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Studying the electronic characteristics and physisorption of OTS on the pure silver surfaces (Ag_{10}), (Ag_{15}) and (Ag_{18})

1st Fatima Thamer
Physics Department/College of science
University of Thi-Qar
Nasiriya/Iraq
fatima.thamer@sci.utq.edu.iq

2nd Abbas Shwya alwan
Physics Department/ College ofscience
University of Thi-Qar,
Nasiriya /Iraq
abbasshwaa_ph@sci.utq.edu. iq

3rd Ali Ben Ahmed
Physics Department/ College ofscience
University of Sfax
Sfax /Tunisia
ali.benahmed@isbs.usf.tn

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***Abstract*— The interaction between organic Nano molecules and solid surfaces play a prominent role in numerous applications such as charge transfer and physisorption. Density functional theory (DFT) by utilizing sophisticated algorithms in Gaussian 09 software package at LANL2DZ, B3LYP level at the ground state energy had been utilized to attain the merits, molecular structure, contour maps density, electrostatic potentials (ESPs), density of states , infrared spectra (IR), electronic states, HOMO and LUMO energies, Energy gaps (Eg), electron affinity (E.A), ionization potential (I.P), dipole moment, the eigen values of the polarizabilities tensor α_{xx} ,α_{yy} and α_{zz} , average polarizability <α> ,and symmetry to the geometrical nanostructures $(Ag1_0)$, (Ag_{15}), (Ag_{18}), $(Ag_{10}$-OTS), $(Ag_{15}$-OTS) and $(Ag_{18}$-OTS). Physisorption phenomena impact tremendously to the symmetry of the geometrical structure. Molecular bonds of the (σ, σ^*, π, π^*, δ and δ^*) originate because the overlap between (s or p atomic orbitals) in the organic nanomaterials and (d atomic orbitals) in the silver nanosurface. The distortion in contour maps interprets happening physisorption or charge transfer. According infrared spectra it can be seen new bonds because of the physisorption. Density of states diagrams demonstrates changing in the magnetic properties after physisorption. Simulation of silver (Ag) in nano dimensions make it semiconductor as compared with the bulk. The values of energy gaps of all hybrid nanostructures are in the range of semiconductor. Physisorption procedure impact randomly to the ionization potential and electron affinity, this takes place because many factors, just like, geometrical parameters, topological coordinates, symmetry and the geometrical structure. The geometrical nanostructure $(Ag_{18}$-OTS) stands for the highest value of dipole moment nanostructure among all hybrid and pure nanostructures in this research, it has the value (6.24 Debye). Physisorption phenomena lead to decrease in the values of average polarizability. Three classes of point group symmetries demonstrate, (D_{2h}/C_1), (C_{2h}/C_1) (C_1) .**

***Keywords*— Physisorption, DFT, DOS, HOMO, LUMO, Energy gap, Polarizability, Symmetry.**

I.INTRODUCTION

Due to the potential significance in numerous applications, including catalysis, molecular switches, sensors, photovoltaics, energy materials, organic molecules adsorption at metal surfaces study is garnering significant interest [1, 2]. Combining different material classes such as the metals organic nanomolecules may produce novel functions that none of the materials alone could have [3]. The adsorbate structure and intermolecular interactions have a significant impact to the electronic, optical, and transport properties of hybrid systems [4, 5].

The interaction between the organic nanomaterial and the metal surface represent physisorption phenomena [5]. Dipoles "physically" connect the atoms or molecules together. The Van der Waals (VdW) interaction is physisorption counterpart in surface physics. This classification is supported by the strength of the physisorption, which occurs when small molecules or atoms are physisorbed and then desorb when heated to normal temperatures, which are infrequently above the adsorbate's bulk-boiling point (e.g. 77 K for physisorbed N2) [6]. Therefore, understanding and controlling the functionality of such hybrid systems depends on an accurate description of the bonding between adsorbates and substrates. This poses a theoretical challenge because bonding in complex organic/metal systems is the result of a delicate balance of covalent bonds, Van der Waals (VdW) forces, charge transfer, hydrogen bonds and Pauli repulsion [5].

Density Functional Theory (DFT) is a quantum computational method that employs quantum physics and quantum chemistry to achieve geometrical structure (at the ground state) for many molecular systems through the

