



## Theoretical study of physisorption of tosylate on $Au_{10}$ , $Au_{15}$ and $Au_{18}$ surfaces utilizing DFT approach

## Estudio teórico de la fisisorción de tosilato en superficies $Au_{10}$ , $Au_{15}$ y $Au_{18}$ utilizando el enfoque DFT

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### ABSTRACT

Charge transfer from organic nanomaterial to the coinage metal surfaces occur as a result to the physisorption phenomena. Physisorption plays a major role in many applications. A set of properties such as, molecular geometries, contour density maps, electrostatic potentials (ESPs), infrared spectra (IR), electronic states, HOMO and LUMO energies, Energy gaps (Eg), ionization potential (I.P), electron affinity (E.A), dipole moment, polarizabilities  $\alpha_{xx}$ ,  $\alpha_{yy}$  and  $\alpha_{zz}$ , average polarizability  $\langle \alpha \rangle$ , symmetry and density of states by using Gaussian 09 software package algorithms were investigated at LANL2DZ, B3LYP and the ground state energy of ( $Au_{10}$ -OTS), ( $Au_{15}$ ), ( $Au_{15}$ -OTS), ( $Au_{18}$ ) and ( $Au_{18}$ -OTS), but the structure of ( $Au_{10}$ ) has been submitted at LANL2MB, B3LYP basis sets. The research study physisorption phenomena from the organic nanomaterial to sylate (OTS) to the coinage metal surface (gold surfaces), also the research concentrate if charge transfer procedure gets at the surface. Physisorption phenomena and charge transfer procedure that happen at the surface can be known throughout some properties such as the closed energy contour maps, electrostatic potentials, symmetry and density of states. Electronic states and energy gap property have been studied in this research to recognize importance of the geometrical structures in the electronic devices and the different electronic applications in different branch of knowledges. The research had the ionization potential and electron affinity credits to demonstrate if the geometrical structure will behave as a donor or an acceptor because the ionization energy demonstrate ability of the geometrical structure to donate the electrons in an interaction, but the electron affinity describes the capacity of the geometrical structure to accept electrons in an interaction.

**Keywords:** Physisorption, DFT, DOS, Symmetry, Polarizability, Electrostatic Potential, Energy gap.

### RESUMEN

La transferencia de carga desde los nanomateriales orgánicos a las superficies de metales preciosos ocurre como resultado del fenómeno de fisisorción. La fisisorción desempeña un papel importante en muchas aplicaciones. Se investigaron un conjunto de propiedades, como geometrías moleculares, mapas de densidad de contorno, potenciales electrostáticos (PE), espectros infrarrojos (IR), estados electrónicos, energías HOMO y LUMO, brechas de energía (Eg), potencial de ionización (I.P), afinidad electrónica (E.A), momento dipolar, polarizabilidades  $\alpha_{xx}$ ,  $\alpha_{yy}$  y  $\alpha_{zz}$ , polarizabilidad promedio  $\langle \alpha \rangle$ , simetría y

densidad de estados utilizando algoritmos del paquete de software Gaussian 09 con bases LANL2DZ y B3LYP. Se investigó la energía del estado fundamental de (Au10-OTS), (Au15), (Au15-OTS), (Au18) y (Au18-OTS), pero la estructura de (Au10) se ha presentado con bases LANL2MB y B3LYP. El estudio de investigación aborda el fenómeno de la fisorción desde el nanomaterial orgánico hasta el silano (OTS) en la superficie de metal precioso (superficies de oro), y se concentra en si ocurre un procedimiento de transferencia de carga en la superficie. Los fenómenos de fisorción y el procedimiento de transferencia de carga que ocurren en la superficie se pueden conocer a través de algunas propiedades, como los mapas de contorno de energía cerrada, los potenciales electrostáticos, la simetría y la densidad de estados. Se estudiaron los estados electrónicos y la propiedad de la brecha de energía en esta investigación para reconocer la importancia de las estructuras geométricas en los dispositivos electrónicos y las diferentes aplicaciones electrónicas en diversas ramas del conocimiento. La investigación incluyó el potencial de ionización y la afinidad electrónica para determinar si la estructura geométrica se comportará como donante o aceptor, ya que la energía de ionización demuestra la capacidad de la estructura geométrica para donar electrones en una interacción, mientras que la afinidad electrónica describe la capacidad de la estructura geométrica para aceptar electrones en una interacción.

**Palabras claves:** Fisorción, DFT (Teoría de la Funcional Densidad), DOS (Densidad de Estados), Simetría, Polarizabilidad, Potencial Electrostático, Brecha de Energía.

## 1. INTRODUCCIÓN

The interaction of molecules and organic materials with metal surfaces is a topic of great interest in both basic science and technology (Hoppe & Sariciftci, 2004). Moreover, there are significant commercial uses for comprehending the interactions of an aromatic adsorbate with a metallic surface (Stanislaus & Cooper, 1994). Organic thin-film devices, such as transistors, light-emitting diodes, and organic photovoltaic cells are depending on the cooperative qualities of the contacting interface between organic molecule semiconductors and metallic substrates (Kronik et al., 2010; Tseng et al., 2010). In order to design the features and quality of these devices, it is critical to precisely account for the many types of interaction and to forecast interface structure and stability (Pai et al., 2010; Ruiz et al., 2012). Density functional theory (DFT) has becoming more widely used to study molecule adsorption on metal surfaces (Wellendorff et al., 2010). Density functional theory has successfully demonstrated its utility in characterizing a variety of strongly interacting systems employing exchange and correlation (XC) functionals within the generalized gradient approximation (GGA) including those involving adsorption on surfaces of transition and noble metals (J. K. Nørskov, T. Bligaard, 2009; Kohn et al., 1996; Neurock, 2003). Density Functional theory use the density function rather than the wave function to calculate electronic characteristics (Grimme, 2006). In 1998, John Boyle and Walter Kohn were awarded Nobel Prize in Chemistry for being they developed the DFT theory mathematically based on the principles of quantum mechanics (Anandakumar & Umamaheswari, 2017). In DFT the evaluations agree quite satisfactorily with the experimental values (Brown, 1967b). Gold surface atoms have been used as adsorbent in recent years, golden nucleonic particles have attracted great attention due to their quantitative properties and small size, leading to a wide range of potential applications as catalysts and molecular devices compared to their counterparts of large molecules, the reason for this is that the physical and chemical properties of Au NPs, they are greatly affected by their shape, size and spatial arrangement (Soydaner, 2012). Organic Tosylate molecule used as adsorbate, organic molecules can easily be modified chemically and possess semiconductor features, such as electron structure and charge transport. When one make a comparison to other semiconductors and inorganic metals, organic semiconductors stand out because they do not develop dielectric oxide on their surface when exposed to air, which allows operating systems to build clean destinations with materials. Metals and other operating systems, for example, since 2000 , as insulators, electromagnets, and biological organisms become more important to the operation of organic electronic devices, interest in the interfaces that govern the intertransfer of electrons and ions as well as the operation of organic electronic devices as a whole is growing. (Hofmann et al., 2021).

