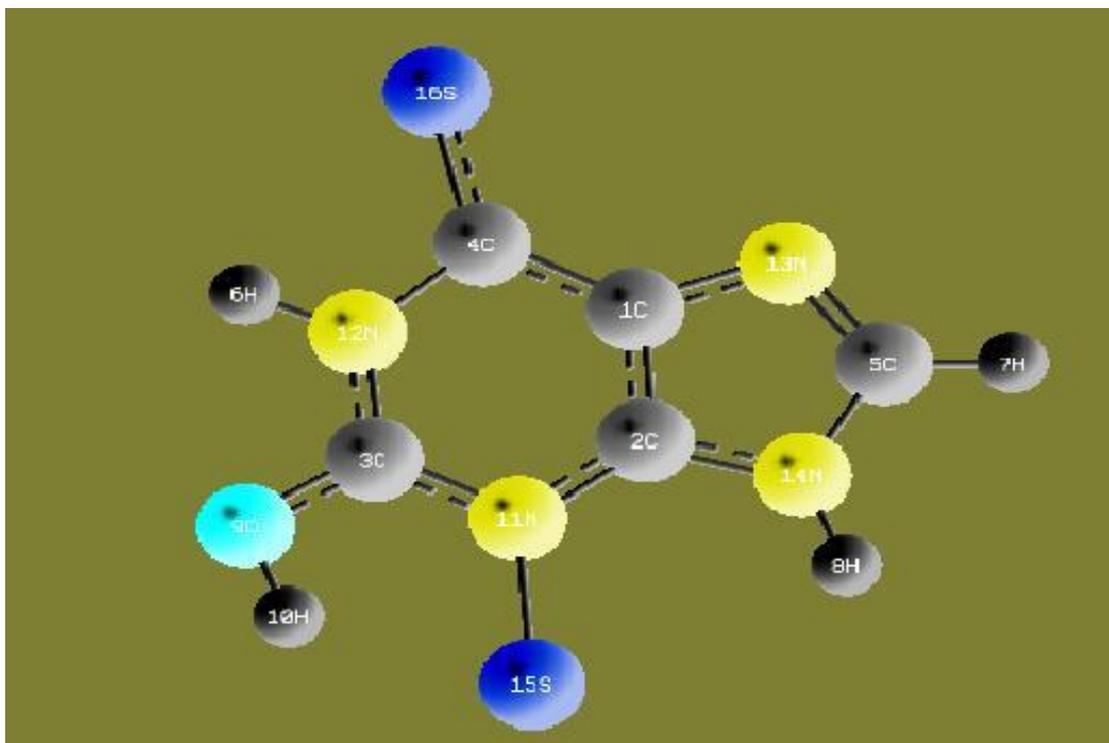
Density function theory is one of the largest popular and successful quantum mechanical approaches [14]. It is a powerful computational quantum physical and chemical technique method that allows the calculation of the geometries and energies of reactants [15]. It has become a popular tool for electronic structure calculations in recent years due to its favorable combination of low computational cost and good accuracy for the calculated results. In analogy with wave mechanics methods, there are two main parameters controlling the accuracy of the results, the inherent approximations in the Hamiltonian and the size of the basis set used for expanding the Kohn–Sham (KS) orbital's [16,17].

The foundation of DFT was laid by Hohenberg and Kohn, who showed that a unique functional of the electron density determines the ground-state electronic energy exactly [18]. In present work, density functional theory has been performed to study the electronic properties of the fluorine benzene molecules to determine the effects of the substituent groups

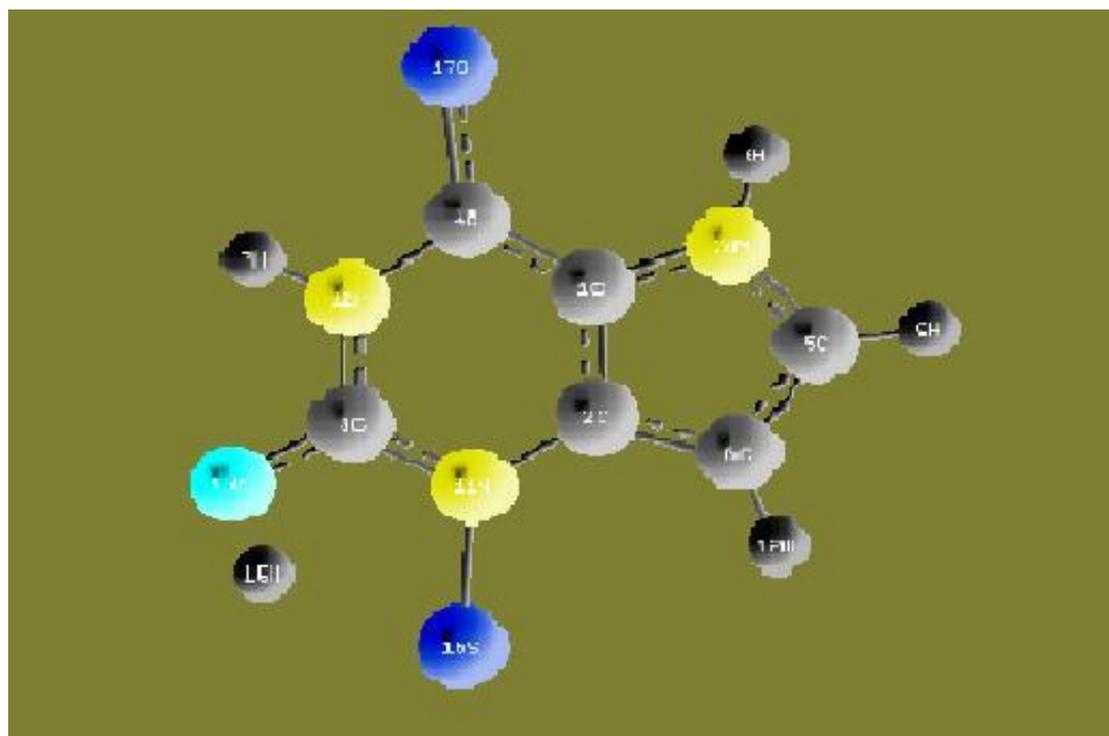
## **2. COMPUTATIONAL DETAILS**

Figure 1 represents the molecules under study. All the computational studies were carried out using the density functional theory (DFT) methods implemented in the Gaussian 03 suite of programs [19].