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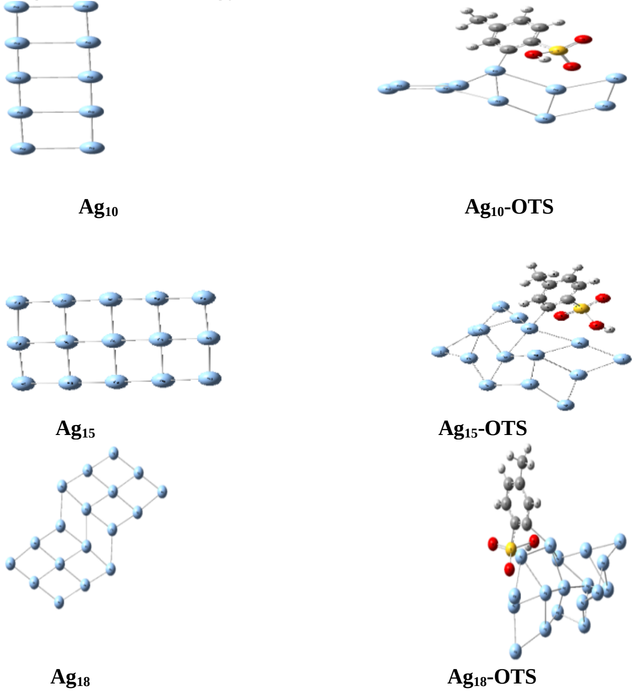
utilizing of sophisticated algorithms in the Gaussian 09 software [7-9]. DFT is used to calculate the electronic properties of systems with multiple molecules that are dependent on the electron density instate the wave function [10]. There are several researches that thoroughly discussed the calculations of density functional theory for solid state molecules and concluded that they agreed satisfactorily with practical data [11]. Applications for silver nanoparticles have been around for a while: [12] in 1897, "Collargol," a silver product with a mean silver particle size of 10 nm, was introduced to the medical market. Since then, nanosilver has been widely usage in a variety of products, including pigments, cameras, wound healing, composites that are conductive and antistatic, catalysts, and biocides. Silver nanoparticles are currently used in registered products primarily as biocide additives, algaecides, and disinfectants. These are the product categories for nanotechnology that are expanding the fastest [13]. Annually, more of silver nanoparticles are utilized in the industrial products [12]. Organic Tosylate(OTS) molecule used as adsorbate. Organic nanomaterials are drawing interest from a wide range of industries, including biotechnology, nanomedicine, and basic and clinical research. Organic nanomaterials have a wide range of uses, including image-guided therapy, pharmacological formulations, and molecular imaging [14]. The research aims to study the electronic properties, physisorption phenomena and charge transfer procedure, and then showing their importance in the electronic applications.

II.RESULTS AND DISCUSSION

One of the most well-known methodologies that have been used in solid state physics density functional theory (DFT). Density functional theory has been presented in two seminal papers in the sixties by Kohn-Sham and Hohenberg Kohn [15]. With density functional theory basis sets such as LANL2DZ and B3LYP. The basis set LANL2DZ means Los Alamos National Laboratory 2 Double Zeta, but the he basis set B3LYP means Becke three parameters Lee-Yang-Parr. Basis sets are a collection of the vectors that can be used to describe the atomic orbitals in which the molecular orbitals stand for the linear combination of atomic orbitals (LCAO). Density functional theory utilizes functionals in which a functional is a function of another function. Most of semi-empirical methods employ predefined basis sets, but Ab-initio methods and density functional theory calculations need determined basis sets. Geometry optimization procedure has been submitted to find out the results of ground state (stationary state) [16-19]. Geometry optimization seeks on the arrangement of the lowest energy of the molecular systems. The procedure begins at elementary geometry and continues to seek on new geometry. The procedure evaluates the forceeffect on each atom through calculating the gradient (first derivative) of energy in regard to positions of atoms in order to obtain rapid convergence to the geometry of the minimum energy. At the end step of the geometrical optimization the force resultant on each atom must equal to zero (stationary state). Actually the procedure geometry optimization stops when a stationary point at the potential surface had been find out. During the optimization the second derivative of energy in regard to the atomic positions had also used. Goals of geometrical optimization are find out the minimum structure, transition state structure and global minimum structure [20, 21].

A. *Molecular Geometry*

Geometry optimization is a procedure for finding the minimum energy composition, in which at the ending of the lowest energy geometry, the force acting on each atom will be zero, and the geometric parameters and optimization coordinates will be the optimum [22,23].Density functional theory (DFT) techniques had been used to determine the molecular structure for (Ag_{10}), (Ag_{15}), (Ag_{18}), (Ag_{10}-OTS) , (Ag_{15}-OTS) and (Ag_{18}-OTS) by utilizing Gaussian 09 software package algorithms at LANL2DZ, B3LYP level at the ground state energy.