Physisorption phenomena is sometimes called physical adsorption, The adsorption of the atoms and molecules on the surfaces of solid states ( i.e. physisorption ) originates at the surface because of the interaction force between the atom or molecule with the metal surface.

### 1.1. Molecular Geometry

Molecular Geometry is an important factor for determining the properties of molecules, as it plays an important role for determining the magnetic properties, polarization and some other properties of the molecule. After submitting, the geometrical structure gives the optimized geometrical arameters like bond lengths, bond angles and dihedral angles, they are governed by the principles of quantum mechanics (Devi & Umamaheswari, 2020). Gaussian 09 software package algorithms were employed at LANL2DZ, B3LYP to investigate the molecular structure at the ground state energy of ( $\text{Au}_{10}$ -OTS), ( $\text{Au}_{15}$ ), ( $\text{Au}_{15}$ -OTS), ( $\text{Au}_{18}$ ) and ( $\text{Au}_{18}$ -OTS), but the structure of ( $\text{Au}_{10}$ ) has been submitted at LANL2MB, B3LYP basis sets.

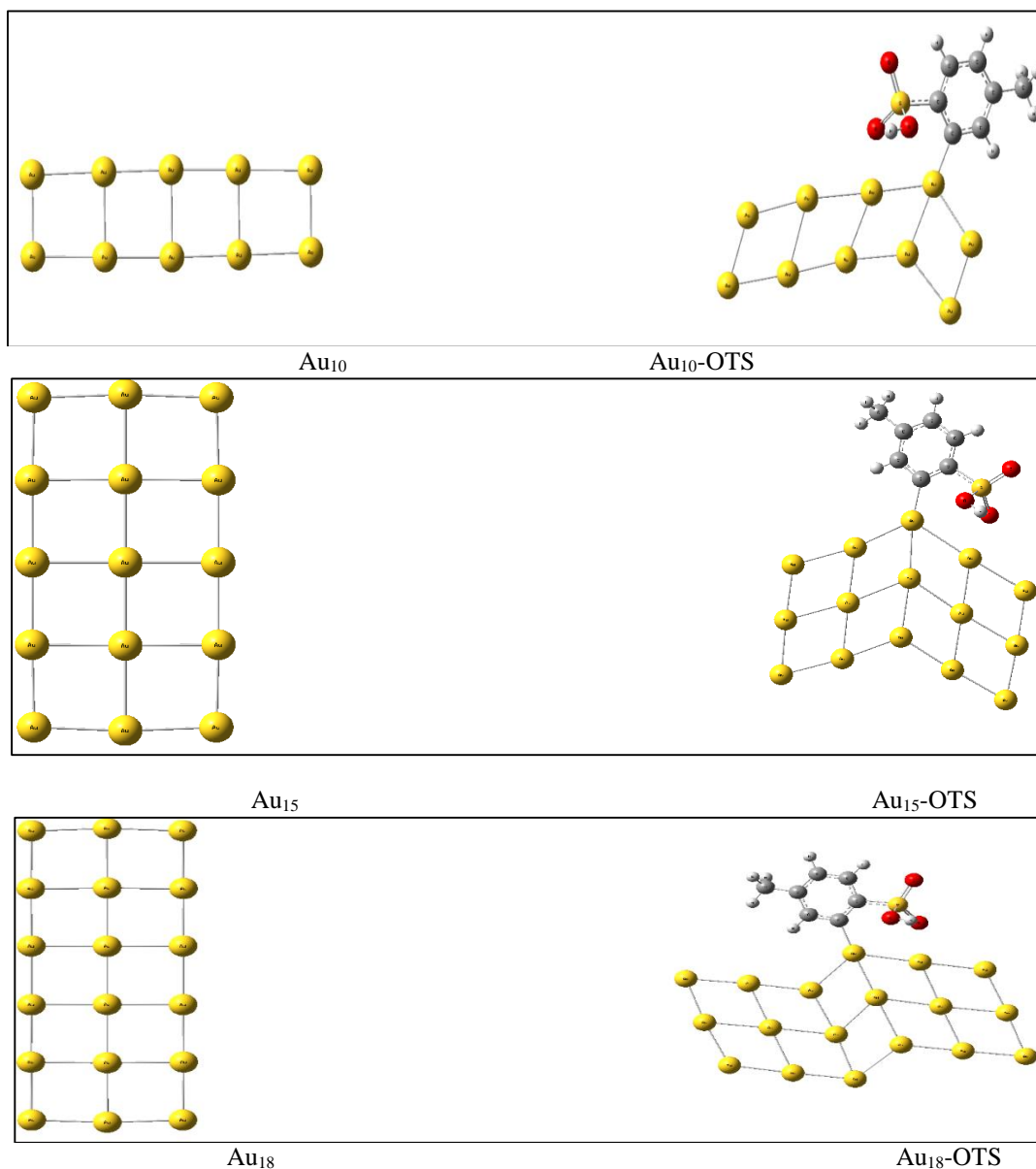
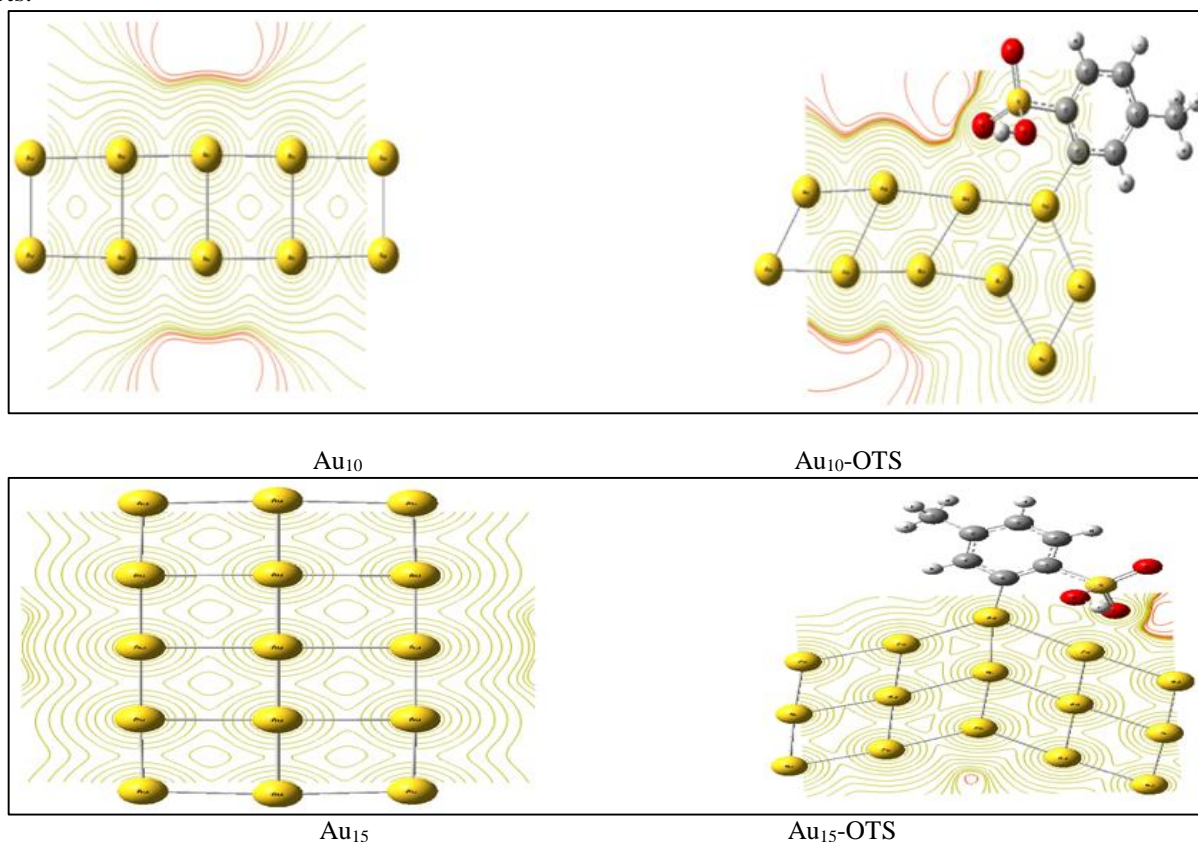