The molecular properties of the compounds had been computed by DFT using the standard 6-31G\*\* basis set. In the DFT calculations, Lee, Yang and Parr correlation functional is used together with Becke's three parameters [19] exchange functional B3LYP. Conformational analysis of the molecules had been performed to have an idea about the lowest energy structures of the species.

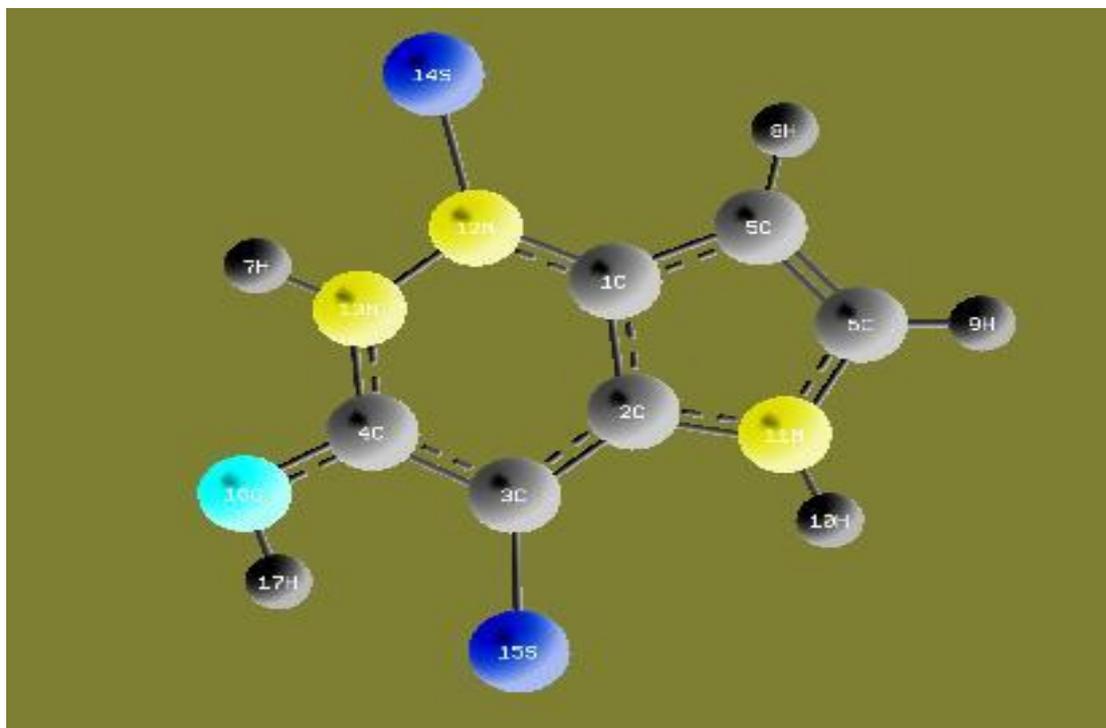


Structure (1)

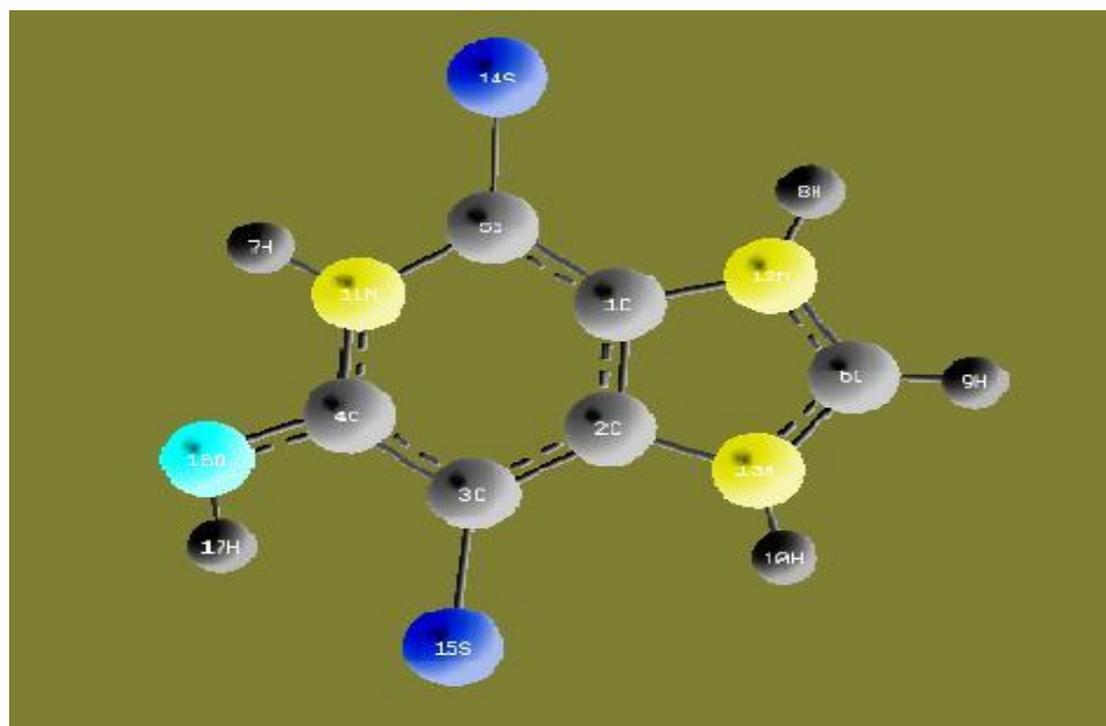


Structure (2)