Ag_{10} **Ag_{10}-OTS**

Ag_{15} **Ag_{15}-OTS**

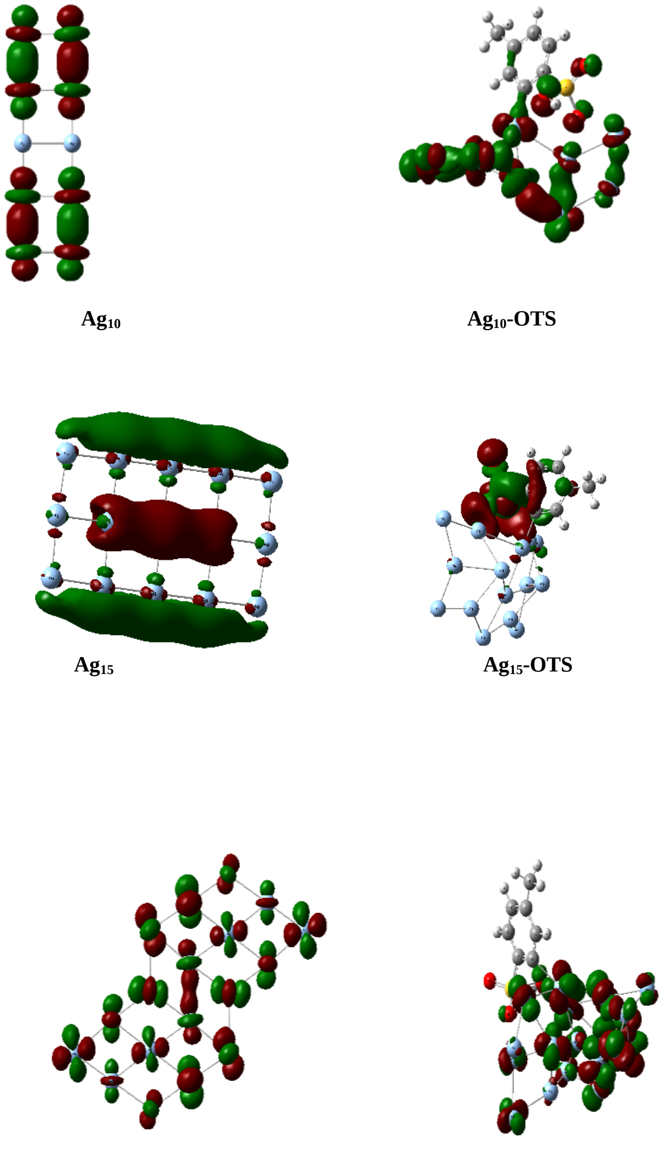
Ag_{18} **Ag_{18}-OTS**

Fig. 1: Molecular structure for (Ag_{10}), (Ag_{15}), (Ag_{18}), (Ag_{10}-OTS), (Ag_{15}-OTS) and (Ag_{18}-OTS).

Fig. 1 demonstrates the silver atoms with cyan color, carbon in dark lead color, oxygen in red color, sulfur in yellow color and eventually hydrogen in light lead color. The addition of organic molecules to the metal surface changes he geometry of the coinage metal (silver) and this is very clear through scan to change in the order of the atoms in the geometrical system, this new structure (pure silver-tosylate) due to the interaction between the organic molecule tosylate (OTS) and the coinage metal surface silver (Ag). Through visualization the pictures of the geometrical structures after physisorption process, it has been noted that the molecular geometry become quite dissimilar as a result to the interaction between the organic material (OTS) and the metallic surface. This scenario leads to new values of the geometrical dimension (bond lengths, bond angles and dihedral angles). Also physisorption phenomena impact tremendously to the symmetry of the geometrical structure, this can be observed apparently by making spot on the dissimilarity in symmetry in the pictures before and after the physisorption, just like the bigger difference in symmetry figure between (Ag_{18}) and (Ag_{18}-OTS).

B. Surfaces

After submitting the paradigm in Gaussian 09 codes and putting it through the geometrical optimization process using (MOs) order, the electrostatic potential surface produces high occupied molecular orbits and low unoccupied molecular orbits. The geometry optimization stops when stationary point is found at the potential surface [24, 25]. Gaussian 09 software package algorithms applied at LANL2DZ basis set, B3LYP to investigate the electrostatic potential at the ground state energy of (Ag_{10}), (Ag_{15}), (Ag_{18}), (Ag_{10}-OTS), (Ag_{15}-OTS) and (Ag_{18}-OTS).


Ag_{10} **Ag_{10}-OTS**

Ag_{15} **Ag_{15}-OTS**

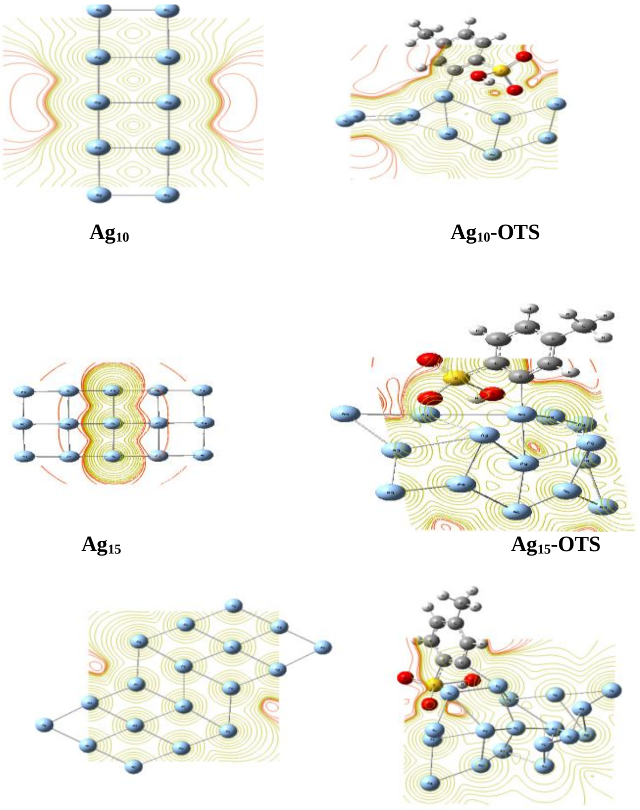
Ag_{18} **Ag_{18}-OTS**

Fig. 2: Electrostatic Potential for (Ag_{10}), (Ag_{15}), (Ag_{18}), (Ag_{10}-OTS) , (Ag_{15}-OTS) and (Ag_{18}-OTS).