Figure 1. Molecular structure for ( $\text{Au}_{10}$ ), ( $\text{Au}_{10}$ -OTS), ( $\text{Au}_{15}$ ), ( $\text{Au}_{15}$ -OTS), ( $\text{Au}_{18}$ ) and ( $\text{Au}_{18}$ -OTS).

Figure (1) demonstrates atoms in yellow color indicates to the atoms of the surface of gold. The atoms of organic material it contains four types of different atoms, where hydrogen appears in light gray and carbon in dark gray color, and there are three atoms of oxygen in red and finally one atom of sulfur in yellow color. The figure clarify physisorption of tosylate (OTS) on the golden surfaces and charge exchange between the organic material (OTS) and the surfaces of gold ( $Au_{10}$ ) surface, ( $Au_{15}$ ) surface and ( $Au_{18}$ ) surface. The interaction between the organic material leads to new values of the geometrical parameters (bond lengths, bond angles and dihedral angles). Simplification comparison between ( $Au_{15}$ ) and ( $Au_{15}$ -OTS) gives a clear picture around impact of physisorption phenomena to the geometrical structure. It is very apparent that the physisorption gives new symmetry for ( $Au_{15}$ -OTS) differs from the structure ( $Au_{15}$ ).

## 1.2. Contours

The closed curved geometries (energy contours) can be used to identify the Fermi surface. Contour maps concept can also depict the electrical charge distribution around atoms, it is appropriate here to say that charge density or concentrations near atoms are described by contours. The contour problem can also give a description interpret charge transfer and charge exchange between the interacting materials (Alwan & Talib, 2021; Jones et al., 1991). Gaussian 09 software package algorithms were employed at LANL2DZ, B3LYP to investigate the contours at the ground state energy of of ( $Au_{10}$ -OTS), ( $Au_{15}$ ), ( $Au_{15}$ -OTS), ( $Au_{18}$ ) and ( $Au_{18}$ -OTS), but of the structure of ( $Au_{10}$ ) it has been submitted at LANL2MB,B3LYP basis sets.



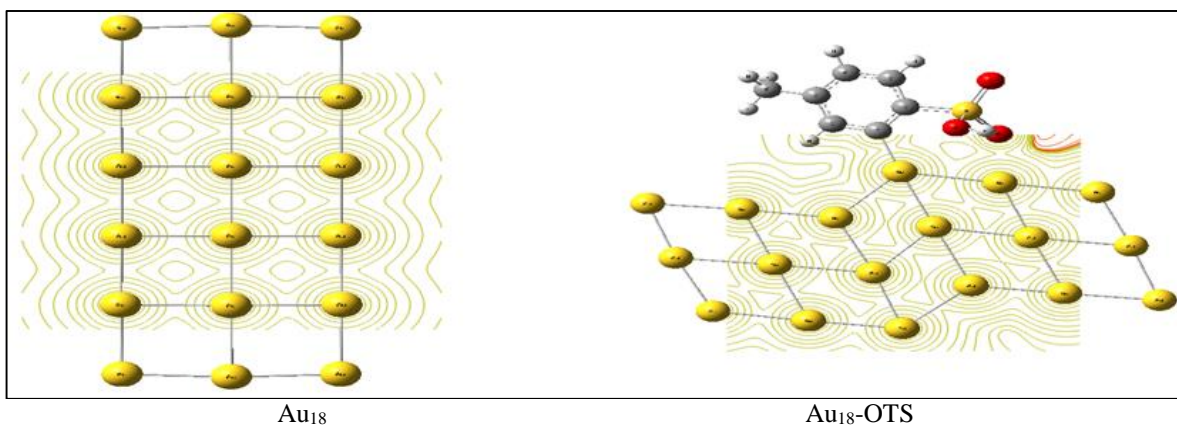
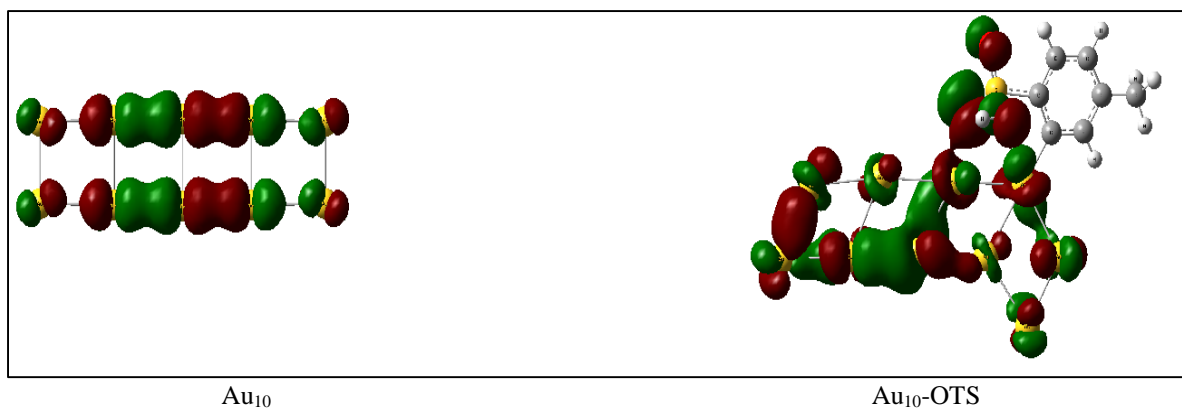


Figure 2. Contour energy maps for (Au<sub>10</sub>), (Au<sub>10</sub>-OTS), (Au<sub>15</sub>), (Au<sub>15</sub>-OTS), (Au<sub>18</sub>) and (Au<sub>18</sub>-OTS).

