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Charge transfer and physisorption mechanism between tosylate , pyrimidine and the surfaces of nanocopper (Cu_9) and (Cu_{10}) utilizing algorithms of (DFT)

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Abstract:

The physisorption procedure and charge transfer phenomena are very important features in surface physics, it contribute to many of important applications in solid state physics. Density functional theory (DFT) with the package of Gaussian 09 at the basis set LanL2Dz, B3LYP level has been utilized to attain the geometrical nanostructure, density contour maps, infrared spectra, electrostatic potential, LUMO energy, HOMO energy, energy band gap, electron affinity, ionization potential, density of states, dipole moment and the polarizability for the geometrical nanostructures (Cu_9), (Cu_{10}), (Cu_9 -OTS), (Cu_9 -Pyrimidine). Calculations of the geometrical nanostructure (Cu_{10} -OTS) has been accomplished at the basis set 6-31G, but the calculations of the geometrical nanostructure (Cu_{10} -Pyrimidine) has been accomplished at basis set LanL2MB. The interactions between the tosylate (OTS) and the nanocopper surface leads to charge transfer phenomena. The interaction between pyrimidine and the nanocopper surface leads to physisorption phenomena. Charge transfer phenomena and physisorption precedures demonstrate apparently in the pictures of contour density maps. Calculations of the energy band gap of the pure geometrical nanostructure (Cu_9) and (Cu_{10}) show that the value of energy gap of those nanostructures is pioneering in the manufacture of the electronic devices. Calculations of the ionization energy and electron affinity disclosure the best geometrical

nanostructure to endow the electrons in an interaction, so the calculations disclosure the best geometrical nanostructure to acquire the electrons in an interaction. Calculations of dipole moment and polarizability disclosure the largest dipole moment and the highest activity geometrical nanostructure in the research under the treatise. Physisorption procedure and charge transfer phenomena make all hybrid geometrical nanostructures have the symmetry C_1 . Physisorption phenomena makes some geometrical nanostructures have anti-ferromagnetic features, but it makes other geometrical nanostructures loses the anti-ferromagnetic feature.

Keywords: Physisorption, DFT, DOS, HOMO(Highest Occupied Molecular Orbital), LUMO (Lowest Unoccupied Molecular Orbital), Symmetry, Contours

1-Introduction

The interaction between organic nanomaterial and solid state surfaces play an active role in many researches in a number of different applications in many branch of knowledge such as surface physics and surface chemistry [1][2]. After the interactions between the organic nanomaterials and the solid state surface, new electronic applications produce in the new geometrical system, the new characteristics did not find in the organic nanomaterial or solid surface [3][4]. Several phenomenas originate when an organic nanomaterial interacts with a solid surface just like physisorption, chemisorption adsorption, ions scattering and resonance charge transfer[5][6]. Density Functional Theory (DFT) is a computational quantum mechanical method can be utilized in physics, chemistry, and nanomaterials science in order to study the electronic properties at the ground state of many geometrical systems. DFT also can utilized to investigate the geometrical structures of nanoclusters, nanotubes and nanoribbons [7][8].The name DFT derived from utilization of electron density instead of the wave function [9]. DFT is one of the most popular and versatile methods in the fields of condensed matter physics, computational physics, and computational chemistry [10]. Many functionals are employed to enhance DFT calculations, such as exchange-correlation functionals. Many approximations also important in density functional theory calculations such as generalized gradient methods (GGA), local density methods (LDA), and local spin density methods (LSDA) [11] [12][13]. DFT needs many basis sets to make the calculation more accurate, just like (3-21G), (LanL2DZ), (LanLMB), and the hybrid functional (B3LYP). The atomic orbitals can be described by a wave function, in which the molecular orbitals result from the linear combinations of the atomic orbitals,. Alex Becke (1993) proposed (B3LYP) to express the correlation-exchange energy. The geometry optimization procedure search on a stationary point at the potential surface. Nobel Prize in Chemistry

awarded to Walter Kohn and John Pople (1998) for their vast enhancements in DFT calculations by utilizing ideas of quantum chemistry [14][15]. In 1881 the German physicist Heinrich Kayser utilizes the expression adsorption [16].

Metals are a group of materials with high electrical and thermal conductivity as well as plasticity, ductility and optical reflectivity [17][18]. Copper (Cu) it was chosen adsorbent, The symbol (Cu) comes from cuprum (Latin). Copper owns atomic number equals to 29. In fact, recently interest has turned to copper surfaces for the potential extension of technological applications to such substrates [19]. Tosylate is a functional group in organic chemistry, tosylate (OTS) owns the chemical formula (C₇H₇O₃S). Tosylate also can be described as an ester functional group, it owns a tosyl group and sulfite group, with a (-ve) charge at one of oxygen atoms. Tosylate can be utilized as an excellent leaving group and impact as protecting group for alcohols. Tosylate also can be employed in the elimination and substitution groups. Unlike alcohols, tosylate can interact with a salt, just like sodium chloride (NaCl) and sodium bromide (NaBr). Tosylate is utilized not only for the halogenation of alcohols, tosylate could easily convert the hydroxide (OH) into a good leaving group [18]. Pyrimidine was chosen adsorbate, it is a six-membered heterocyclic compound composed of nitrogen atoms and carbon. They occur in nature in different forms and form the building blocks of many natural compounds, from antibiotics to vitamins to liposugars. The most common pyrimidines are the bases of RNA and DNA, rich in cytosine, thymine or uracil. The origin of the word pyrimidine dates back to 1884, when Pinner utilizes the term from a combination of the words pyridine and amidine due to the structural similarity to these compounds [19].

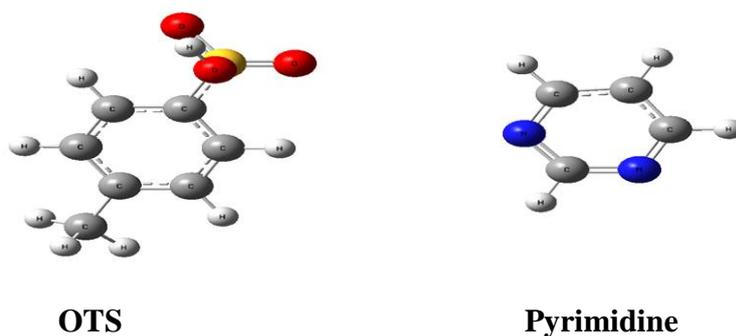
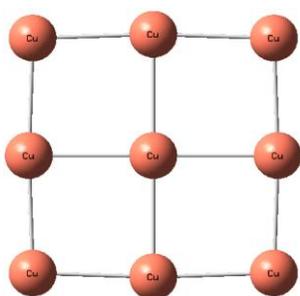


Fig.(1):Molecular geometry for (Tosylate (OTS) and Pyrimidine).