Figure.2 Give a sight about the electronic charge distribution about the atoms in the electrostatic potential geometrical structures. The Gaussian 09 program's use of molecular orbitals theory, which stand for the linear combination of reactive atomic orbitals to produced HOMO and LUMO surfaces**.** The colors here may be interpret as the following, the green color denotes the positive wave function partition, but the red color points out to the negative partition of the wave function. As a result to the physisorption procedure between the nanomaterials (OTS) and the nanosilver surfaces ($Ag_{10,}$ Ag_{15} and Ag_{18}) molecular bonds of the type $(\sigma, \sigma^{*}, \pi, \pi^{*}, \delta$ and $\delta^{*})$ will be originate. The cause of origination the molecular bonds is the overlap between (s or p atomic orbitals) in the organic nanomaterials and (d atomic orbitals) in the silver nanosurface. The electrons or electron pairs will transfer from s or p orbitals in nano OTS to the d oribitals in the nanosilver. One can assert here the interaction will be between p atomic orbital of oxygen and d atomic orbital of nanosilver surface to formulate new orbitals of the type$(\pi, \pi^{*}, \delta$ and $\delta^{*})$.

C. Contours

The contours of the electronic density are used to characterize the electrostatic potentials forms. Occasionally, brillion zones are described by contour density maps. The electrostatic potential of a surface is sometimes described by its contours system. In the paradigm's geometry, it looks for active spots. Moreover, some studies use the contour term to describe how the space's electron density is distributed. Density of contour maps is very beneficial in the study of charge distribution, charge exchange and energy transfer mechanics [26]. Gaussian 09 software package algorithms submitted at LANL2DZ, B3LYP to investigate contour maps illustrations at the ground state energy of (Ag_{10}), (Ag_{15}), (Ag_{18}), (Ag_{10}-OTS) , (Ag_{15}-OTS) and (Ag_{18}-OTS).


Ag_{10} **Ag_{10}-OTS**

Ag_{15} **Ag_{15}-OTS**

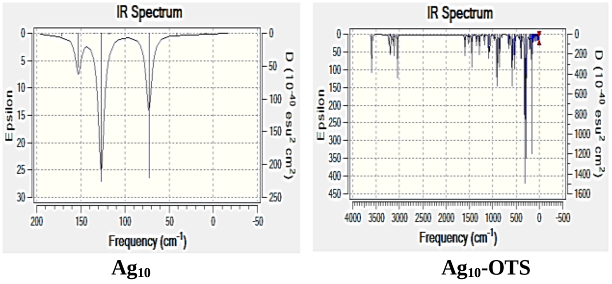
Ag_{18} **Ag_{18}-OTS**

Fig. 3: Charge density distribution for (Ag_{10}), (Ag_{15}), (Ag_{18}), (Ag_{10}-OTS) , (Ag_{15}-OTS) and (Ag_{18}-OTS).

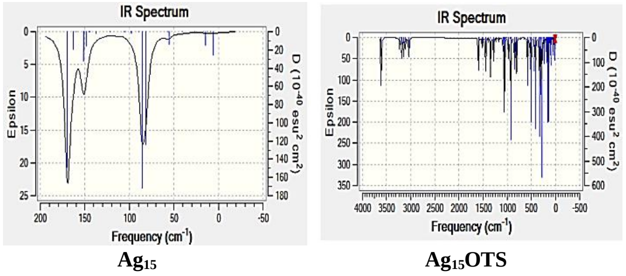
Fig.3 Epitomizes Brillion zones and so epitomizes electrostatic potentials surfaces of the pure silver nanosurfaces and hybrid geometrical nanostructures (Agn-OTS) , (n=10, 15, 18). Contour maps describe the distortion as a consequence of the resonance charge transfer between (OTS) and the surfaces of the pure silver metal. Charge transfer between some carbon atoms and (OTS) or between sulfur atoms and (OTS) or between oxygen atoms and (OTS). One can visualize very clear picture to the concentration of the charges in a common region near two carbon atoms and two silver atoms, the reasonable interpretation here is happening resonance charge transfer between the two nanocarbon atoms and the nanosilver atoms in the common high concentration charge region. Simplified comparison between the two figures (Ag_{15}) and (Ag_{15})-OTS disclosure that the charge distribution around the same silver atoms became dissimilar this point out possibility obtaining charge transfer from (OTS) atoms to some atoms in the silver surface. Studying contour density maps owns huge priority in the charge transfer mechanisms in surface physics just like resonance charge transfer and physisorption phenomena.

D. Infrared spectra

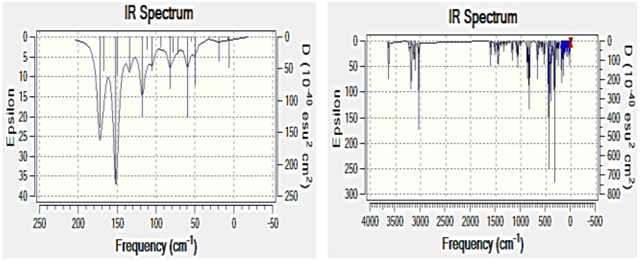
The infrared spectroscope explains how a material reacts with the infrared radiation. It expresses the symmetry or asymmetry of the vibration modes. When atoms with identical classes vibrate to produce the symmetric mode, but atoms with different classes vibrate to produce the asymmetric mode. The vibrational modes could be elastic and inelastic. Infrared spectroscopy is utilized to identify between the compounds through types of the active group. IR diagrams also determines the kinds bonds between the interacting atoms, in other words infrared spectra can be utilized to diagnose the geometrical structure [27]. Density functional theory (DFT) idea had been implemented to investigate the contour maps diagrams for (Ag_{10}), (Ag_{15}), (Ag_{18}), (Ag_{10}-OTS) , (Ag_{15}-OTS) and (Ag_{18}-OTS), at LANL2DZ basis set, B3LYP level at the ground state.by using Gaussian 09 software package.