One can visualize in figure (2) contour maps which gives the interaction behavior and signs locations of strong physisorption, in the figure of (Au<sub>10</sub>-OTS) the strong interaction near some gold atoms and some of the oxygen atoms. The distortion in shape of energy contour maps can describe Fermi surface, Fermi surface is very beneficial in the explanation some physical phenomena, especially in solid state physics, like electronic properties. A simple comparison between (Au<sub>15</sub>) and (Au<sub>15</sub>-OTS) clarify that charge concentration increase near one of the oxygen atoms and some gold atoms, here one can see apparently physisorption (OTS) on (Au<sub>15</sub>) surface, i.e. (Au<sub>15</sub>-OTS) interaction draw new contour map different pretty much tremendously from the contour map of the pure gold surface (Au<sub>15</sub>). Contour maps give an apparent sight around the disinformation as a result to charge transfer and charge exchange. So, in the geometrical structure (Au<sub>18</sub>-OTS) one can find that physisorption procedure gets between oxygen atom and gold surface.

### 1.3. Electrostatic Potential (ESP)

The fundamental tenet of the molecular orbital theory is that molecular orbitals can be constructed by combining several atomic orbitals. In order to create molecular orbitals. After achieving the optimization geometry, high occupied orbitals and low unoccupied orbitals can be visualized and updated by selecting MOs in Gaussian 09, which depict picture of the surface by utilizing the Gauss View 05 program, here one can put it Gaussian 09 algorithms find a stationary point at the potential surface (Alwan & Talib, 2021; Frisch et al., 2009). Gaussian 09 software package algorithms were employed at LANL2DZ, B3LYP to investigate the electrostatic potential (ESP) at the ground state energy of (Au<sub>10</sub>-OTS), (Au<sub>15</sub>), (Au<sub>15</sub>-OTS), (Au<sub>18</sub>) and (Au<sub>18</sub>-OTS), but of the structure of (Au<sub>10</sub>) it has been submitted at LANL2MB, B3LYP basis sets.



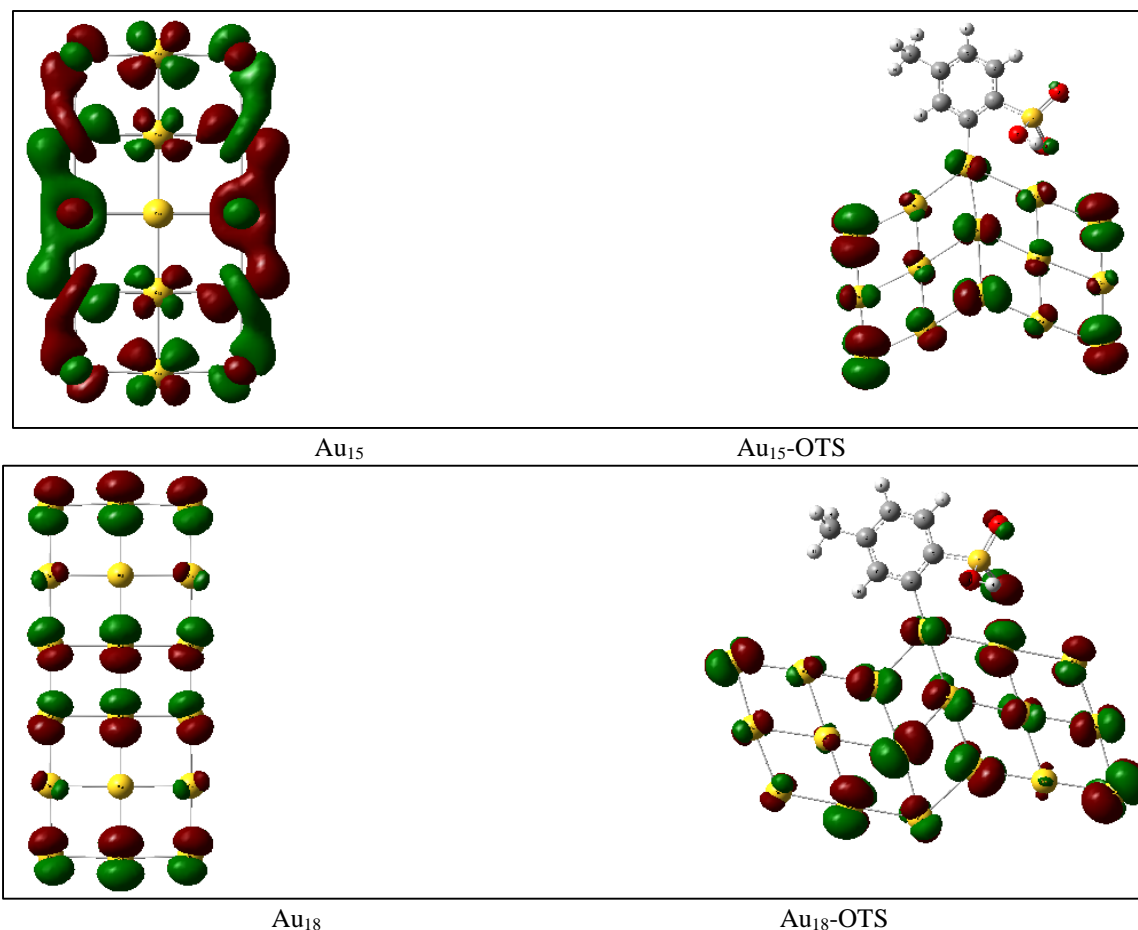


Figure 3. Electrostatic Potential for  $(Au_{10})$ ,  $(Au_{10-OTS})$ ,  $(Au_{15})$ ,  $(Au_{15-OTS})$ ,  $(Au_{18})$  and  $(Au_{18-OTS})$ .