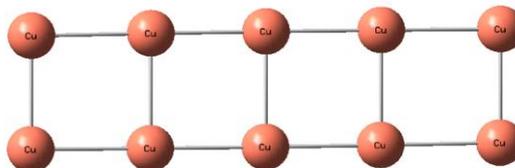
2- Results and Discussion

2.1- Molecular Geometry

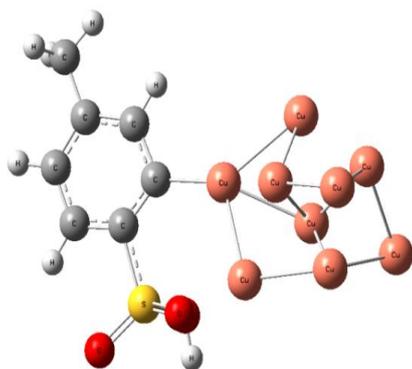
One of the most important factors for describing molecular geometries containing single bonds is the repulsion between electrons. The repulsion is related to the number of electron pairs around the central atom. Repulsion forces should be minimal and allow ideal composition based on the electrons surrounding the central atom. In other words, it can be said that the best possible composition of a molecule consists of the number of electrons around the central atom. The electrons have to move into the orbital, they are in the direction of least repulsive force[21][13]. Molecular geometry for (Cu₉), (Cu₁₀), (Cu₉-OTS), (Cu₉-Pyrimidine) have been investigated utilizing sophisticated codes in DFT with the package of Gaussian 09 at the basis set LanL2Dz, B3LYP level, the structure (Cu₁₀-OTS) has been accomplished at the basis set 6-31G, but the structure (Cu₁₀-Pyrimidine) has been accomplished at basis set LanL2MB.



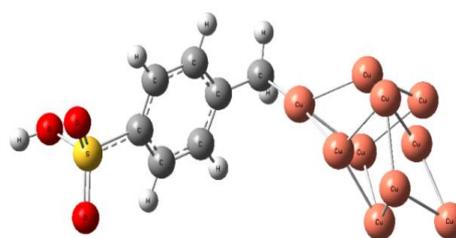
Cu₉



Cu₁₀



Cu₉-OTS



Cu₁₀-OTS

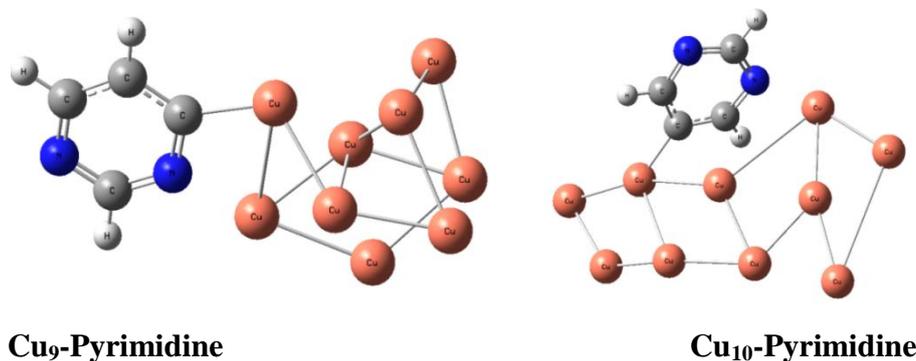


Fig.(2):Molecular geometry for (Cu₉), (Cu₁₀), (Cu₉-OTS), (Cu₁₀-OTS) (Cu₉-Pyrimidine) and (Cu₁₀-Pyrimidine).

Fig.(2):the copper atoms depicts in the light brown color, the nitrogen atoms demonstrates in the blue color, the oxygen atoms demonstrates in the red color, the carbon atoms is noted that have dark lead color, the hydrogen atoms have the light lead color, but the sulfur atom has the yellow color. Physisorption procedure of the organic nanomaterials pyrimidine and OTS on the surfaces (Cu₉) and (Cu₁₀) manipulate vividly on the geometrical structure, one can find out this manipulation by holding simplified counter-posing between (Cu₉) and (Cu₉-OTS), (Cu₁₀) and (Cu₁₀-OTS), (Cu₉) and (Cu₉-Pyrimidine), so (Cu₁₀) and (Cu₁₀-Pyrimidine). Physisorption phenomena leads to big variance in the symmetry shape, (Cu₉) more symmetric than (Cu₉-OTS), (Cu₉-Pyrimidine) and (Cu₁₀) more symmetric than (Cu₁₀-OTS), (Cu₁₀-Pyrimidine). The dimensions between atoms before physisorption are approximately equal, but after the physisorption this dimensions changed. Geometrical optimization makes the bond angles and dihedral angles are the optimal, also the topological dimensions are the optimal. According to bond angles and dihedral angles, the electrons can be presented in some orbitals, but it kept out to be presented in other orbitals. Existence of the forces of interatomic attractive is capable of the stability of the geometrical nanostructures. :

2.2- Electrostatic Potential (ESP)

A surface is a two-dimensional shape with length and width and no thickness. The current surface is an electrostatic potential surface generated by visualizing the molecular structure with the Gaussian 09 program on a Gauss view 5 screen. Surfaces can be probed according to HOMO and LUMO electronic states, where HOMO stands for highly occupied molecular orbitals and LUMO stands for low unoccupied molecular orbitals. The geometry optimization process stops when there is a stagnation point on the potential surface[22]. Electrostatic potential surfaces of (Cu₉), (Cu₁₀), (Cu₉-OTS), (Cu₉-

Pyrimidine) have been investigated utilizing sophisticated codes in DFT with the package of Gaussian 09 at the basis set LanL2Dz, B3LYP level, the structure (Cu_{10} -OTS) has been accomplished at the basis set 6-31G, but the structure (Cu_{10} -Pyrimidine) has been accomplished at basis set LanL2MB.

