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Quantum study of symmetrical/asymmetrical charge/energy transfer in a simple candidate molecular switch

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Abstract

Based on molecular nanoelectronic knowledge, field-effect molecular electronic devices can be designed for use in nano-circuits. Therefore, in this study, a candidate field-effect molecular switch (isolated, M, and non-isolated, Au-M-Au/Au₄-M-Au₄, molecular systems) is studied, using density function/pseudopotential model (DFT/LANL2DZ). This molecular switch's switching mechanism (ON/OFF) we performed by applying an external electric field-effect. In this regard, some computational studies related to this molecular switch's electronic/vibrational transfer properties were investigated. Also, used from the quantum theory of atoms in the molecule (QTAIM), Landauer's theory (LT), and energy/charge transfer mechanisms were used at the atomic scale to predict this molecular switch's voltage-current (IV) behavior. Analysis of these results showed that when the intensity of the applied electric field increases to 0.008 au, the molecular switch is in the ON state. In addition, the role of gold electrodes on some of the electronic/vibrational properties of this molecular switch was investigated. Analysis of the results showed that gold electrodes play an essential role in the local distribution of charge and intramolecular energy and, consequently, the I/V diagram of this molecular switch. It is expected that such quantum-based research (without using numerical methods such as Green's function methods) could open new horizons in the quantum study of molecular parts at the atomic-intramolecular scale.

Keyword Molecular nanoelectronics, Molecular switch, Atoms in molecule theory (AIM) and Landauer theory, symmetrical/asymmetrical charge/energy transfer coefficients.

Introduction

Molecular electronics is the most widely used part of nanotechnology [1-3]. In this technology, the efficiency of electronic circuits can be increased [4,5]. In molecular electronics, single molecules are used to build a circuit [6-8]. The use of single molecules (in electronic devices) can remove the limitations of reducing the size of electronic devices [9,10]. The use of these structures provides the ability to make precise electrical connections (by molecules). Due to the size effect, by reducing the size of electronic devices (to nanoscale), the quantum properties of these components become more apparent [11,12]. Therefore, careful study of molecular nanoelectronics systems requires the use of quantum mechanical knowledge [13]. For example, the quantum study of the transport-electron and vibrational properties (at the atomic-molecular scale) is critical in studying the properties of molecular devices of the field-effect (such as wire and molecular switch) [14,15]. If a molecular device can be used to lose or gain electrons (oxidation/reduction), the electron exchange process will create the electromotive force (e.m.f) in the system [16]. In this case, a molecular motor is created that operates under the effect of electric force (because electrons move throughout the system) [17]. The molecular switch acts as a molecular motor in nanoelectronics systems. Studies show that the position of atoms in a molecule (molecular switch) changes due to the external electric field effect [18-21]. A molecular switch reacts according to the direction of the electrical field effect. In this case, the molecular switch is in the ON/OFF position [22-26].

Several studies show that each molecular key used in electrical circuits must pass four evaluation steps [27,28]. These steps include evaluating molecular properties such as the geometric structure of the molecule, energy gap (HLG) related to the difference in energy levels of the HOMO and LUMO frontier molecular orbitals, electrical polarizability, and evaluating the molecule's response to different external electrical field intensity [29-30]. In this work, an ab initio (computational/quantum) study was performed on some electronic/vibrational transport properties of a field-effect molecular switch (in two states in two isolated states M, and conjunct to the electrode, Au-M-Au, and Au4-M-Au4). In this case, the electric current-voltage diagram (I-V) of this molecular switch (as the response of the molecular switch to the electric field effect) will be checked in two isolated states (M) and conjuncted to the electrode (Au-M-Au and Au4-M-Au4). By applying an electric field, the electronic and vibrational properties change. These changes cause the thermoelectric effect to appear as heat in the system. The heat generated can cause electrical disturbances in the circuit. Therefore, control of thermal, electrical interference in molecular nanoelectronic circuits is essential. The Joule (symmetrical, Lsy) and Peltier (asymmetrical, Lasy) effect play an important role in studying thermoelectric effects in nanosystems [31]. When a current I passes through an n/p-type semiconductor thermoelectric device, heat is absorbed in the lower temperature junction (as p junction) and released at the higher temperature junction (as n junction). In this case, the asymmetrical effect defines according to the following equation:

$$\frac{dQ}{dt} = L_{np}I = (L_n - L_p)I \quad (1)$$

Where L_{np} is the overall asymmetrical coefficient of the n/p-type semiconductor thermoelectric device, and L_n and L_p are the asymmetrical coefficients of the n and p materials jointed at the two points (which altogether constitute the asymmetrical circuit) [32]. Molecular properties, such as electric and magnetic moments, are observable measures of how the molecular geometry and the electron density and configuration change due to interactions with external electric and magnetic fields. These molecular response properties can also be decomposed into atomic response properties. The QTAIM also allows

determining the extent of transferability of the field-induced atomic properties and understanding the physical factors governing their values in given situations [33–35].