In figure (3) one can note clear pictures to the charge distribution around atoms in pure and hybrid geometrical surfaces. It is possible to compare  $(Au_{15})$  with  $(Au_{15-OTS})$  to discover that new type of symmetry is caused by physisorption, Also charge distribution around gold atoms in  $(Au_{15})$  differ from charge distribution around same gold atoms in  $(Au_{15-OTS})$  because of the resultant distortion in potential surface because of the interaction. In the geometrical surface  $(Au_{18})$  charge distribution about all gold atoms except two gold atoms, but in the geometrical structure  $(Au_{18-OTS})$  and because of the physisorption between the organic material and the surface one can visualize charge concentration is about all oxygen atoms and one hydrogen atom, here one can interpret the new charge concentration positions as a result to the interaction between the organic material with the metal surface ( the gold here). Physisorption of OTS on  $(Au_{10})$  surface changes the geometrical map dramatically , this point out the strong physisorption of tosylate atoms on the gold surface among all hybrid (gold-tosylate) interactions.

## 2. RESULTS AND DISCUSSION

### 2.1. Infrared Spectra (IR)

Symmetric vibration and asymmetrical vibration can be classified as extended vibrations .Symmetric oscillation occurs when identical atoms oscillate at the same phase, but asymmetric expansion occurs when bonds vibrate in a different phase (Abdulzahra & Abbood, 2014). Vibrational frequencies are produced across the infrared spectra. Each band or value of the bond length indicates a vibration mode. Inelastic vibration as well as elastic vibration can be classified as vibratory modes (Abood, 2014). Gaussian 09 software package algorithms were employed at LANL2DZ, B3LYP to investigate the

infrared spectra (IR) at the ground state energy of (Au<sub>10</sub>-OTS), (Au<sub>15</sub>), (Au<sub>15</sub>-OTS), (Au<sub>18</sub>) and (Au<sub>18</sub>-OTS), but of the structure of (Au<sub>10</sub>) it has been submitted at LANL2MB,B3LYP basis sets.

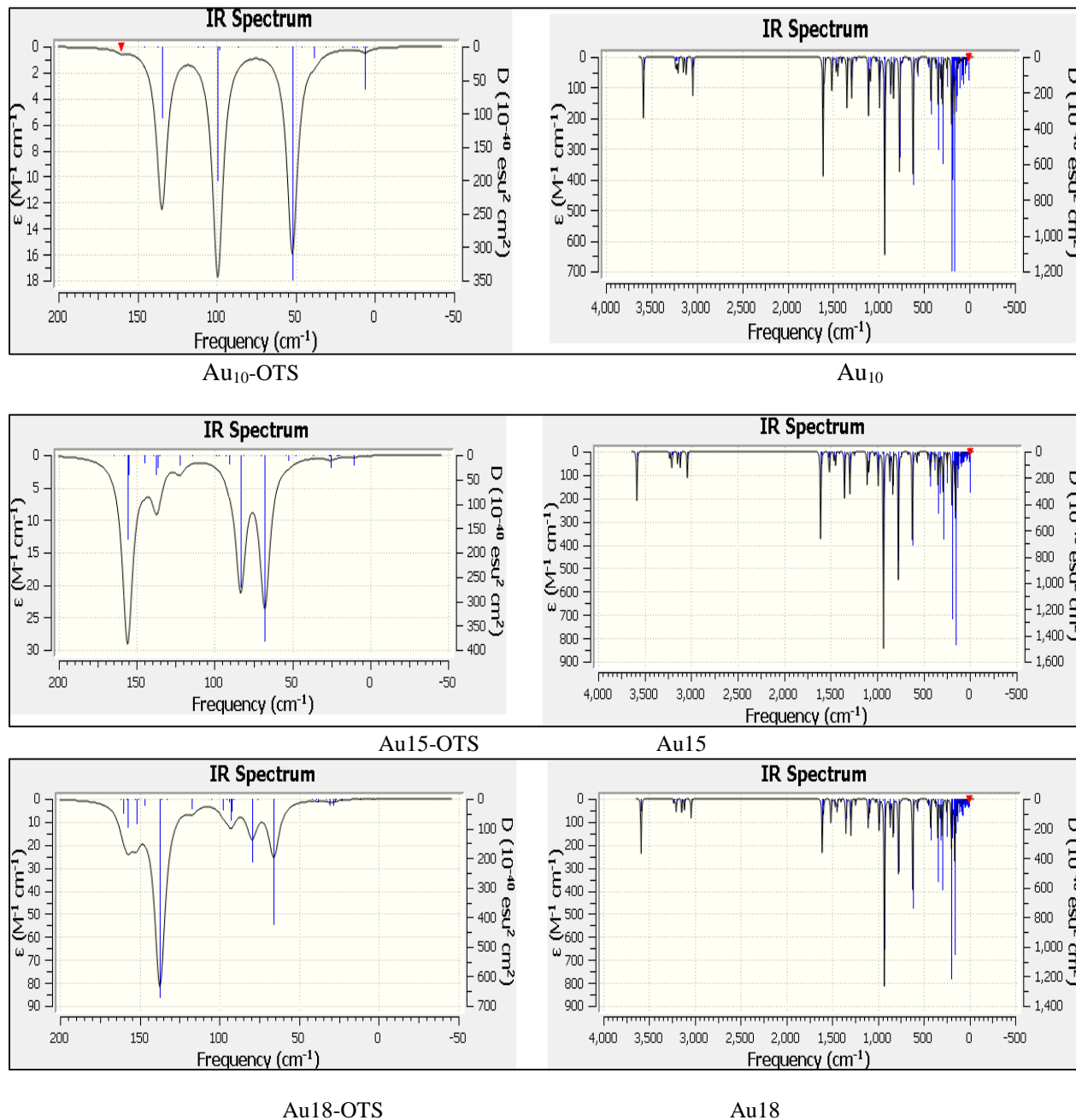


Figure 4. Infrared spectra for (Au<sub>10</sub>), (Au<sub>10</sub>-OTS), (Au<sub>15</sub>), (Au<sub>15</sub>-OTS), (Au<sub>18</sub>) and (Au<sub>18</sub>-OTS).

On can watch in the pictures of infrared spectra in figure (4) by making comparison between pure surfaces of gold and tosylate gold surfaces, there is new bonds have been originated of the types (Au-O), (Au-C), (Au-S) and (Au-H). In the geometrical structure (Au<sub>10</sub>), the apexes emerge at the wave numbers (50 cm<sup>-1</sup>), (100 cm<sup>-1</sup>) and (140 cm<sup>-1</sup>), but after getting physisorption procedure i.e. in (Au<sub>10</sub>-OTS) new apparent apexes demonstrate near new wave numbers (700 cm<sup>-1</sup>), (950 cm<sup>-1</sup>), (1600 cm<sup>-1</sup>) and (3600 cm<sup>-1</sup>). Also, as a comparison between (Au<sub>10</sub>) and (Au<sub>10</sub>-OTS) one can see the variation in the values on the perpendicular axis the largest value of intensity is less than (18 km/mole), while the physisorption gives

intensity approximately (700 cm<sup>-1</sup>). Generally, it can be discovered the new bonds throughout change the domain of wavelength in the horizontal axis (x-axis), while y-axis stands for intensity in (km/mole) unit. Infrared spectra is very important characteristics that has been utilized to diagnose the substances. Also one can visualize in the IR figures how the interaction between the coinage metal surfaces (Au15) and (Au18) and the organic material (OTS) happen dramatically changes in bond lengths and intensity.