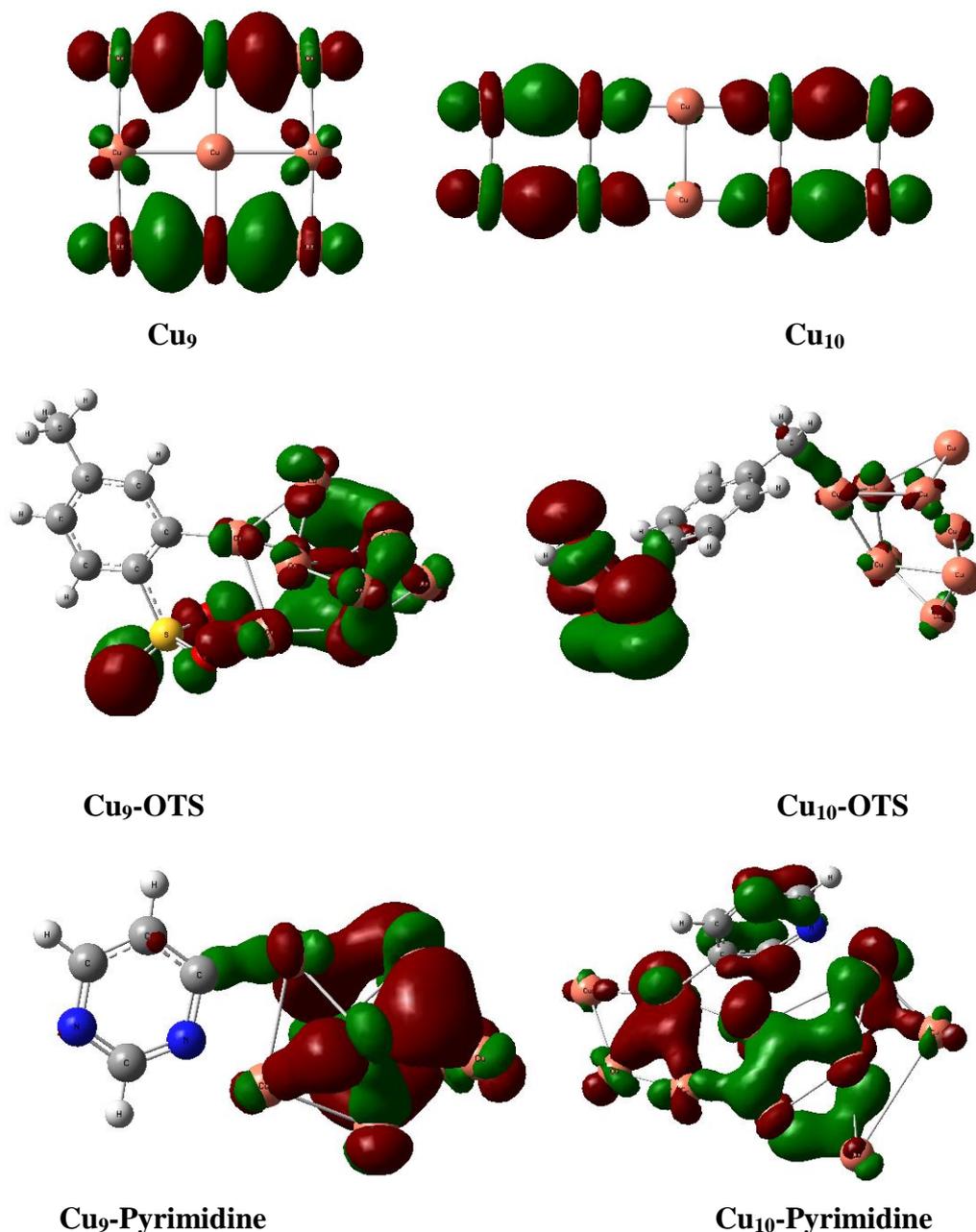
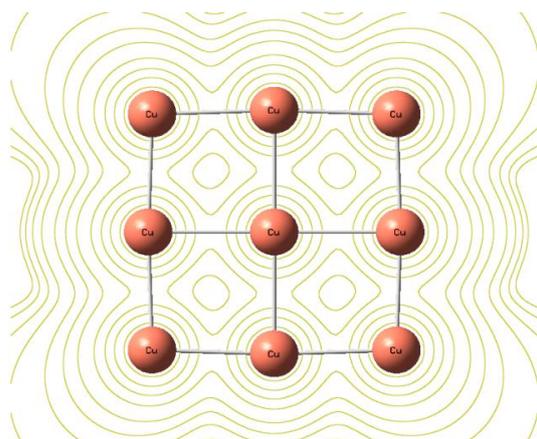


Fig.(3):Electrostatic potential (ESP) for (Cu_9), (Cu_{10}), (Cu_9 -OTS), (Cu_{10} -OTS) (Cu_9 -Pyrimidine) and (Cu_{10} -Pyrimidine).

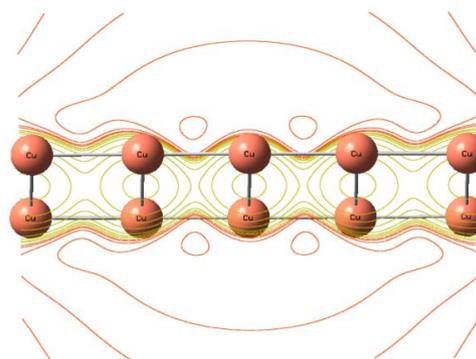
Fig.(3):demonstrates diffusion the electronic charges about the atoms is quite dissimilar in the pure nanostructure as compared with the hybrid nanostructure. Physisorption of the organic nanostructures Pyrimidine and (OTS) on the surface of pure copper (Cu_9) and Cu_{10}) is clarifying that charge diffusion around the atoms in the pure nanostructures is semi-systemizing with comparison to the hybrid nanostructure (Cu_9 -OTS), (Cu_9 -Pyrimidine), (Cu_{10} -OTS) and (Cu_{10} -Pyrimidine). Scan the pictures of electrostatic potential in the figure shows that the charge distribution about the atoms in (Cu_9) is considered semi-homogeneous with comparison to (Cu_9 -OTS) and (Cu_9 -Pyrimidine), either that the charge distribution about the atoms in (Cu_{10}) is considered semi-homogeneous with comparison to (Cu_{10} -OTS) and (Cu_{10} -Pyrimidine). Physisorption procedure causes appearance new credits of the electrostatic potential surface. The atomic orbitals s and p in (OTS) and pyrimidine overlap with the atomic orbitals d of copper atoms to produce molecular orbitals σ , σ^* , π and π^* . The colors (dark red and green) in the potential surface structures can be interprets as follows, the dark red color points out the negative potential region, but the green color indicates to the positive potential region. Also the colors may be interpreted as, the dark red color indicates to the negative partition of the wave function($-\Psi$) , but the green color point out the negative partition of the wave function($+\Psi$).