Structure (5)



Structure (6)

**Figure 1.** Structures for iso indene and its derivatives discussed in this work.

Koopman's theorem states that if the single particle energies are not affected by adding or removing a single electron, then the ionization energy is energy of the highest occupied single particle molecular orbital (the HOMO) and the electron affinity is the energy of the lowest unoccupied molecular orbital (the LUMO) with the negative sign as the following [20]

$$IP = - E_{HOMO} \dots\dots\dots(1)$$

$$EA = - E_{LUMO} \dots\dots\dots(2)$$

where IP: ionization potential, EA: electronic affinity.

$E_{HOMO}$ : energy of the highest occupied molecular orbital.

$E_{LUMO}$ : energy of the lowest unoccupied molecular orbital

Koopman's theorem is extremely useful in predicting ionization energies and spectra [20]. Energy gap generally refers to energy difference between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) according to the Koopmans theorem [21,22]

$$E_g = E_{LUMO} - E_{HOMO} \dots\dots\dots(3)$$

Ionization energy (IP) defined as the minimum energy required to removing an electron from the atom in a gaseous phase. Ionization energy is expressed in units of electron volt (eV) [22].

Chemical hardness is the resistance of a species to lose electrons [23], for insulator and semiconductor, hardness is half of the energy gap [24]. From equations (1) and (2), we can calculate the chemical hardness ( $\eta$ ):

$$\eta = (IP - EA)/2 \dots\dots\dots(4)$$

The softness can be defined as the inverse of the hardness [25]

$$S = 1/(2\eta) \dots\dots\dots(5)$$

Electro negativity is defined as "the power of an atom in a molecule to attract electrons to itself" by Pauling [22,23]. R. Mulliken defined electro negativity as the average of the ionization energy and electron affinity as follows [26]

$$\chi = (IP + EA)/2 \dots\dots\dots(6)$$

Within the validity of Koopmans' theorem, we can be defined as the negative value for average of the energy levels of the HOMO and LUMO [21,26].

$$\chi = -(E_{HOMO} - E_{LUMO}) \dots\dots\dots(7)$$

The Electrophilicity is definition as a index measures the stabilization in energy when the system acquires an additional electronic charge from the environment. On the other word, it can be defined as a measure of energy lowering due to maximal electron flow between donor and acceptor [27,28].

$$\omega = \chi^2 / (2\eta) \quad \dots\dots\dots(8)$$

### 3. RESULTS AND DISCUSSION

#### 3. 1. Energies

Table (1) shows the values of the total energy and electronic states for the analyzed structures and the energy gap ( $E_{LUMO} - E_{HOMO}$ ) of the studied molecules. The total energy for all study molecules as a linear function of (OH, N & S) side group number adding to the molecule. The final total energy of the product is the collection of total energy of all small molecules which build the product molecule, that means:

$$E_{tot} \approx E_{tot}(molecule) + nE_{tot}(radical) \quad \dots\dots\dots (9)$$