Ag_{10} **Ag_{10}-OTS**



Ag_{15} **Ag_{15}OTS**



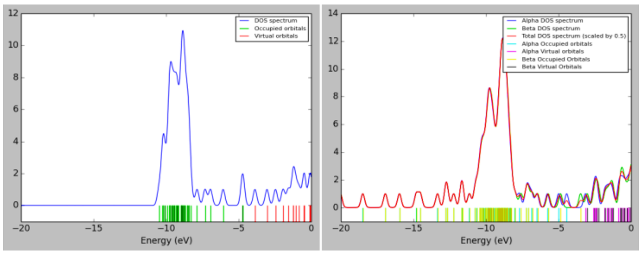
Ag_{18} **Ag_{18}-OTS**

Fig. 4: Infrared spectra schematics for (Ag_{10}), (Ag_{15}), (Ag_{18}), (Ag_{10}-OTS) , (Ag_{15}-OTS) and (Ag_{18}-OTS).

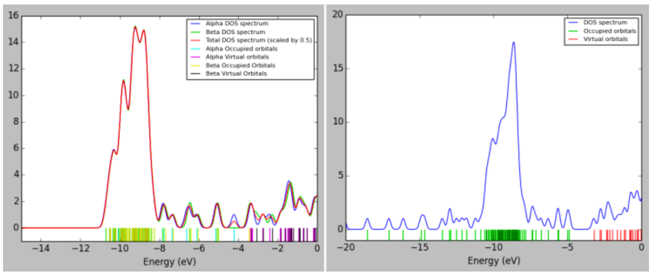
Fig. 4 Depicts effect of physisorption phenomena on the infrared spectra (IR). It can be seen there is disturbance and distortion in the diagrams of infrared spectra by holding simplified comparison between pure and hybrid geometrical structures. Physisorption procedure participates to originate new active regions as a result to the interaction between the organic nanomaterial (OTS) and coinage metal surfaces (Ag_{10}), (Ag_{15}), (Ag_{18}). Physisorption impact to both frequency (cm^{-1}) and intensity (km/mole), the frequency dissimilarity demonstrates apparently on $(x - \text{axis})$, but the intensity dissimilarity demonstrates on $(y - \text{axis})$. Let's make a modest comparison between (Ag_{10}) and (Ag_{10}-OTS) to note that the clear peaks for the geometrical structure (Ag_{10}) are in the domain (50) cm^{-1} to (200) cm^{-1}, while after happening physisorption procedure at the coinage metal surface new clear peaks demonstrate at the domain from (350) cm^{-1} to(1700)cm^{-1} and also at the domain from (3000) cm^{-1} to (3600)cm^{-1}. New bonds of the type (Ag-O), (Ag-S), (Ag-H) and (Ag-C) will emerge in the hybrid geometrical nanostructures (Ag_{10}-OTS), (Ag_{15}-OTS) and (Ag_{18}-OTS). From the other hand the intensity on $(y - \text{axis})$ does not exceed (38) cm^{-1} in the pure nanostructure (Ag_{18}), but the intensity increase clearly in the hybrid nanostructure, the geometrical nanostructure (Ag_{10}-OTS) has apparent peak at the intensity approximates to the value (350) cm^{-1}.

E. Density of states

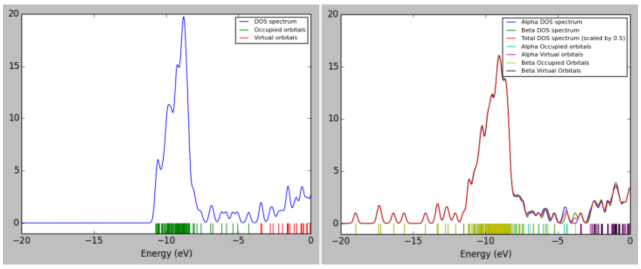
The density of states can be defined in solid state physics as the number of states that are allowed or occupied in quantum physics, the wave-like particles and waves can occupy states or situations with definite wavelengths the direction of propagation determine that only certain states will be allowed to be occupied by the electrons. The crystal geometry structure of the materials permits to the waves to propagate in a direction while it prevents the wave to propagate in other directions. Density of states can be investigated for photons, electrons, and phonons according to quantum physics principles. The electrons will occupy energy levels in the orbitals. The places of electrons in the energetic levels express quantum states. Studying the quantum states has huge importance in the physics of solids and physics of quanta [28-30].



Ag$_{10}$ **Ag$_{10}$-OTS**



Ag$_{15}$ **Ag$_{15}$OTS**



Ag$_{18}$ **Ag$_{18}$-OTS**

Fig. 5: Density of States for (Ag$_{10}$), (Ag$_{15}$), (Ag$_{18}$), (Ag$_{10}$-OTS) , (Ag$_{15}$-OTS) and (Ag$_{18}$-OTS).