2.3- Contours

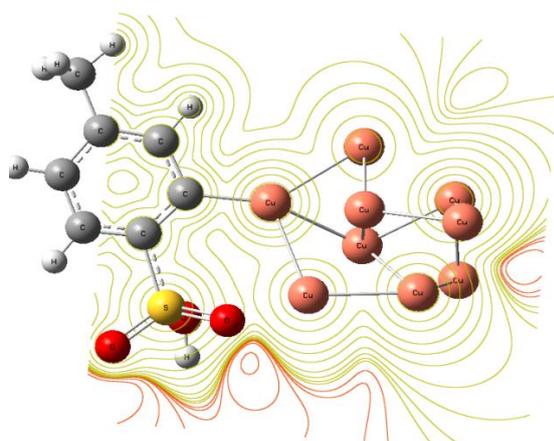
Electron density contours describe the shape of the electrostatic potential. Contour maps are sometimes express Fermi level. Fermi level energy is from the most important quantities in solid state physics and quantum physics. Density contour maps picture give active locations in molecular geometry. So contour geometries occasionally had been utilized to clarify electron density distribution around the atoms in the space [23]. Contour maps for (Cu_9) ,(Cu_{10}) , (Cu_9 -OTS) ,(Cu₉-Pyrimidine) have been investigated utilizing sophisticated codes in DFT with the package of Gaussian 09 at the basis set LanL2Dz, B3LYP level, the structure (Cu_{10} -OTS) has been accomplished at the basis set 6-31G , but the structure (Cu_{10} -Pyrimidine) has been accomplished at basis set LanL2MB.



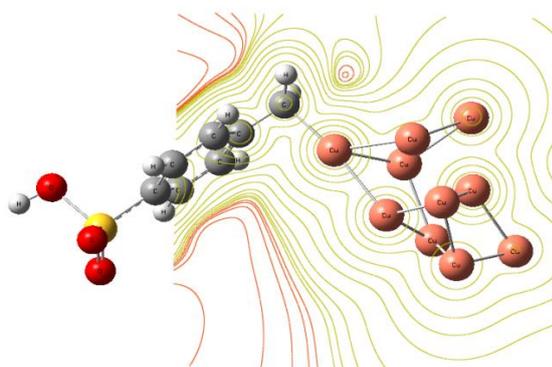
Cu₉



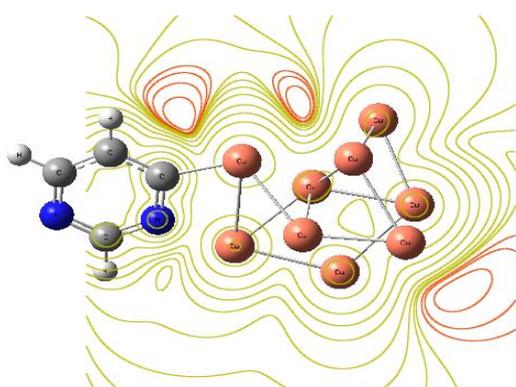
Cu₁₀



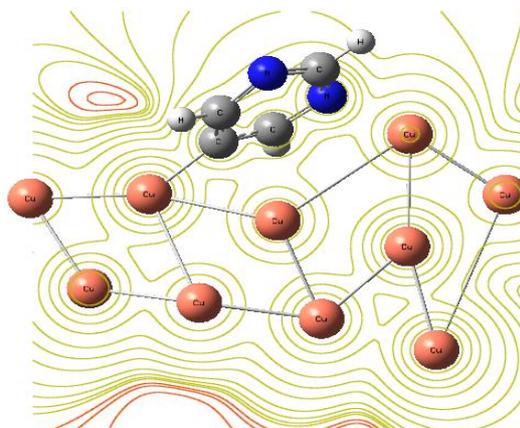
Cu₉-OTS



Cu₁₀-OTS



Cu₉-Pyrimidine



Cu₁₀-Pyrimidine

Fig.(4):Density of contour maps for (Cu₉), (Cu₁₀), (Cu₉-OTS), (Cu₁₀-OTS)

(Cu₉-Pyrimidine) and (Cu₁₀-Pyrimidine).

In fig.(4): it could be observed that charge transfer phenomena demonstrates as a result to the interaction between (Cu₉) and (OTS), the electronic charges concentrate apparently near oxygen atoms. Also charge transfer phenomena happen because the interaction between (Cu₁₀) and (OTS), the electronic charges concentrate clearly near carbon atoms. The interaction between pyrimidine and the surfaces (Cu₉) and (Cu₁₀) leads to physisorption process, one could note by rapprochement between (Cu₉) and (Cu₉-Pyrimidine), electronic charges concentrate around copper atoms. Also the rapprochement between (Cu₁₀) and (Cu₁₀-Pyrimidine) shows electronic charges concentrate around copper atoms. Contour density maps occasionally are expressed by Fermi surface, Fermi surface has significant importance in many of solid state characteristics just like charge transfer. The electrons near Fermi surface is moving at very large speed, around one-hundredth of the speed of light. Fermi energy is determined primarily by electrons concentrations. Either Brillion zones sometimes utilize for pointing out contour curves (contour circles). The electrons cannot exceed the 1st Brillion zone to cross to the 2nd Brillion zone unless the electrons have the enough energy that permit to exceed the area between 1st and 2nd Brillion zones, this energy make the electrons capable of crossing the prohibition region, in this case the electrons will be able to transfer, hence the charge transfer will accomplish.

2.4-Infrared spectra (IR)

There are two types of stretching vibrations: symmetrical and asymmetrical. Stretching vibrations occur when atoms oscillate in the same phase. Non-stretching vibrations occur in atoms oscillate with different phases[24]. Infrared spectroscopy provides harmonic vibrational frequencies. The number of modes depends on the number of atoms in the geometrical structure. Each value or range represents a vibration pattern. The vibration modes are either elastic or inelastic [25]. Infrared spectra for (Cu₉), (Cu₁₀), (Cu₉-OTS), (Cu₉-Pyrimidine) have been investigated utilizing sophisticated codes in DFT with the package of Gaussian 09 at the basis set LanL2Dz, B3LYP level, the structure (Cu₁₀-OTS) has been accomplished at the basis set 6-31G, but the structure (Cu₁₀-Pyrimidine) has been accomplished at basis set LanL2MB.