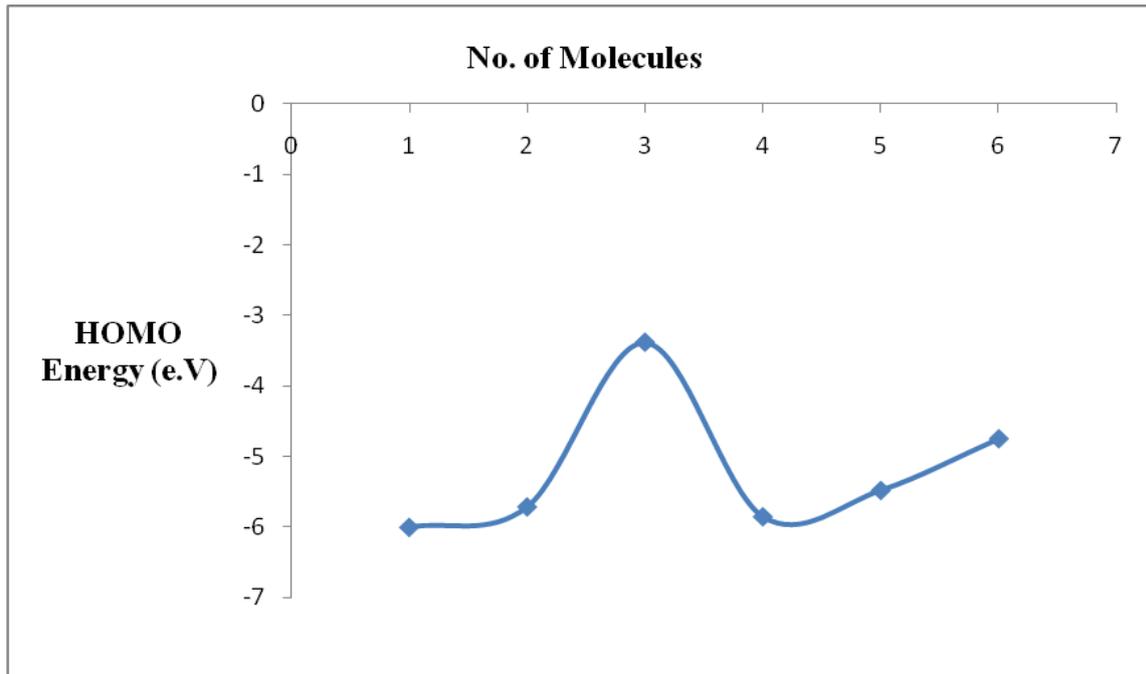
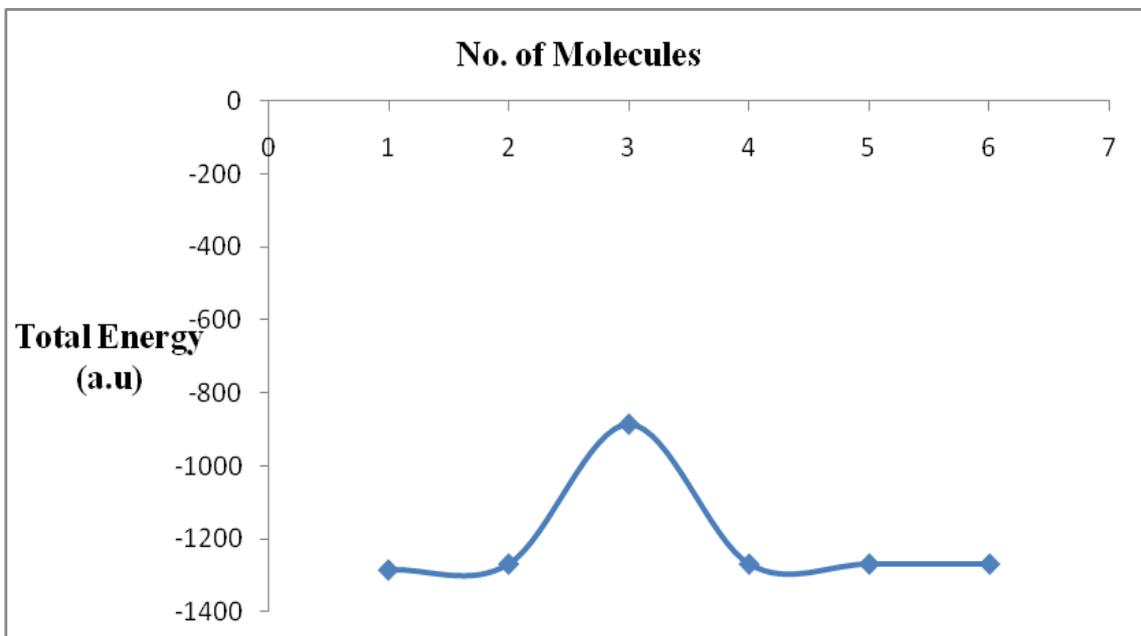
where n is the number of (OH, N & S) radicals.

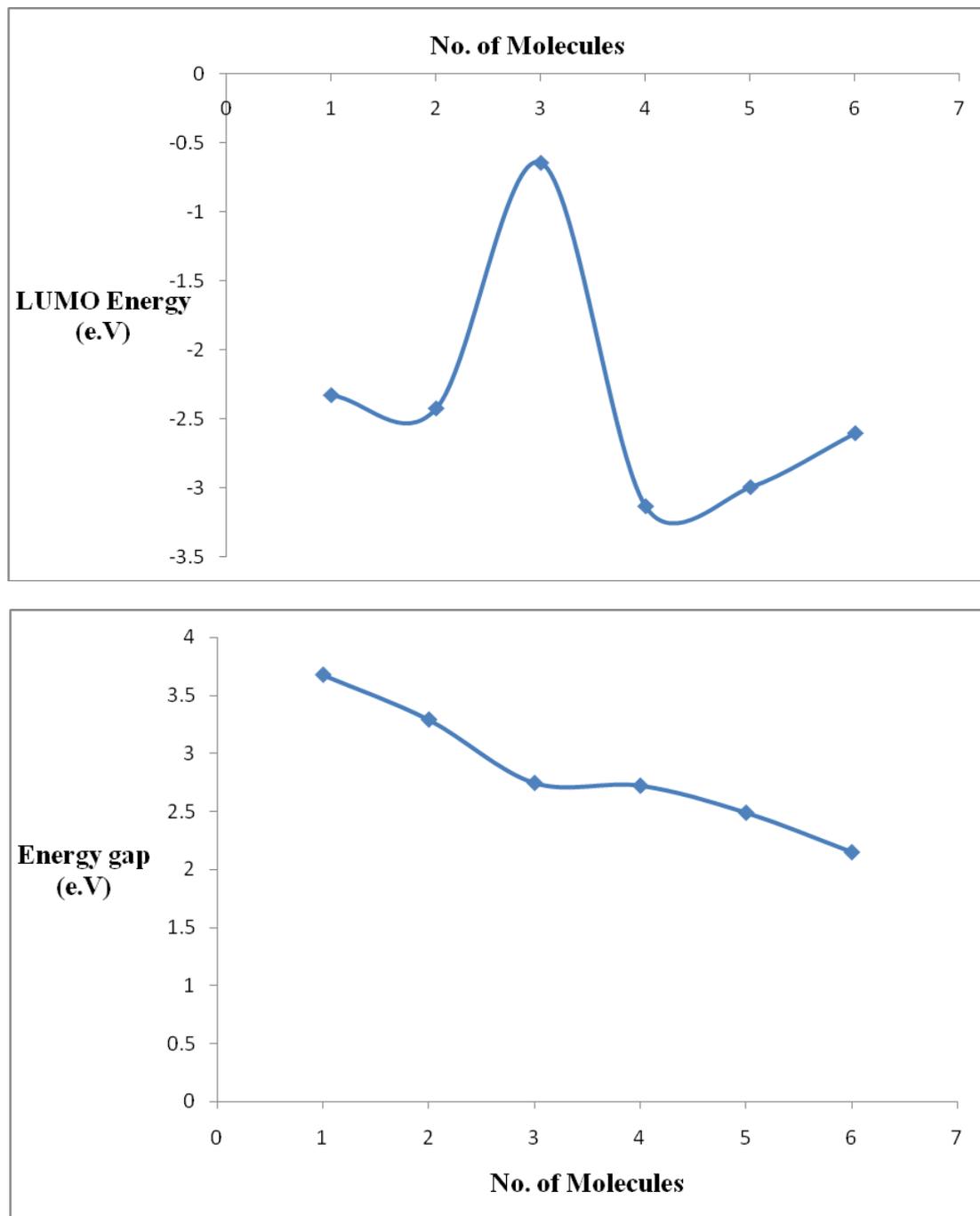
It is clear that from Table (1), the total energy for all molecules study is approximately the same in which this refer to that the total energy is independent on the position of the (OH, N & S) radical in the ring, and it is observed that substitution of OH ion and (N, S) atoms groups (electron with drawing) causes increasing the HOMO and decreasing LUMO energy [22], and energy gap decreased are less than that of the original molecules. Therefore, the presence of substituent decreases the energy gaps improves the semi conductivities and also enhances the solubility's of these molecules, with decreasing energy gap, electrons can be easily excited from the ground state. This effect of the side group was the largest in molecule (1) it has energy gap of (3.677 eV). The Table (1) show also the symmetry of study molecules, all the molecules from (1-6) is planar with inversion center and have  $D_s$  symmetry (low symmetry) and have higher electro negativity.