## 2.2. Electronic states and Energy Gap (E<sub>g</sub>)

The energy that an electron possesses in the highest occupied orbital of a molecular orbital is known as EHOMO, while the energy that an electron possesses in the lowest unoccupied orbital of a molecular orbital is known as ELUMO. The energy gap E<sub>g</sub> is the difference between them i.e. ELUMO and EHOMO. One of the most significant numbers in physics is the band energy gap, which allows one to determine if a substance is a conductor, semiconductor, semi-metal, or an insulator. According to band theory, there are two bands, the valence band, which is entirely filled with electrons, and the conduction band, which is entirely devoid of electrons. Between these two bands is a region known as the forbidden energy gap. The equation that can be utilized to represent the energy gap (E<sub>g</sub>) mathematically (Abood, 2014; Talib & Alwan, 2022).

$$E_g = E_V - E_C \quad \dots \quad (1)$$

Table 1. illustrates HOMO, LUMO energies and energy gaps (E<sub>g</sub>) for (Au<sub>10</sub>), (Au<sub>10</sub>-OTS), (Au<sub>15</sub>), (Au<sub>15</sub>-OTS), (Au<sub>18</sub>) and (Au<sub>18</sub>-OTS)

System	HOMO (eV)	LUMO (eV)	Energy gap (eV)
Au <sub>10</sub>	-5.929059	-5.047455	0.881604
Au <sub>15</sub>	-5.2711212	-4.8485499	0.4225713
Au <sub>18</sub>	-5.8836183	-4.5840687	1.2995496
Au <sub>10</sub> -OTS	-5.5274394	-4.3546884	1.172751
Au <sub>15</sub> -OTS	-5.9600784	-4.6534542	1.3066242
Au <sub>18</sub> -OTS	-5.5151949	-4.5008061	1.0143888

Table (1) shows values of energy gap of all structures in the domain of energy gaps of semiconductors, but the structure (Au<sub>15</sub>) can be classified as a semi-metal material, it has value of energy gap less than (0.43 eV). The energy gap of the geometrical structure (Au<sub>10</sub>-OTS) approaches the energy gap of silicon. The material that have energy gap like this value have very importance in the electronic applications such as the electronic pieces of laptops, mobiles and sensors. Simulation of the gold surfaces in nanoscale make it have non-zero energy gap values as compared with bulk which has zero value of energy gap. HOMO is connected with molecules' capacity to donate electrons, but LUMO is linked to particles ability to accept electrons. The geometrical structure that has higher value of HOMO donates the electrons easier than the others. The geometrical structure that has higher value of LUMO accepts the electrons easier than the others. The carbon atom electrons in the p orbital or oxygen atom electrons in the p orbital can be adsorbed on empty place on d orbitals of the coinage metal surface, here any (Au) surface.

## 2.3. Ionization potential and electron affinity

The ionization potential can be defined as the required energy that can remove an electron from a neutral atom in its gaseous state. The bonding force between the atom and the electron can be measured by the ionization potential. The atoms which have more electrons in the outer shell have more than one ionization energy for each electron but In hydrogen there is one ionization energy because there is one electron in the outer shell (Beistel, 1973) As for electron affinity, it is the energy that is released from a certain atom



when it acquires an electron. It is equivalent to the energy required to remove an electron from negative ions. Electron affinity is sometimes called zero ionization energy. Electron affinity is high in atoms containing seven electrons in their outer shell, but small in atoms of closed shells. According to Koopman theory (Lee et al., 1988).

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

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

Table 2. illustrates Ionization energy and electron affinity for (Au<sub>10</sub>), (Au<sub>10</sub>-OTS), (Au<sub>15</sub>), (Au<sub>15</sub>-OTS), (Au<sub>18</sub>) and (Au<sub>18</sub>-OTS)

system	I.P (eV)	E.A (eV)
Au <sub>10</sub>	5.929059	5.047455
Au <sub>15</sub>	5.2711212	4.8485499
Au <sub>18</sub>	5.8836183	4.5840687
Au <sub>10</sub> -OTS	5.5274394	4.3546884
Au <sub>15</sub> -OTS	5.9600784	4.6534542
Au <sub>18</sub> -OTS	5.5151949	4.5008061

In table (2) it has been seen that the minimum value of ionization potential is for the geometrical structure (Au<sub>15</sub>), it is about (5.27 eV) here one can put it that the electrons in this geometrical structure surface break free easier than the electrons in other surfaces, one can interpret this issue the electrons need lowest energy to escape from the metal surface. The ionization potential measures force of donor, hence it can donate the electrons from HOMO level, charge transfer procedure occurs easier from the surface of (Au<sub>15</sub>). The geometrical structure (Au<sub>10</sub>) is the maximum value of electron affinity, it is about (5.05 eV), so that this geometrical structure accept the electrons easier than the other gold structures in the table, hence the physisorption procedure at the surface of (Au<sub>10</sub>) takes place simpler than the surfaces of (Au<sub>15</sub>) and (Au<sub>18</sub>). Because of electron affinity scale acceptor force, the electron affinity represents the energy that result when an electron adds to LUMO. Ionization potentials and electron affinities are very beneficial credits to find another important credits, like softness, electronegativity, hardness and electrophilicity.

#### 2.4. Dipole moment

According to the conventional definition of the dipole moment, there exist two charges that have the same magnitude but they have different signs. The unit Debye became the unit of dipole moment in honor of Peter Debye, who was the first physicist who examine bipolar systems. Dipole moment can be either induced or permanent. Dipole moment typified the multiplication of charge and displacement. If the symbol (*d*) denotes to the distance between the two charge, and the symbol (*μ*) indicates to the dipole moment. One can express the dipole moment mathematically as the equation below (Balwa, n.d.)

$$\mu = q \cdot d \quad \dots \quad (4)$$

Table 3. illustrates Dipole moment for (Au<sub>10</sub>), (Au<sub>10</sub>-OTS), (Au<sub>15</sub>), (Au<sub>15</sub>-OTS), (Au<sub>18</sub>) and (Au<sub>18</sub>-OTS).