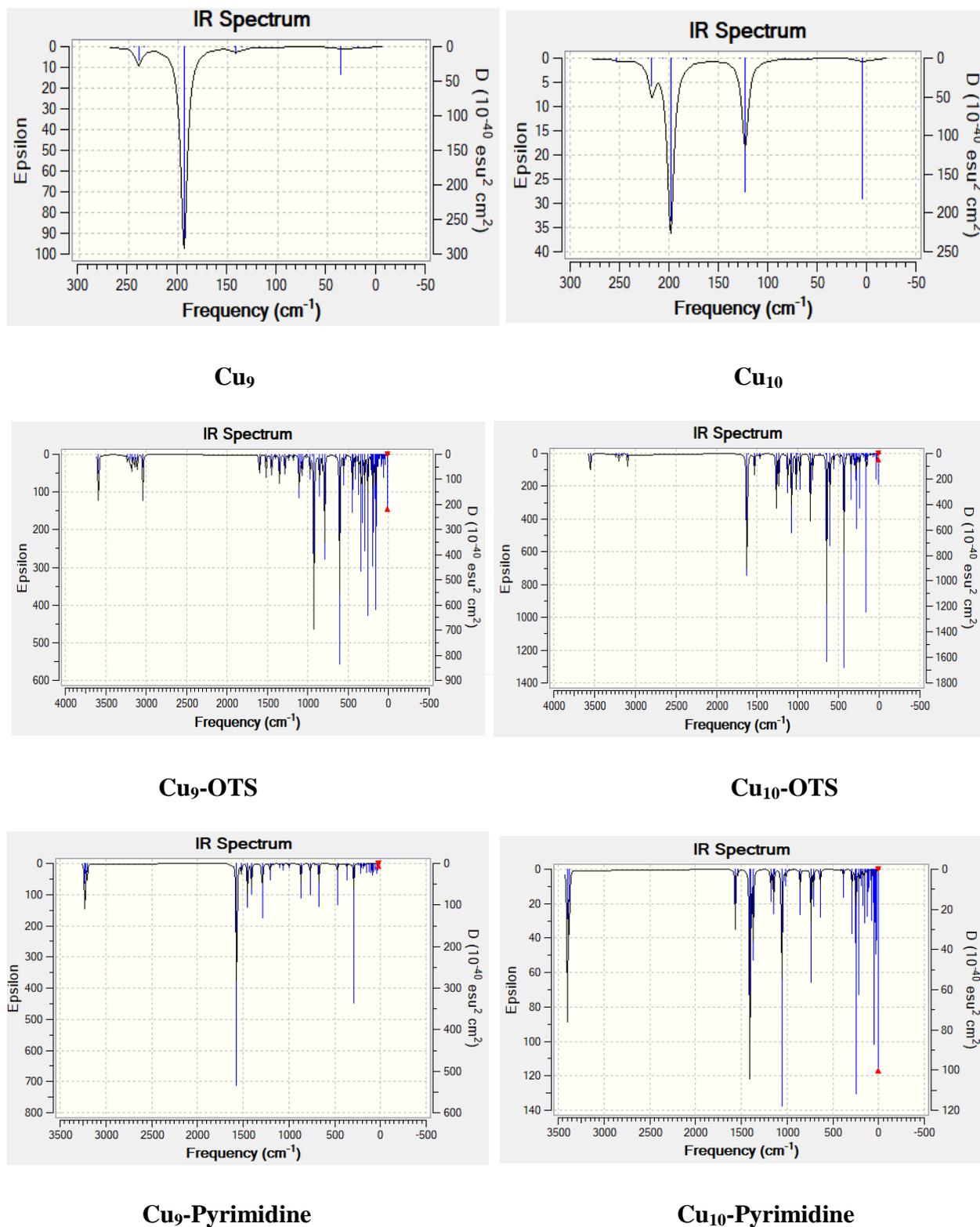


Fig.(5):Infrared spectra schematics for (Cu₉), (Cu₁₀), (Cu₉-OTS), (Cu₁₀-OTS) (Cu₉-Pyrimidine) and (Cu₁₀-Pyrimidine)

In fig.(5):the diagrams demonstrate effect of physisorption procedure on the active areas. One of IR schematics advantages is to diagnosis the compounds, theoretically IR schematics could be obtained by submitting codes (sophisticated algorithms) computationally in Gaussian 09 package with density functional theory, but tentatively the diagnostics could be held by utilizing special devices in chemistry laboratories. The diagnostic theoretically and tentatively demonstrates the active groups. The rapprochement between (Cu₉) and (Cu₉-OTS) , (Cu₁₀) and (Cu₁₀-OTS) shows manipulation of the charge transfer phenomena in demonstration the new active groups. New bonds (Cu-O), (Cu-S), (Cu-C) and (Cu-H) will result in the geometrical nanostructures (Cu₉-OTS) and (Cu₁₀-OTS) with rapprochement to (Cu₉) and (Cu₁₀) respectively. The rapprochement between (Cu₉) and (Cu₉-Pyrimidine) , (Cu₁₀) and (Cu₁₀-Pyrimidine) demonstrates influence physisorption procedure on the active groups. New bonds (Cu-N), (Cu-C) and (Cu-H) will show in the geometrical nanostructure (Cu₉-Pyrimidine) and (Cu₁₀-Pyrimidine) with rapprochement to (Cu₉) and (Cu₁₀). Charge transfer phenomena make the maximum apex approximately (600 km/mole) concerns the geometrical nanostructure (Cu₁₀-OTS), at the wave number (1650 cm⁻¹). Physisorption procedure make the maximum apex approximately (310 km/mole) concerns the geometrical nanostructure (Cu₉-yrimidine) , at the wave number close approximately (1600 cm⁻¹).

2.5-Electronic states and Energy Gap (E_g)

HOMO and LUMO energies are electronic states. They refer to specific sites where electrons with quantized energies exist, where HOMO energy indicates high occupied molecular orbitals, and LUMO energy indicates low unoccupied molecular orbitals. The molecular orbitals are produced by linear combinations of the atomic orbitals. The difference between HOMO and LUMO gives the energy gap (E_g). Mathematically the energy gap (E_g) can be expressed as the equation[26] [27]

$$E_g = E_{LUMO} - E_{HOMO} \quad (1)$$

Table1. Illustrates HOMO, LUMO energies and energy gaps for (Cu₉), (Cu₁₀), (Cu₉-OTS), (Cu₁₀-OTS), (Cu₉-Pyrimidine) and (Cu₁₀-Pyrimidine)

System	E _{HOMO} (eV)	E _{LUMO} (eV)	E _g (eV)
Cu ₉	-4.0918398	-3.1827537	0.9090861
Cu ₁₀	-4.682841	-3.7193349	0.9635061
Cu ₉ -OTS	-5.393022	-2.5343394	2.8586826
Cu ₉ -Pyimidine	-5.1301734	-2.6091669	2.5210065
Cu ₁₀ -OTS	-4.4452977	-3.1830258	1.2622719
Cu ₁₀ -Pyrimidine	-4.3187712	-2.6546076	1.6641636

Table1.Demonstrates the values of band gap in the pure geometrical nanostructures (Cu₉) and (Cu₁₀) with semiconductor properties, one can say the pure copper in those two nanostructures become semiconductor with rapproachment to the bulk copper. Interaction of the organic nanomaterial (OTS) and pyrimidine with the geometrical nanostructure (Cu₉) causes apparent increasing in band gap values as compared with the interaction of the organic nanomaterial (OTS) and pyrimidine with (Cu₁₀). Semiconductor substances is pioneering in manufacturing of the electronic devices such as laptop and mobile species. When the energy gap of the compound at room temperature be less than (2 eV), the compound is described as a semiconductor, but the compound is described as an insulator if the energy gap be large. The reason of originating the energy gap in the compounds is that the electrons own dissimilar values of the potentials at dissimilar regions. HOMO is at most involved to capability of the geometrical nanostructure to endow the electrons, but LUMO is involving to capability of the geometrical nanostructure to acquire the electrons. So that the geometrical nanostructure can be considered has high trend to endow the electrons if it has high value of HOMO, likewise the high trend of acquire electrons is involving to consumption LUMO.