**Table 1.** Total energy, electronic states and energy gap for molecules.

Structure molecule	Total Energy (a.u)	Symmetry	Electronic States (eV)		Energy Gaps (eV) Our data
			HOMO	LUMO	
1	-1283.614	$C_s$	-6.005	- 2.328	3.677
2	-1267.576	$C_s$	-5.715	-2.424	3.291
3	-886.527	$C_s$	-3.388	-0.643	2.745
4	-1267.532	$C_s$	-5.855	-3.134	2.721

5	-1267.526	C <sub>s</sub>	-5.483	-2.995	2.488
6	-1267.507	C <sub>s</sub>	-4.752	-2.604	2.148





**Figure 2.** Energies per unit a.u & e.V corresponding the No. of molecules.

### 3. 2. Some important variables

B3LYP functional used in this study has a high efficient to calculate the electronic properties for the organic studied molecules, such as ionization potentials (IP), electron affinities (EA), electronegativity ( $\chi$ ), absolute hardness ( $\eta$ ), absolute softness (S) and electrophilic index ( $\omega$ ). The properties are displayed in Table (2) lists the electronic properties for the molecules

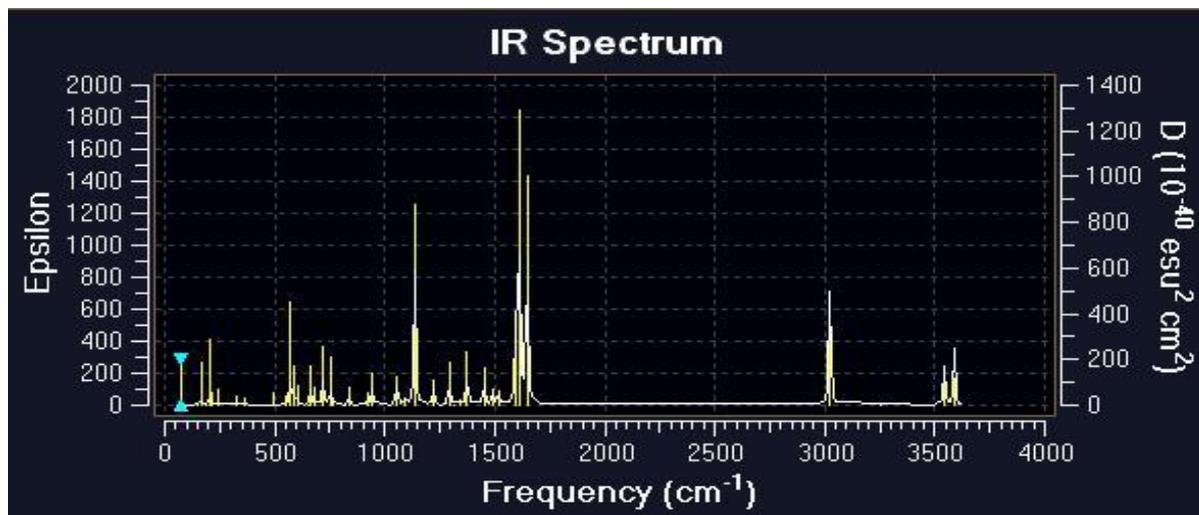
under study. It is clear from Table (2) that the ionization potential for iso-indene molecules group is lowest from different location the adding atoms (OH, N, S ) but in the (3) molecule is very low from the molecules study. The electron affinity for iso-indene are different from molecule to the another molecules. It is obvious from this table that all molecules under study have hardness less than that for molecule one; The behavior of electro negativity but in the (3,6) molecules are lowest from molecule one, (softness and electrophlicity) index for the studied molecules shows the magnitude large than these for the original ring (iso-indene), adding the atoms (N, S) and OH ion give the molecule more softness, it is a new electronic material.