Fig. 5 Illustrates density of states of the pure and hybrid geometrical nanostructures. The distance between valence band and conduction band stands for band gap in (eV). The geometrical nanostructure (Ag$_{10}$-OTS) , (Ag$_{15}$) and (Ag$_{18}$-OTS) have two types of orbitals alpha (α) and beta (β) but (Ag$_{10}$) , (Ag$_{15}$-OTS) and (Ag$_{18}$) have only alpha (α) orbitals, hence one can say (Ag$_{10}$-OTS) , (Ag$_{15}$) and (Ag$_{18}$-OTS) have anti-ferromagnetic properties. Some geometrical nanostructure acquire anti-ferromagnetic properties after occurring the physisorption, they are (Ag$_{10}$-OTS) and Ag$_{18}$-OTS), but the geometrical nanostructure (Ag$_{15}$-OTS) losses the anti-ferromagnetic characteristic. Electrons will transfer from the orbital p in sulfur , oxygen or carbon to empty d orbital in the coinage metal surface because of the physisorption procedure between the organic geometrical nanostructure (OTS) and coinage metal surfaces (Ag$_{10}$) , (Ag$_{15}$) and (Ag$_{18}$). A modest counter-posing between (Ag$_{10}$) and (Ag$_{10}$.OTS) shows the increasing in density of state value from the value (11) to the value (12). The comparison between (Ag$_{18}$) and (Ag$_{18}$-OTS) shows the decreasing in the value of density of state from the value (20) to the value (16). The new values of the density of states point out new energetic levels at the coinage metal surface can be occupied by electrons. Electronic states and Energy gap (Eg)

F. Electronic state and Energy gap (Eg)

High-occupied molecular orbitals (HOMO) and low-unoccupied molecular orbitals (LUMO) are two abbreviations that stand for the most crucial electronic states for the existence of the electrons in molecular orbitals; they are examples of relevant terminologies for energy gaps, through values of them, the value of energy gap can be determined. The energy gap (Eg) is also derived from the difference in energy between two electrical levels that the equation has established [31].

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

TABLE 1. ILLUSTRATES HOMO, LUMO ENERGIES AND ENERGY GAPS (EG) FOR (AG$_{10}$), (AG$_{15}$), (AG$_{18}$), (AG$_{10}$-OTS) ,(AG$_{15}$-OTS) AND (AG$_{18}$-OTS).

System	HOMO(eV)	LUMO(eV)	E_g(eV)
Ag $_{10}$	-4.698622	-3.86844	0.83017
Ag $_{15}$	-4.21183	-3.3849	0.82691
Ag $_{18}$	-4.29264	-3.46165	0.83099
Ag $_{10}$.OTS	-4.42924	-3.13812	1.29111
Ag $_{15}$-OTS	-4.90705	-3.22356	1.68348
Ag $_{18}$-OTS	-4.8428358	-3.1620741	1.6807617

Table 1. Summarizes the values of HOMO , LUMO and energy gaps (E$_g$). HOMO energy is frequently connected with tendency of the geometrical structure to donate electrons; a high value of HOMO energy suggests a high propensity to donate electrons. Whereas LUMO energy is linked to the tendency of the geometrical structure to accept electrons, a small value of LUMO denotes to a strong propensity of the geometrical structure to take electrons. It is known that silver (Ag) is a conductor material as bulk material, in the table all values of energy gap for pure silver structures are values of semiconductor materials, all of them approach to the value of (E$_g$) for germanium. Therefore one can say simulation of silver (Ag) in nano dimensions make it semiconductor as compared with the bulk. The values of energy gaps of all hybrid nanostructures are in the range of semiconductor. This property i.e. semiconductor credit appends biggest importance in the electronic devices just like, solar cells , sensors and laptop parts. In order to cross the electrons from the valence band to the conduction band, it ought to have energy equal to or greater than the band gap, the electrons occupy an empty place (a hole) in the conduction band. The electrons are constraint to Fermi-Dirac statistics and Pauli's exclusion principle.

G. Ionization potential and electron affinity

The lowest amount of energy that required eliminating an electron from a molecule structure or an atom in the gaseous state can be estimated from the ionization energy or ionization potential of a molecule or an atom.

Electron affinity can be expressed by the modification in the potential energy of the atom (in the neutral state) in the gaseous phase, i.e. electron will be yield to an atom in order to formation a negative ion , so one can express as the probability that the atom will gain electron. Koopman suggest the following math relations for the ionization potential and electron affinity [32].

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

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

TABLE 2. ILLUSTRATES IONIZATION ENERGY AND ELECTRON AFFINITY FOR (AG_{10}), (AG_{15}), (AG_{18}), (AG_{10}-OTS) , (AG_{15}-OTS) AND (AG_{18}-OTS).

system	*I.P(*eV)	*E.A*(eV)
Ag_{10}	4.6986228	3.8684457
Ag_{15}	4.2118359	3.384924
Ag_{18}	4.2926496	3.4616562
Ag_{10}-OTS	4.4292438	3.1381293
Ag_{15}-OTS	4.9070514	3.2235687
Ag_{18}-OTS	4.8428358	3.1620741

Table 2. Summarizes the values of ionization potentials and electron affinities for the pure silver nanostructures and the hybrid silver nanostructures. The minimum value of ionization potential belongs to the nanostructure Ag_{15}, it is approximately (4.211 eV). Therefore, the electrons in the nanostructure (Ag_{15}) needs the lowest value of energy to break free the surface, hence physisorption procedure make it has the best value of ionization potential in the table. Also one can assert that the nanostructure (Ag_{15}) needs the minimum energy to become cation. Ionization potential connects to the released energy when an atom endows electron from HOMO. The maximum value of electron affinity belongs to the pure nanostructure (Ag_{10}), it is approximately (3.87 eV), therefore the electrons in the pure nanostructure (Ag_{10}) can be regarded the finest nanostructure to accept the electrons among all pure and hybrid nanostructures in the table. The electron affinity connects to the released energy when an electron occupies LUMO. Physisorption procedure impact randomly to those two electronic characteristics, this takes place because many factors, just like, geometrical parameters, topological coordinates, symmetry and the geometrical structure. Values of the two characteristics ionization potential and electron affinity is very advantageous, they contribute actively to achieve the calculations of hardness, chemical potential, electro-philicity and softness.