2.6-Ionization potential and electron affinity

The ionization potential measures the binding force between electrons and atoms and corresponds to the energy required to take away an electron from a neutral atom in the gaseous state. The electrons in the outer shell have ionization energies [28] [29] [28]. Electron affinity can be defined as the energy released when an atom accepts an electron. Electron affinity is sometimes referred to as zero ionization energy. Atoms with an outer shell of seven electrons have high electron affinity, while atoms with closed electron shells have low electron affinity [28]. According to Koopman's theory [30][29].

$$I.P = -E_{HOMO} \quad (2)$$

$$E.A = -E_{LUMO} \quad (3)$$

Table 2.Reveals Ionization potentials (I.P) and electron affinities (E.A) for (Cu₉), (Cu₁₀), (Cu₉-OTS), (Cu₁₀-OTS), (Cu₉-Pyrimidine) and (Cu₁₀-Pyrimidine).

System	I.P(eV)	E.A(eV)
Cu ₉	4.0918398	3.1827537
Cu ₁₀	4.682841	3.7193349
Cu ₉ -OTS	5.393022	2.5343394
Cu ₉ -Pyrimidine	5.1301734	2.6091669
Cu ₁₀ -OTS	4.4452977	3.1830258
Cu ₁₀ -Pyrimidine	4.3187712	2.6546076

Table2. Demonstrates that the pure geometrical nanostructure (Cu₉) owns the minimum value of the ionization potential in the table, this pure geometrical nanostructure has ionization potential approximately equals to (4.09 eV). Therefore the electrons in (Cu₉) need the minimum energy for breaking free of the surface of (Cu₉), also one can put it this geometrical nanostructure endows the electrons simpler than the other nanostructures in the table to become cation. The pure geometrical nanostructure (Cu₁₀) owns the maximum value of the electron affinity in the table, this pure geometrical nanostructure has electron affinity approximately equals to (3.72 eV). Therefore the pure geometrical nanostructure (Cu₁₀) stands for the finest nanostructure for acquiring the electrons, also one can assert this geometrical nanostructures can be regarded the best nanostructure for accepting the electrons in LUMO level to become anion. Ionization potential is an influence factor on the charge transfer procedures, transfer levels. Binding energy of the nanostructure and the stability of the geometrical nanostructure. Many other electronic properties can be evaluating by utilizing electron affinity and ionization potential, just like, electrophilicity, hardness, electronegativity and softness.

2.7-Polarizability

It shows the ability of molecules to polarize. It determines the dynamic response of the bonded system to external fields. It also implies a linear response of electron density to an infinite electric field. The polarizability represents a second-order change in energy[31] [32].

$$\alpha = -\left(\frac{\partial^2 E}{\partial F_a \partial F_b}\right)_{a,b} = x, y, z \quad (4)$$

Assume the quantities α_{xx} , α_{yy} and α_{zz} typify the eigen values to the polarizability tensor, the average polarizability can be calculated using those eigenvalues of the polarizability tensor. Mathematically it can be calculated by the equation [33]

$$\langle \alpha \rangle = \left(\frac{\alpha_{xx} + \alpha_{yy} + \alpha_{zz}}{3}\right) \quad (5)$$

Table 3. Summarizes polarizabilities and average polarizabilities for for (Cu₉), (Cu₁₀), (Cu₉-OTS), (Cu₁₀-OTS), (Cu₉-Pyrimidine) and (Cu₁₀-Pyrimidine)

System	α_{xx}	α_{yy}	α_{zz}	$\langle \alpha \rangle$
Cu ₉	462.478	462.478	162.218	362.3913333
Cu ₁₀	186.974	1098.998	365.381	550.451
Cu ₉ -OTS	540.899	379.903	313.229	411.3436667
Cu ₉ -Pyrimidine	426.942	319.459	274.655	340.352
Cu ₁₀ -OTS	731.667	406.124	366.433	501.408
Cu ₁₀ -Pyrimidine	844.813	432.957	258.32	512.03

Table 3. Summarizes values of the eigen values of polarizabilities α_{xx} , α_{yy} , α_{zz} and the average polarizability $\langle \alpha \rangle$ for the geometrical nanostructures in the table in atomic units. The geometrical nanostructure (Cu₁₀) owns the maximum numerical value of the average polarizability, $\langle \alpha \rangle$ equal to (550.451 a.u), therefore, the geometrical nanostructure is the maximum activity nanostructure in the table. The highest eigen value of the polarizability tensor α_{xx} be for the geometrical nanostructure Cu₁₀-Pyrimidine (844.813 a.u), the highest eigen value of the polarizability tensor α_{yy} be for the geometrical nanostructure (Cu₁₀), it is (1098.998a.u), but the highest eigen value of the polarizability tensor α_{zz} be for the geometrical nanostructure (Cu₁₀-OTS), it is (366.433 a.u). The polarizability be as result to, the fact that, the building blocks of the geometrical nanostructures are composed of nucleie (+ve) charges and electrons (-ve) charges. The polarized geometrical nanostructures are that have

permanent moment (till with absence of the electric field). The polarizability produce in the geometrical nanostructures when the $(-ve)$ charge be displaced in the opposite direction of the displacement of the $(+ve)$ charge. The importance of polarizability feature in physics is derived from the fact that the polarizability supplies informations over the internal nanostructure and the dipole moment of the geometrical nanostructures without holding calculations. One of the most advantades of the polarizability feature, it is utilized in the nonlinear optics science.

2.8-Dipole moment

A common definition of a dipole moment indicates the presence of two charges with the same value but different signs. Peter Debye was the first physicist to study bipolar systems. In honor of this, the Debye unit became the dipole moment unit. Dipole moments can be permanent or induced. The dipole moment is the product of charge and displacement. Dipole moments occur in heteronuclear molecules, but homonuclear molecules usually do not have dipole moments. The dipole moment varies with each change in the direction of displacement and can be given by [34]:

$$P = q * r \quad (6)$$

P : dipole moment , q : charge , r : displacement.

Table 4. Appears dipole moments for (Cu₉) ,(Cu₁₀) , (Cu₉-OTS), (Cu₁₀-OTS) , (Cu₉-Pyrimidine) and (Cu₁₀-Pyrimidine).