**Table 2.** Computed energies for hydroxyl iso indene molecules.

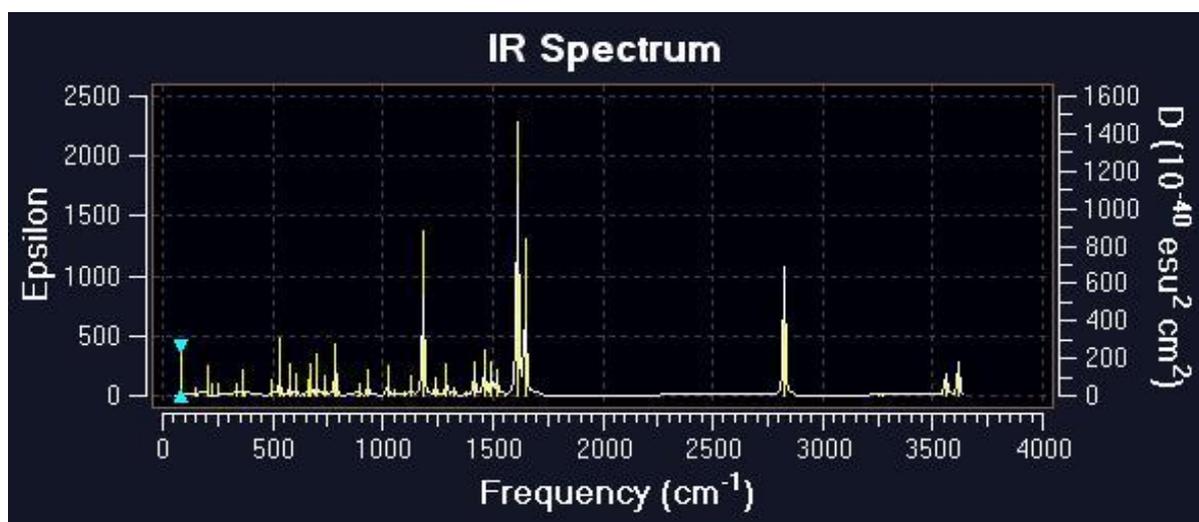
Species	IP (eV)	EA (eV)	$\chi$ (eV)	$\eta$ (eV)	S (eV) <sup>-1</sup>	$\omega$ (eV)
1	6.005	2.328	4.166	1.838	0.272	4.721
2	5.715	2.424	4.069	1.645	0.304	5.032
3	3.388	0.643	2.015	1.373	0.364	1.478
4	5.855	3.134	4.495	1.360	0.368	7.428
5	5.483	2.995	4.239	1.244	0.402	7.222
6	4.752	2.604	3.678	1.074	0.465	6.297

### 3. 3. Infrared spectra

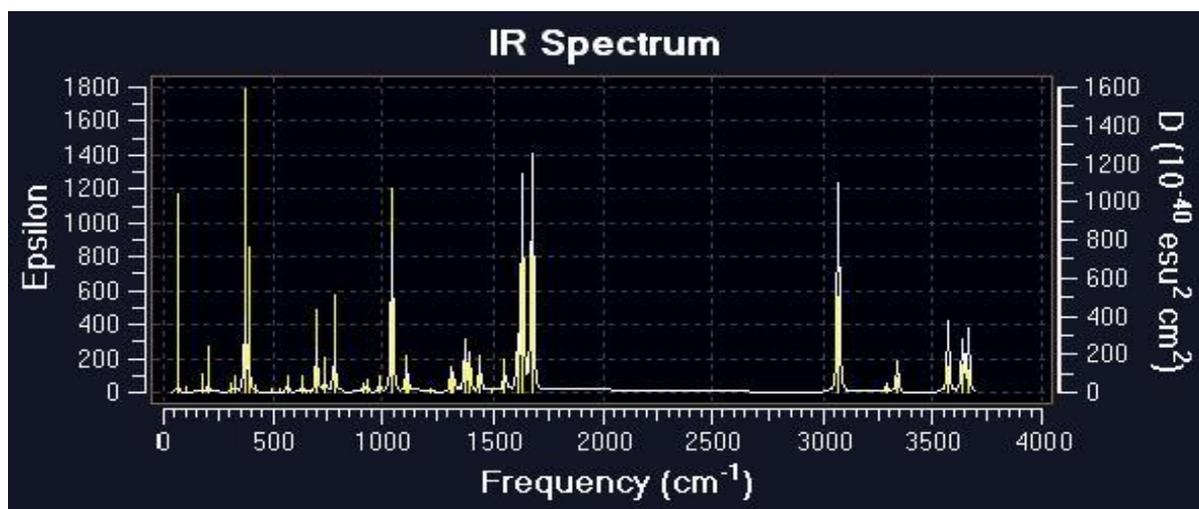
The harmonic vibrational frequencies calculated for studied molecules at B3LYP functional using the 6-31G\*\* basis sets. The (C – H) stretching vibrations of aromatic molecules in the region (2900-3250) cm<sup>-1</sup> which is characteristic region for ready identification of (C – H) stretching vibrations and particularly the region 3250-3100 cm<sup>-1</sup> for asymmetric stretching and 3100-2900 cm<sup>-1</sup> for symmetric modes of vibration. Figure (3) shows the vibration frequencies calculated of the studied molecules using B3LYP/6-31G\*\* method. The strong peak computed by B3LYP/6-31G\*\* observed due to the bending of (C – H) bond, and due to the stretching of (C – C) bond. It is clear from Figure (3) that the IR spectrum for group molecules characters from that of tri fluorine benzene molecule, the stretching and bending of these bonds caused to new peaks or band of peaks to be appeared. There are two types for stretching vibration symmetric and asymmetric, the symmetric stretching is happened when the bonds of the same atoms vibrate in the same phase, and the asymmetric stretching is happened when the bonds vibrate in different phases.