H. *Dipole moment*

The definition of dipole moment clarifies presence of two charges have dissimilar signals but the charges have the same value. The first who attempts to study dipoles was the physics scientist Peter Debye, so that the dipole moment unit takes the name Debye. The dipole moment is probably to be induced or permanent. Dipole moment does not emerge in the homonuclear systems, but in the heterogeneous molecules the dipole moment will appears. If the direction of displacement changes, the dipole moment will change. The dipole moment can be given by the equation below [33].

$$P = q * r \qquad (4)$$

TABLE 3. ILLUSTRATES DIPOLE MOMENT FOR (AG_{10}), (AG_{15}), (AG_{18}), (AG_{10}-OTS) , (AG_{15}-OTS) AND (AG_{18}-OTS).

System	Dipole moment (Debye)
Ag_{10}	0
Ag_{15}	0
Ag_{18}	0.008
Ag_{10}-OTS	2.1088
Ag_{15}-OTS	3.2475
Ag_{18}-OTS	6.24

Table 3. Summarizes the numerical values of dipole moments in Debye unit for the pure silver nanostructures and the hybrid silver nanostructures. The dipole moment for the geometrical nanostructures (Ag_{10}) and (Ag_{15}) is equal to zero, the dipole moment of the geometrical nanostructure (Ag_{18}) is very small, it approximates to zero, those zero values and none-zero values of dipole momentbecause they are homonuclear nanostructure. Because those homonuclear nanostructures do not possess dipole moments vary through the rotation, they do not give rotational spectrums. In the table one can find out dissimilar values of dipole moment of the hybrid nanostructures, many physical and geometrical factors cause this is dissimilarity in the values of dipole moments of the hybrid nanostructures, just like, physisorption, topological dimensions (x, y, z) and the geometrical parameters dihedral angles and bond angles. The geometrical nanostructure (Ag_{18}-OTS) stands for the highest value of dipole moment nanostructure among all hybrid and pure nanostructures in the table, it has the value (6.24 Debye). Dipole moment feature stands for public scale of the bonding characteristics and charge density distribution in the chemical nanostructure.

I. *Polarizability*

The term polarizability gives an apparent picture about the capacity of the molecule to become polarized. The term polarizability is also an expression of the linear response of the electron density in the presence of an infinite electric field F. Mathematically and in terms of the second partial derivative of energy one can describe the polarizability by the following equation [34].

$$\alpha = -\left(\frac{\partial^2 E}{\partial F_a \partial F_b}\right)_{a,b} = x, y, z \qquad (5)$$

$< \alpha >$ Typifies the polarizability mean, and it may be calculated mathematically by the equation

$$< \alpha > = \frac{1}{3}(\alpha xx + \alpha yy + \alpha zz) \qquad (6)$$

The symbols α_{xx}, α_{yy} and α_{zz} point out the polarizability tensor eigen values.

TABLE 4 . ILLUSTRATES POLARIZABILITIES FOR (AG_{10}), (AG_{15}), (AG_{18}), (AG_{10}-OTS) , (AG_{15}-OTS) AND (AG_{18}-OTS).

System	α_{xx}	α_{yy}	α_{zz}	$< \alpha >$
Ag_{10}	465.472	1470.132	232.379	722.661
Ag_{15}	310.114	919.720	1763.924	997.919
Ag_{18}	1986.522	1343.787	353.326	1227.878
Ag_{10}-OTS	1090.573	610.697	425.021	708.763
Ag_{15}-OTS	1287.891	1021.554	525.879	945.108
Ag_{18}-OTS	1069.580	888.277	843.517	933.791

The table 4. Shows the eigen values of polarizabilities (α_{xx}) , (α_{yy}) , (α_{zz}) and the average polarizability $< \alpha >$ of the pure silver nanostructures and hybrid silver nanostructures. The pure nanostructure (Ag_{18}) have the maximum numerical value of average polarizability $< \alpha >$ among all nanostructure in the table, it has the numerical value ($< \alpha >$ =1227.8783 a.u), so that (Ag_{18}) is the maximum activity among them. One can observe in the table how the physisorption procedure on the values of average polarizability, it leads to decrease in the values of average polarizability. The maximum numerical value of eigen value of the polarizability tensor α_{xx} is for the geometrical nanostructure (Ag_{18}) , it equals to (1986.522 a.u), the maximum numerical value of eigen value of the polarizability tensor α_{yy} is for the geometrical nanostructure (Ag_{10}) , it equals to (1470.132 a.u), but the maximum numerical value of eigen value of the polarizability tensor α_{zz} is for the geometrical nanostructure (Ag_{15}) , it equals to (1763.924 a.u). Polarizability deems intriguing merit in physics because it yields information over internal structure and electric dipole moment of the geometrical nanostructures. Polarizability merit is also intriguing in the nonlinear optics science.