System	Dipole moment (Debye)
Cu ₉	0
Cu ₁₀	0
Cu ₉ -OTS	3.6373
Cu ₉ -Pyrimidine	1.8051
Cu ₁₀ -OTS	9.108
Cu ₁₀ -Pyrimidine	3.298

Table 4.Demonstrates values of dipole moments of the pure copper nanostructures and hybrid copper nanostructures. The pure copper nanostructure (Cu₉) and (Cu₁₀) have zero values dipole moment, the reason here is the homonuclear nanostructures. The dipole moment is a vector physical quantity, so

that, the dipole moment can take a zero value, in which, the (+ve) dipole moments can cancel the (-ve) dipole moments, therefore the resultant will be zero. The hybrid geometrical nanostructures ($\text{Cu}_9\text{-OTS}$), ($\text{Cu}_9\text{-Pyrimidine}$), ($\text{Cu}_{10}\text{-OTS}$) and ($\text{Cu}_{10}\text{-Pyrimidine}$) have non-zero values of dipole moment because they are heteronuclear nanostructures. The hybrid nanostructure ($\text{Cu}_{10}\text{-OTS}$) owns the maximum value of dipole moment (9.108 Debye), hence the physisorption procedure impact dramatically tremendously on the value of dipole moment of this geometrical nanostructure. The dipole moment be considered standard for bond strength and charge density in the chemical nanostructure. Dipole moment yields informations about the polarizability, because it predicts to the activity of the geometrical nanostructure. Dipole moment is happening as a consequence to the dissimilarity in the electric negativity between two atoms. The dipole moment of the geometrical nanostructure in the table typifies the resultant of the moments vectors of the dissimilar bonds in molecular nanostructure, the reason here, they are many atoms systems. **2.9-Symmetry**

In order to understand symmetry idea, it is most suitable to know the following terms that involved the symmetry project, they are center of inversion, plane of reflection and centerpiece of rotation. Point group symmetries are implicit all the possible operations (rotation, inversion and reflection) which leave one point remains invariant. One must retain in the mind, the name point group symmetry derived from the fact that there is point must be fixed. Symmetry elements are, identity, proper axis, horizontal plane, vertical plane, dihedral plane, improper axis and inversion center or center of symmetry[35][36][35].

Table 5. Appears point group symmetries for (Cu_9), (Cu_{10}), ($\text{Cu}_9\text{-OTS}$), ($\text{Cu}_{10}\text{-OTS}$), ($\text{Cu}_9\text{-Pyrimidine}$) and ($\text{Cu}_{10}\text{-Pyrimidine}$).

System	Point group symmetry
Cu_9	D_{4h}/C_1
Cu_{10}	D_{2h}/C_1
$\text{Cu}_9\text{-OTS}$	C_1
$\text{Cu}_9\text{-Pyrimidine}$	C_1
$\text{Cu}_{10}\text{-OTS}$	C_1
$\text{Cu}_{10}\text{-Pyrimidine}$	C_1

Table 5. Summarizes point group symmetries of the pure copper and hybrid copper. There are three types of point group symmetries demonstrate in the table, they are, D_{4h}/C_1 , D_{2h}/C_1 and C_1 .

Physisorption and charge transfer phenomena leads to make all hybrid nanostructures own the sort C_1 . The geometrical nanostructure (Cu_9) has the point group symmetry D_{4h}/C_1 , therefore, one could say this pure copper nanostructure owns four fold axes vertical to C_n , so it owns plane of horizontal mirror. The geometrical nanostructure (Cu_{10}) owns the point group symmetry D_{2h}/C_1 , therefore, one could say this pure copper nanostructure has two fold axes vertical to C_n , so it owns plane of horizontal mirror. The hybrid geometrical nanostructures (Cu_9 -OTS), (Cu_9 -Pyrimidine), (Cu_{10} -OTS) and (Cu_{10} -Pyrimidine) possess the point group symmetry C_1 , the point group symmetry of the hybrid geometrical nanostructures can be classified as C_n symmetry, in this kind, the symmetry is happening over $(360^\circ/n)$, the repetition of those geometrical nanostructures is taking place over (360°) , here $(n=1)$. Determination of the point group symmetry permits to make some of deductions around the geometrical nanostructure without holding extra evaluations. The symmetry gives the possibility to decide if the molecular nanostructure owns dipole moment or not. Symmetry idea is beneficial in biocomplexes applications.

2.10-Density of States (DOS)

In solid-state physics, the density of states can be defined as the number of allowed states of an energy level that can be occupied. In quantum physics, waves and wave-like particles can adopt modes or states at specific wavelengths, with the direction of propagation determined by the system [37]. Most of the time there are certain allowed states, that is, the number of certain allowed wavelengths are with certain energy levels [38][39]. The density of states of electrons, photons and phonons can be studied through quantum mechanics. The density of states is a very important property in solid state physics and quantum physics[40]. Density of states for (Cu_9), (Cu_{10}), (Cu_9 -OTS), (Cu_9 -Pyrimidine) have been investigated utilizing sophisticated codes in DFT with the package of Gaussian 09 at the basis set LanL2Dz, B3LYP level, the structure (Cu_{10} -OTS) has been accomplished at the basis set 6-31G, but the structure (Cu_{10} -Pyrimidine) has been accomplished at basis set LanL2MB.