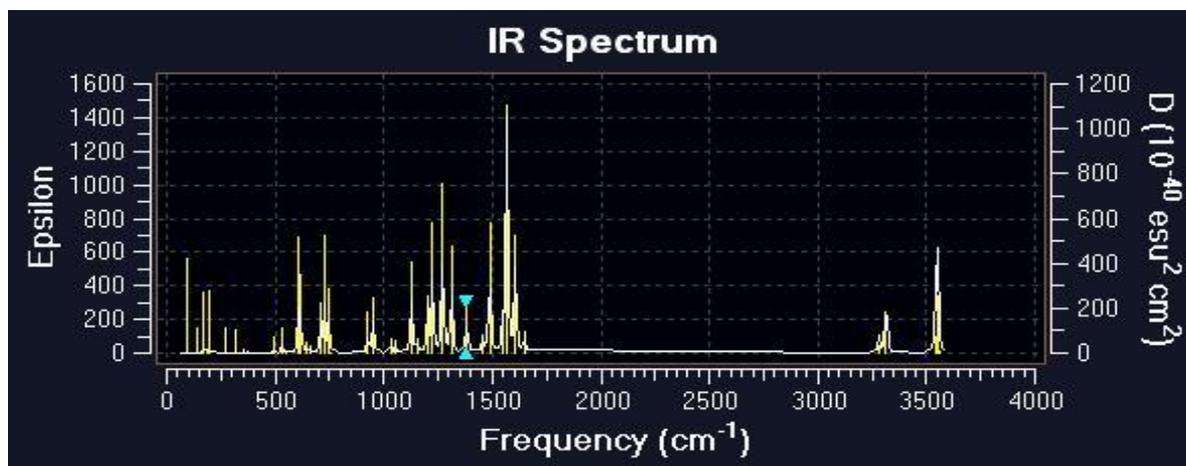
Vibration for structure (1)



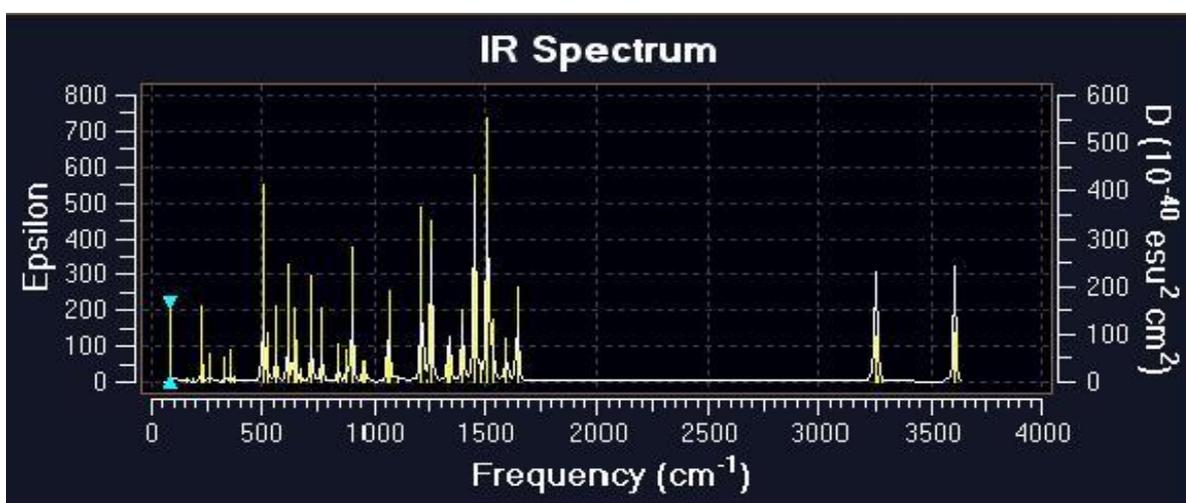
Vibration for structure (2)



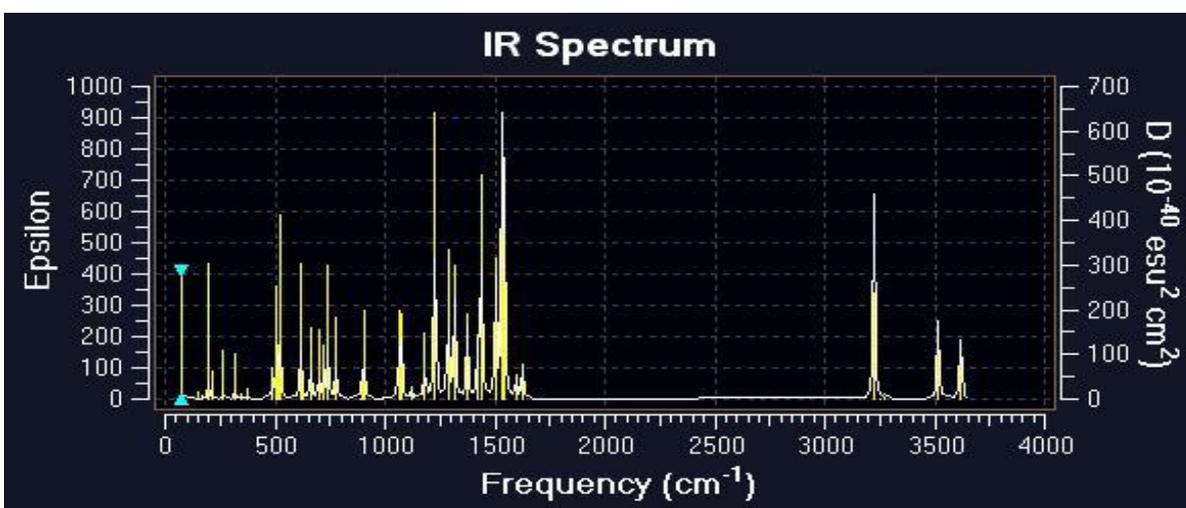
Vibration for structure (3)



Vibration structure (4)



Vibration structure (5)



Vibration structure (6)

Figure 3. The IR spectra of molecules under study, Epsilon  $\equiv$  Intensity (Km/mol).