System	Dipole moment (Debye)
Au <sub>10</sub>	0
Au <sub>15</sub>	0
Au <sub>18</sub>	0.0001
Au <sub>10</sub> -OTS	7.4562
Au <sub>15</sub> -OTS	3.1457
Au <sub>18</sub> -OTS	3.4476

Table (3) demonstrates (Au<sub>10</sub>) and (Au15) with zero values of dipole moment, the reason here is very apparent, the atoms in the two geometrical structures are in the same type, but the geometrical structure (Au18) has semi-zero dipole moment. Physisorption procedure of the organic nanomaterial (OTS) on the surfaces of the coinage metal (gold) make huge changes tremendously in the values of dipole moment. The geometrical structure (Au<sub>10</sub>-Tosylate) has (7.4562 Debye) dipole moment, it is the highest value of dipole moment among the hybrid geometrical structure. The huge dissimilarity in the values of dipole moment result in the hybrid structures because they are hetro structure, hence one can put it the physisorption contribute to generate dipole moment in the hybrid structures. Dipole moment property give information about the bonding properties and charge concentration to the chemical structure. Also physisorption phenomena yield rotational spectrums lead to changes in the dipole moment during the rotation. Also dipole moments result in the hybrid geometrical structure because of the unequal distribution of the charges in this geometrical structures.

## 2.5. Polarizability

Electro polarization is one of the most important quantities used to know the properties of nanomaterials. Polarizability demonstrates the capacity of geometrical structure to be polarized. Polarizability shows the linear response of the electron concentration in the presence of a seminal infinite electric field F, and it stands for a second order variance in the energy. Mathematically the polarizability can be expressed by the following equation (Hait & Head-Gordon, 2018)

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

Let the quantities  $\alpha_{xx}$ ,  $\alpha_{yy}$  and  $\alpha_{zz}$  indicates to the eigenvalues of the polarizability tensor and  $\langle \alpha \rangle$  typifies the average of polarizability. The following equation calculate the average polarizability (Ali, 2009)

$$\langle \alpha \rangle = \frac{1}{3} (\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \quad \dots (6)$$

Table 4. illustrates Polarizabilities for (Au<sub>10</sub>), (Au<sub>10</sub>-OTS), (Au15), (Au15-OTS), (Au18) and (Au18-OTS).

System	$\alpha_{xx}$	$\alpha_{yy}$	$\alpha_{zz}$	$\langle \alpha \rangle$
Au10	1258.845	388.889	215.589	621.1076667
Au15	789.479	1551.837	262.302	867.8726667
Au18	879.627	2008.522	306.001	1064.716667
Au10-OTS	1235.526	624.852	256.305	705.561
Au15-OTS	1312.24	1197.75	317.391	942.4603333
Au18-OTS	2057.041	1202.397	358.157	1205.865

In table (4) It can be seen that the geometrical structure (Au18-OTS) is the largest value of the average polarizability, as it is close to (1205.865a.u). It can be said that this geometrical structure is the most vital geometrical structure among all pure and hybrid coinage metal ( gold and gold-tosylate). When one compare the average value of polarization for all models ( gold and gold-tosylate) before and after the physisorption process can note that , there increases in vitality, thi is meaning that the physisorption is the reason for the increase in the average value of polarizability. When one compare the models according to the eigenvalues of the polarizability tensor, the highest value of  $\alpha_{zz}$  is for the (Au18-OTS) , it is (358.157 a.u), the highest value of  $\alpha_{yy}$  is for the (Au18) , it is (2008.522 a.u) , but the highest value of  $\alpha_{xx}$  for the (Au18-OTS) , it is (2057.041 a.u). Polarizability characteristic yield beneficial informations about the internal structure and dipole moment of the geometrical structures. Polarizability credit has advantage in the nonlinear optics science applications. Polarizability impact to many coefficients, just like bond lengths, dihedral angles and bond angles, topological properties, hybridization and symmetry.

### 3. SYMMETRY

Symmetry can occur around a point, centerpiece or surface. Symmetry operations implicit the rotations, the reflections and the inversions. There is a identical symmetry element for each symmetry operation, which may be point, line or plane with respect to the symmetry operation. The sphere is more symmetric as compared with the cube, the reason here belong to that the sphere is looking the same after it rotates at any angle around the diameter, but the cube is looking the same after it rotates with certain angles. The geometrical structure has reflection symmetry about a symmetry plane if the geometrical structure does not change after reflection process from the plane. The inversion symmetry is taking place if the geometrical structure has rotation at certain angle and the geometrical structure reflects around straight line at the same time through point on it. (Bishop & Klein, 1975; Lesk, 2004; Öhrn, 2000; Shwya et al., 2020).

Table 5. illustrates Symmetries for (Au10), (Au10-OTS), (Au15), (Au15-OTS), (Au18) and (Au18-OTS).

System	Point group symmetry
Au10	D2h/C1
Au15	D2h/C1
Au18	D2h/C1
Au10-OTS	C1
Au15-OTS	C1
Au18-OTS	C1

In table (4) one can see two kinds of point group symmetries, they are (C1) and (D2h/C1). Physisorption of the organic nanomaterial (tosylate) on the surface of all coinage metals (Au10), (Au15) and (Au18) make apparent changes in the type of point group symmetry, the physisorption changes the symmetry from (D2h/C1) to (C1). (Au10), (Au15) and (Au18) surfaces have (D2h) symmetry, one can say that those surface have two fold axes perpendicular to Cn, and also they have a horizontal mirror plane ( $\sigma_h$ ). Also the geometrical surfaces (Au10), (Au15) and (Au18) have (Cn) type symmetry because they have (C1) symmetry, and in this kind of symmetry the rotation is done by an angle equal to  $(360^\circ/n)$ , here (here  $n=1$ ), therefore the geometrical structure repeat itself through  $(360^\circ)$ . Symmetry treatise is very beneficial for giving conclusions about the molecular geometry properties without making calculations, some of these properties are the degenerate states and dipole moment. Symmetry treatise has an importance in the researches that allocate the optical activity property in the branch of knowledge physical optics.

#### 3.1. Density of States (DOS)

The ability of electrons to occupy energetic levels in orbitals can be assessed using the density of state characteristic. The electrons placements in energetic levels serve to characterize quantum states. Solid state physics can be used to examine these electron quantum states. Quantum statistical physics principles must be considered when discussing phonons and photons and electrons. Since they are fermions, electrons are subject to the Fermi-Dirac statistic, however, phonons and photons must adhere to the Bose-Einstein statistics, and electrons must unquestionably adhere to Pauli's exclusion principle. The electrons are unable to occupy orbitals in the energy level if the density of state is zero. The density of states is greatly influenced by a variety of parameters, just like topological characteristics and symmetry characteristic (Adachi & Sunada, 1993; Brown, 1967a; Honig, 1970; Kittel & McEuen, 2018).