J. Symmetry

Comprehension of symmetry can be understood through the repetition procedure or correspondence of partitions of a geometrical figure about a point, an axis or a surface. As a counter-piece between the cube and sphere, the cube sounds less symmetry, the cube repeats itself at certain angles, while the sphere sounds the same after the rotation with any angle. There are three symmetry operations; they are rotation, inversion and reflection. The point groups symmetries (E , Cn , σ_h , σ_v , σ_d , S_n and i) are the symmetry elements that correspond the procedures of symmetry tabulated in molecular chemistry and physics textbooks [35].

TABLE 5. ILLUSTRATES SYMMETRIES FOR (AG_{10}), (AG_{15}), (AG_{18}), (AG_{10}-OTS) , (AG_{15}-OTS) AND (AG_{18}-OTS).

System	Point group symmetry
Ag_{10}	D_{2h}/ C_1
Ag_{15}	D_{2h}/C_1
Ag_{18}	C_{2h}/C_1
Ag_{10}-OTS	C_1
Ag_{15}-OTS	C_1
Ag_{18}-OTS	C_1

Table 4. Summarizes three classes of point group symmetries, the first class is (D_{2h}/C_1) for the geometrical nanostructure (Ag_{10}) and the geometrical nanostructure (Ag_{15}) , the second class is (C_{2h}/C_1) for the geometrical nanostructure (Ag_{18}) , the third class (C_1) for the geometrical nanostructures (Ag_{10}-OTS) , (Ag_{15}-OTS) and (Ag_{18}-OTS) consecutively. Physisorption of (OTS) on the surfaces of (Ag_{10}) , (Ag_{15}) and (Ag_{18}) makes all those geometrical nanostructure of the type of point group symmetry (C_1) , one can put it the twirl will be with an angle (360^o /n), (n=1) , so that the geometrical nanostructures (Ag_{10}-OTS) , (Ag_{15}-OTS) and (Ag_{18}-OTS) will be repeating itself over (360^o). The geometrical nanostructures (Ag_{10}) and (Ag_{15}) have horizontal mirror plane (σ_h) and they have two fold axes vertical to (Cn), the reason here is , they have the point group symmetry (D_{2h}/C_1). The geometrical nanostructure (Ag_{18}) has horizontal mirror plane because it has the point group symmetry (C_{2h}), also the twirl in this nanostructure will be with an angle (360^o /n), (n=1) , the repetition will be over (360^o) in this nanostructure. Symmetry study is intriguing, it gives conclusions concerning the molecular structure merits wanting holding calculations, just like dipole moment and degenerate states. Symmetry is beneficial in study of optical activity merit.

III. CONCLUSIONS

Physisorption phenomena impact tremendously to the symmetry of the geometrical structure. The bigger difference in symmetry figure between (Ag_{18}) and (Ag_{18}-OTS) explain this. The interaction between p atomic orbital of oxygen and d atomic orbital of nanosilver surface produce new orbitals of the type (π , π^* , δ and δ^*) . Comparison between charge distributions in (Ag_{15}) and (Ag_{15}-OTS) point out possibility obtaining charge transfer from (OTS) atoms to some atoms in the silver surface. New bonds (Ag-O), (Ag-S) , (Ag-H) and (Ag-C) originate in the hybrid geometrical nanostructures (Ag_{10}-OTS) , (Ag_{15}-OTS) and (Ag_{18}-OTS). The geometrical nanostructures (Ag_{10}-

OTS) , (Ag_{15}) and (Ag_{18}-OTS) have two types of orbitals alpha (α) and beta (β) but (Ag_{10}) , (Ag_{15}-OTS) and (Ag_{18}) have only alpha (α) orbitals, hence one can say (Ag_{10}-OTS) , (Ag_{15}) and (Ag_{18}-OTS) have anti-ferromagnetic properties. Pure silver (Ag) had energy gap in the range of semiconductor materials as compare with bulk silver which has conductor materials one can conclude in nano dimensions silver convert from conductor to semiconductor. And this is intriguing in the electronic devices just like, solar cells, sensors and laptop pieces. The ionization potential nanostructure (Ag_{15}) is the minimum, it is approximately (4.211 eV). Therefore the electrons in the nanostructure (Ag_{15}) needs the lowest value of energy to break free the surface, one can put it physisorption procedure make it has the best value of ionization potential, it needs the minimum energy to become cation. The pure nanostructure (Ag_{10}) has the maximum electron affinity , it is approximately (3.87 eV) , the electrons in the pure nanostructure (Ag_{10}) can be regarded the finest nanostructure to accept the electrons among all pure and hybrid nanostructures. The geometrical nanostructure (Ag_{18}-OTS) has the highest value of dipole moment among all hybrid and pure nanostructures in the table; it has the value (6.24 Debye). The pure nanostructure (Ag_{18}) have the maximum numerical value of average polarizability $< \alpha >$ among all nanostructure in the table, it has the numerical value ($< \alpha >$ =1227.8783 a.u), so that (Ag_{18}) is the maximum activity among them. Physisorption of (OTS) on the surfaces of (Ag_{10}), (Ag_{15}) and (Ag_{18}) makes all those geometrical nanostructure of the type of point group symmetry (C_1), Symmetry is intriguing in study of optical activity merit.

CONFLICT OF INTEREST

Authors declare that they have no conflict of interest.

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