#### 4. CONCLUSIONS

- 1- The density functional theory is a powerful method three parameters Lee-Yang-Par (B3LYP) functional is a suitable and an efficient function for studying the electronic properties of aromatic structures.
- 2- The geometric structures, symmetry and total energies for iso-indene and hydroxyl iso-indene molecules group are in a good agreement with those in other references. But for other molecules they have not been found similar studies, thus this study supplies new data in this aspect. The hardness for hydroxyl iso-indene molecules group is lowers' values when adding the (N, S) atoms in different locations.
- 3- The total energies for hydroxyl iso-indene found dependent on the position of the (N, S) atoms and OH ion in the ring causes decreasing total energy and more stability.
- 4- The presence of the substituents decreases the energy gap of the molecules study, this is one of the important properties obtained in this work.
- 5- B3LYP/6-31G\*\* DFT given a large approach in IR spectra calculations for observed peaks computed experimentally of iso-indene, and for new hydroxyl iso-indene this study supplies new data for IR spectrum.

#### References

- [1] C. L. Tang, "Fundamentals of Quantum Mechanics for Solid State Electronics and Optics", NY publishes, Ithaca, 2004.
- [2] H. F. Hameka, "Quantum Mechanics: A Conceptual Approach", Leiden University, John Wiley & Sons, Inc., 2004.
- [3] A. Cox., "Introduction to Quantum Theory and Atomic Structure", Lecture in Organic Chemistry, University of Oxford, 1995.
- [4] [4] P. v. R. Schleyer, "Aromaticity (Editorial)", *Chemical Reviews*, 101 (2001) 1115-1118.
- [5] G.A. Jeffery, W. Saenger, "Hydrogen Bonding in Biological structures", Springer, Berlin, 1991.
- [6] G. Horowitz, D. Fichou, X. Z. Peng, Z. G. Xu, F. Gamier, *Solid State Common*, 72 (1989) 381.
- [7] R.D. Green, "Hydrogen Bonding by C-H groups", Wiley-Inter-Science, New York, 1974.
- [8] S. Scheiner, "Hydrogen Bonding: a Theoretical Perspective", Oxford University Press, Oxford, 1974.
- [9] G. R. Desiraju, T. Steiner, "The Weak Hydrogen Bond", Oxford University Press, Oxford, 1997.
- [10] A. T. Balaban, P. v. R. Schleyer and H. S. Rzepa, Crocker, Armit and Robinson, *Chemical Reviews*, 105 (2005) 3436-3447.

- [11] K. Sadasivam, R. Kumaresan, "Computational and Theoretical Chemistry", *Journal of Energetic*, 963 (2011) 227-235.
- [12] P. Ravi, G. M. Gory, S. P. Tewari, and A. K. Sikder, *Journal of Energetic Materials*, 29 (2011) 209-227.
- [13] K. J. Denniston, J. Topping and T. M. Dwyer, "General Organic and Biochemistry", 5th Edition, Towson University, 2007.
- [14] K. Capelle, "A Bires Eye View of Density Functional Theory", Department de Fisica, Univirsil de Sao Paulo, Caixa Postal, 2006.
- [15] P. P. O. Ryan, "Density Functional Theory Modeling of Partial Oxidation in Millisecond Single-Gauze Reactors", University of Minnesota, Department of Chemical Engineering and Materials Science, 2001.
- [16] J. Frank, "Polarization Consistent Basis Sets: Estimating the Kohn-Sham Basis Set Limit", *J. Chem. Phys.* 7372 (2002) 7372-7379.
- [17] E. Min, K. S. Cheol, and B. Kieron, "Avoiding Unbound Anions in Density Functional Calculations", Institute of Nano-Bio Molecular Assemblies, Department of Chemistry, USA publishes, 2011.
- [18] C. Fiolhais, F. Nogueira and M. Marques, "A Primer in Density Functional Theory", Die Deutsche Bibliothek publishes, Germany, 2003.
- [19] M. J. Frisch, G. W. Trucks, H. B. Schlegel et al., "Gaussian 03", Revision A.02, Gaussian, Inc., PA, Wallingford CT., 2009.
- [20] E. R. Bittner, "Quantum Mechanics: Lecture Notes for Chemistry", University of Houston, Department of Chemistry, 2003.
- [21] H. M. Kampen, "Energy Level Alignment at Molecular Semiconductor/GaAs (100) Interfaces: Where is the LUMO", University of Chemnitz, Institut fur, Germany, 1999.
- [22] T. Saito, "Inorganic Chemistry", Kanagawa University, D. I.Men. publishes, 2004.
- [23] C. E. Sharpe, "Inorganic Chemistry", Pearson Education Limited, Second Edition, 2005.
- [24] G. M. Tarr, "Inorganic Chemistry", John Dalton publishes, Oxford, Third Edition, 1990.
- [25] T. Tatsuo, N. Tanaka and Y. Koichi, "Density Functional Study on the Reactivity of Oxidized Aluminum Surfaces: Effects of Adsorbed Metallic Atoms (Au, Cu, Ti, V)", *J. Thin Solid Films* 409 (2002) 66-73.
- [26] L. Shenghua, H. Yang and J. Yuansheng, "Lubrication Chemistry Viewed from DFT-Based Concepts and Electronic Structural Principles", *J. Molecular Sciences*, 5 (2004) 13-34.
- [27] A. H. Raheem, K. J. AL-Shejyri and D. E. Al-bermany, "Density Functional Theory Calculations For Methyl Benzene Molecules Group", *British Journal of Science*, 5 (2012) 57-64.

- [28] V. Subramanian, “Quantum Chemical Descriptors in Computational Medicinal Chemistry for Chemo informatics”, Central Leather Research Institute, Chemical Laboratory, 2005.

( Received 28 May 2016; accepted 16 June 2016 )