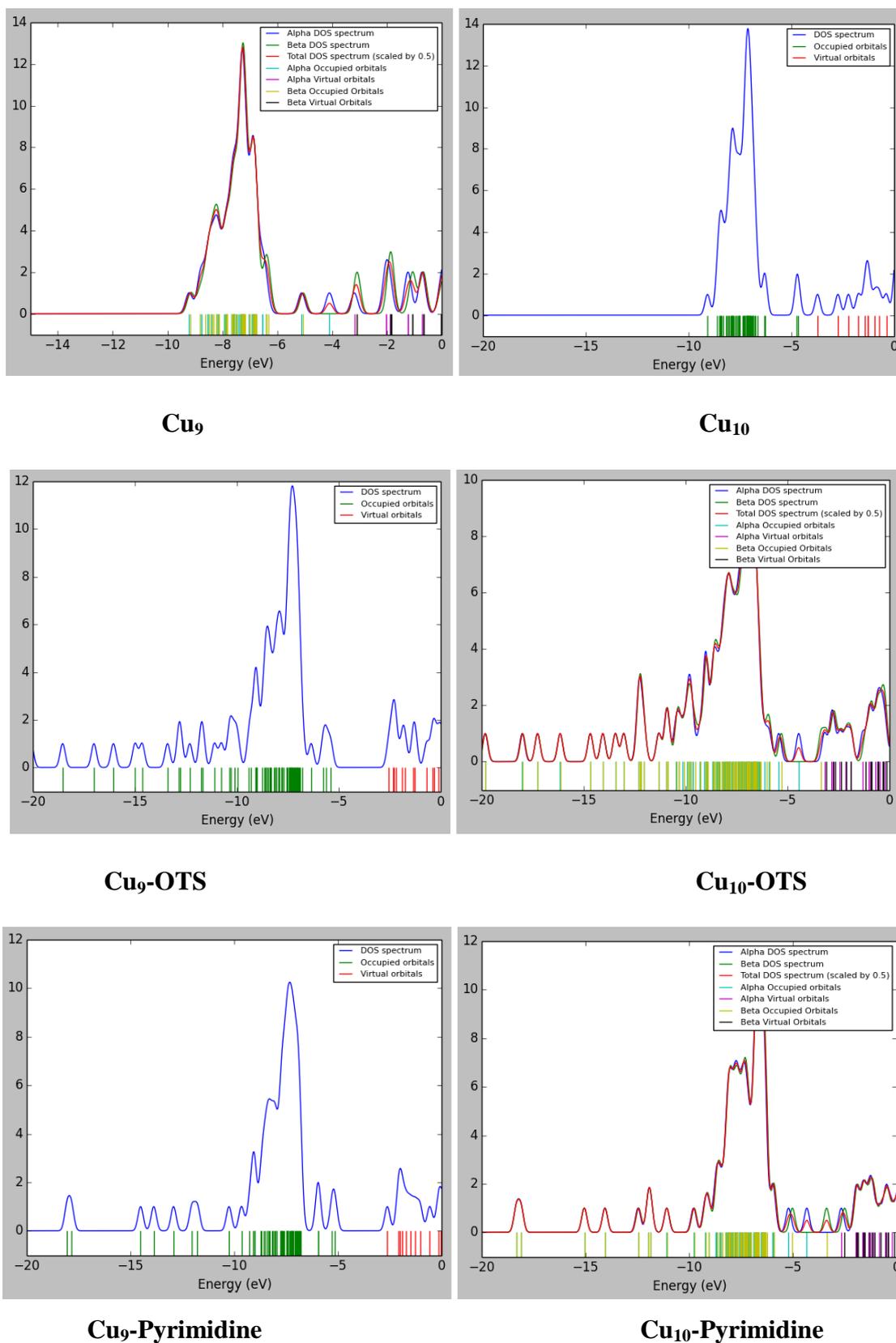


Fig.(6):Density of state charts for (Cu₉), (Cu₁₀), (Cu₉-OTS), (Cu₁₀-OTS),

(Cu₉-Pyrimidine) and (Cu₁₀-Pyrimidine).

Fig.(6):demonstrates the geometrical nanostructure (Cu₉) has anti-ferromagnetism properties, but (Cu₉-OTS) and (Cu₉-Pyrimidine) do not have anti-ferromagnetic properties, hence one could put it charge transfer phenomena and physisorption procedure manipulate apparently tremendously on the magnetic features. The geometrical nanostructures (Cu₉), (Cu₁₀-OTS) and (Cu₁₀-Pyrimidine) have two kinds of orbits, they are alpha (α) and (β) and beta, but (Cu₁₀), (Cu₉-OTS) and (Cu₉-Pyrimidine) have only one type of orbits, it is alpha (α). Anti-ferromagnetization feature demonstrates in many of compounds that have transition metals in their geometrical nanostructure, here the transition metal is copper (Cu). The anti-ferromagnetism feature has dipoles has equal moments, but the neighboring dipoles point will be with opposite directions. The dipole symmetry leads to zero net magnetization. One can observe new states demonstrates between energies ($-20 eV$) and ($-10 eV$) in the geometrical nanostructures (Cu₉-OTS), (Cu₁₀-OTS), (Cu₉-Pyrimidine) and (Cu₁₀-Pyrimidine). The new states in the geometrical nanostructures (Cu₉-OTS) and (Cu₁₀-OTS) are more than the new states in (Cu₉-Pyrimidine) and (Cu₁₀-Pyrimidine). The electrons will occupy the new states, this leads to make the molecular structures more stability.

3-Conclusions

Two types of surface phenomena is taking place at the surfaces of (Cu₉) and (Cu₁₀) as a consequence to the interactions (OTS-Cu) , (Pyrimidine-Cu). The charge distribution of the distortion of the contour density maps of the hybrid nanostructures as rapprochement to the pure nanostructures disclosure clearly the charge transfer mechanics and physisorption phenomena. Charge transfer phenomena make the maximum apex approximately (600 km/mole) concerns the geometrical nanostructure (Cu₁₀-OTS), at the wave number (1650 cm^{-1}). Physisorption procedure make the maximum apex approximately (310 km/mole) concerns the geometrical nanostructure (Cu₉-yrimidine) , at the wave number close approximately (1600 cm^{-1}). The pure geometrical nanostructures (Cu₉) and (Cu₁₀) with semiconductor properties, one can say the pure copper in those two nanostructures become semiconductor with rapprochement to the bulk copper. The pure geometrical nanostructure (Cu₉) has ionization potential approximately equals to (4.09 eV), therefore the electrons in (Cu₉) need the minimum energy for breaking free of the surface of (Cu₉). The pure geometrical nanostructure (Cu₁₀) owns the maximum value of the electron affinity, this pure geometrical nanostructure has electron affinity approximately equals to (3.72 eV), therefore the pure geometrical nanostructure (Cu₁₀) stands

for the finest nanostructure for acquiring the electrons. The geometrical nanostructure (Cu_{10}) owns the maximum numerical value of the average polarizability, $\langle \alpha \rangle$ equals to (550.451 a.u), therefore, the geometrical nanostructure is the maximum activity nanostructure. There are three types of point group symmetries demonstrate, they are, D_{4h}/C_1 , D_{2h}/C_1 and C_1 , therefore, physisorption and charge transfer phenomena leads to make all hybrid nanostructures own the kind C_1 . Symmetry idea is beneficial in biocomplexes applications. The hybrid nanostructure (Cu_{10} -OTS) owns the maximum value of dipole moment (9.108 Debye), hence the physisorption procedure impact dramatically tremendously on the value of dipole moment of this geometrical nanostructure. One can observe new states demonstrates between energies (-20 eV) and (-10 eV) in the geometrical nanostructures (Cu_9 -OTS), (Cu_{10} -OTS), (Cu_9 -Pyrimidine) and (Cu_{10} -Pyrimidine). The new states in the geometrical nanostructures (Cu_9 -OTS) and (Cu_{10} -OTS) are more than the new states in (Cu_9 -Pyrimidine) and (Cu_{10} -Pyrimidine). The electrons will occupy the new states, this leads to make the molecular structures more stability.

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