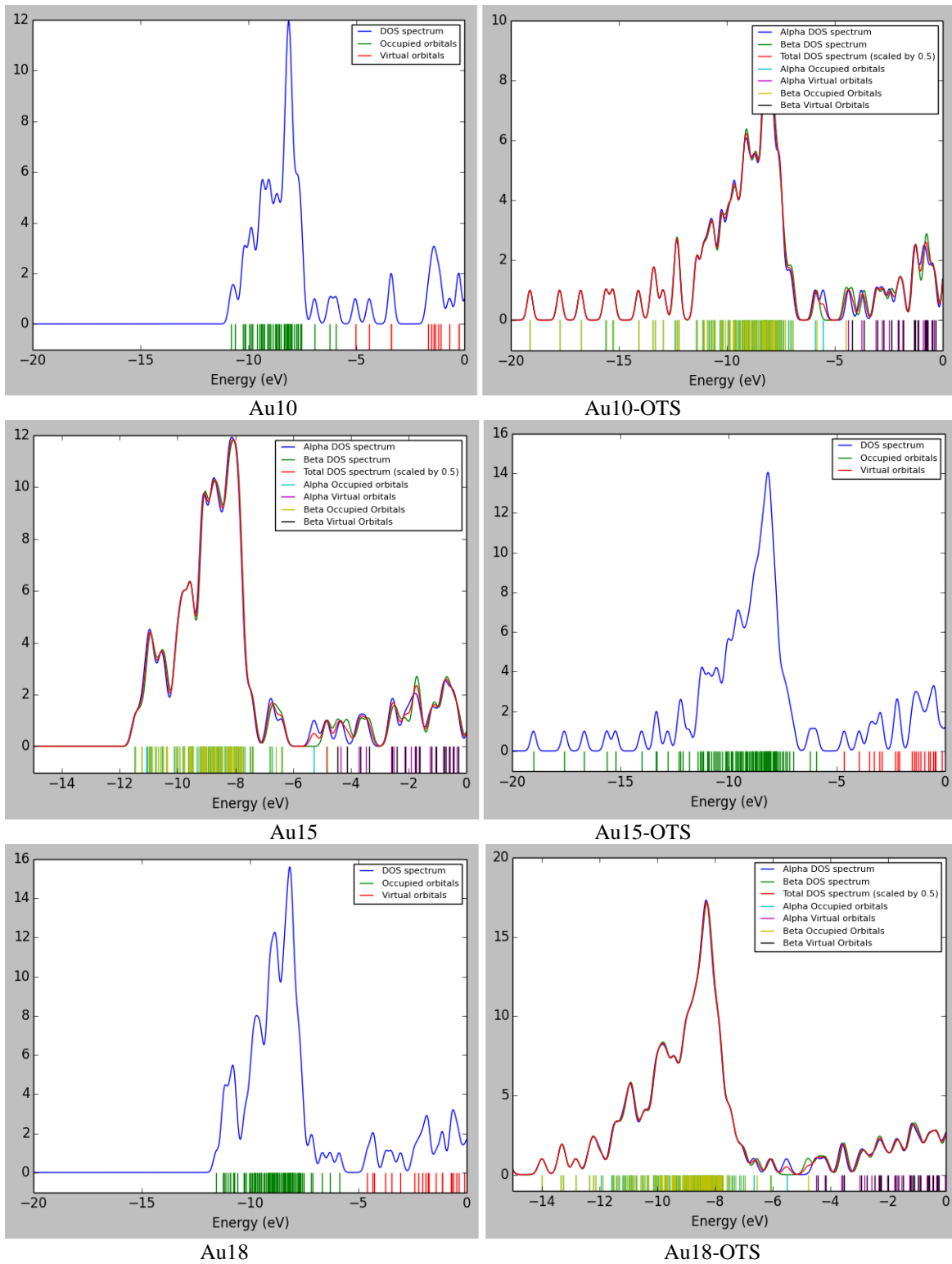


Figure 5. Density of States for Au10,Au15,Au18,Au10-OTS,Au15-OTS and Au18-OTS

The diagrams in figure (5) show that the geometrical structures (Au10-OTS) , (Au15) and (Au18-OTS) implicit two types of orbitals ( $\alpha$ ) And ( $\beta$ ), therefore, they behave as an anti-ferromagnetic nanomaterials this type of open shell system is considered to have the wave functions of electrons in these geometrical structures described by two mathematical equations, one of which is for ( $\alpha$ ), but the other is for ( $\beta$ ). It is very clear when someone spot in the pictures of density of states schematics how the physisorption impact to the magnetic properties. The geometrical structures (Au10) and (Au18) become have anti-ferromagnetic characterstics after physisorption of the organic nanomaterials on those two surfaces, but the geometrical structure (Au15) lose the anti-ferromagnetic property after physisorption. Due to the oscillatory motion of atoms around the equilibrium positions according to the concepts of quantum mechanics and solid-state physics ideas, the local density of states cannot be zero. Local potential, hybridization and molecular geometry are factors impacting the density of state properties. There are other parameters that affect the intensity of cases such as topological characteristics and symmetry.

#### 4. CONCLUSIONS

Physisorption of tosylate (OTS) on the golden surfaces and charge exchange happen between the organic nanomaterial (OTS) and gold surfaces. Physisorption (OTS) on (Au15) surface draw new contour map different pretty much tremendously from the contour map of the pure gold surface (Au15). Charge distribution around gold atoms in (Au15) differ from charge distribution around same gold atoms in (Au15-OTS) because of the distortion in potential surface because of the physisorption phenomena. The largest value of intensity is less than (18 km/mole), while the physisorption gives intensity approximately (700 cm<sup>-1</sup>). Values of energy gap of all structures in the domain of energy gaps of semiconductors, but the structure (Au15) can be classified as a semi-metal material, it has value of energy gap less than (0.43 eV), Simulation the gold surfaces in nanoscale make it have non-zero energy gap values as compared with bulk which has zero value of energy gap, the result values of energy gap is very beneficial in the different electronic applications like solar cells and computer pieces. The minimum value of ionization potential is for the geometrical structure (Au15), it is about (5.27 eV) hence the electrons need lowest energy to escape from the metal surface. The geometrical structure (Au10) is the maximum value of electron affinity, it is about (5.05 eV), hence the physisorption procedure at the surface of (Au10) takes place simpler than the surfaces of (Au15) and (Au18). The geometrical structure (Au10-Tosylate) has (7.4562 Debye) dipole moment, it is the highest value of dipole moment among the hybrid geometrical structure. The geometrical structure (Au18-OTS) is the largest value of the average polarizability, as it is close to (1205.865a.u), it can be said that this geometrical structure is the most activity among all pure and hybrid coinage metal ( gold and gold-tosylate). The physisorption phenomena changes the point group symmetry from (D<sub>2h</sub>/C<sub>1</sub>) to (C<sub>1</sub>) for all pure golden surfaces, Symmetry treatise has an importance in the researches that allocate the optical activity property in the branch of knowledge physical optics. The geometrical structures (Au10) and (Au18) become have anti-ferromagnetic characterstics after physisorption of the organic nanomaterials on those two surfaces, but the geometrical structure (Au15) lose the anti-ferromagnetic property.

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