Therefore, quantum theory of density function (DFT), quantum-atoms- in- molecular theory (QTAIM), and Landauer theory (LT) were used. According to QTAIM theory, the kinetic energy (K), potential energy (V), and total electron energy (E) of a molecular system (using atomic viral theory) are obtained by relations [36,37]. According to AIM theory, the kinetic energy (K), potential energy (V), and total electron energy (E) of a molecular system (using atomic virial theory) calculate by the following equations:

$$K = \sum_{\Omega}^{N_{\Omega}} K(\Omega) ; V = \sum_{\Omega}^{N_{\Omega}} V(\Omega) ; E = \sum_{\Omega}^{N_{\Omega}} E(\Omega) = -2K \quad (2)$$

$$K(\Omega) = \frac{-\hbar^2}{4m} N \int_{\Omega} dr \int [\Psi \nabla^2 \Psi^* + \Psi^* \nabla^2 \Psi] d\tau' \quad (3)$$

Where ψ is a function of the electron wave of the atomic N molecular system and Ω is the basins of each atom [38]. Since a molecular switch plays the role of opening/closing the circuit in nanoelectronics systems, the molecular switch can be ON/OFF by changing the electron transition mechanism [39]. The molecular switch studied in this work is shown in Figure (1, 13). The external electric field effect can convert this molecular switch from structure A to B (ON/OFF states). This state change can be related to the intramolecular charge/energy transfer mechanism and how electrons transfer (π -conjugated bonds) [40,41].

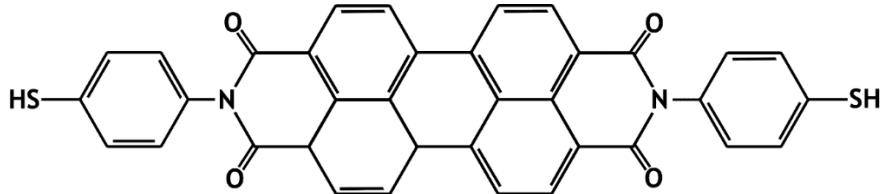


Fig. 1 The isolated molecular switch (M) studied in this work.

Computational and methods

Based on the DFT/UB3LYP /6-311G* computational method, the EF (along the x-axis) effect on geometry optimization and some electronic/vibrational properties of the proposed molecular switch (M and Au-M-Au systems) are investigated. For the gold atoms of the electrodes, the LANL2DZ pseudopotential is used. In addition, Landauer theory (LT) (Equation 4) [42,43], is used to predict current-voltage (Figure I-V) curve of these molecular systems. In addition, starting from the electronic wave functions obtained, at each EF intensity, the atomic basins of the M , Au-M-Au and Au₄-M-Au₄ molecular systems are determined, and thus the average value of the some atomic electronic properties (such as atomic electron density and kinetic energy) of each atomic basins are calculated, using QTAIM.

$$I = \frac{2e}{h} \int T(E, V) [f(E - \mu_L)] - [f(E - \mu_R)] dE \quad (4)$$

In this relation, e is the electron charge, h is Planck constant, T (E , V) is the electron transfer coefficient due to the bias voltage effect (V), $f(E-\mu_L, E-\mu_R)$ is the Fermi-Dirac distribution function for electrochemical potential (μ_L, μ_R) for left and right electrodes [45]. Therefore, the temperature-independence direct-tunneling electric conduction (G) of a single molecule nanoelectronics system can be evaluated using the Landauer formula, i.e. (The simple form of this relationship is as follows):

$$G = \frac{1}{R} = \frac{2e^2 \tau_e}{\hbar} \quad (5)$$

$$\tau = \exp(-\beta L) \quad (6)$$

$$\beta = \left(\frac{2m^* \alpha \varphi}{\hbar^2} \right)^{\frac{1}{2}} \quad (7)$$

where \hbar is $\frac{h}{2\pi}$, φ is the potential barrier height for tunneling through the HOMO or the LUMO level, which is equivalent to the energy difference between the Fermi energy and the molecular HOMO or LUMO level, m^* is the effective mass of the electron ($m^* = 0.16m_0$, m_0 is the free electron mass) and α is the symmetry parameter in the potential profile, in this symmetric case, $\alpha = 1$ [46]. In a particular applied field strength value, φ and L are half the HLG and the distance between the two-ending sulfur S57 and S56 atoms (of the molecular switch), respectively [46]. In addition, the effect of the electric field on some electronic properties (such as electron density of states (DOS), kinetic energy (KEK), and Laplacian density (V)) of this molecular switch were studied (at the atomic scale), using the quantum theory Atom-in-molecule (AIM) [47]. In this regard, Gaussian (G09) and AIM2000 software were used [48]. Also, since the electron potential barrier (φ) has an important role in the electron transfer mechanism in the molecular switch, three Range were defined for the field-effect intensity [49,50]. 1- Position with low field-effect intensity LB ($\varphi > eV$), 2- Threshold effect field intensity ($\varphi \approx eV$), 3- Position with High field-effect intensity HB ($\varphi < eV$) (1a.u.=21.27eV).

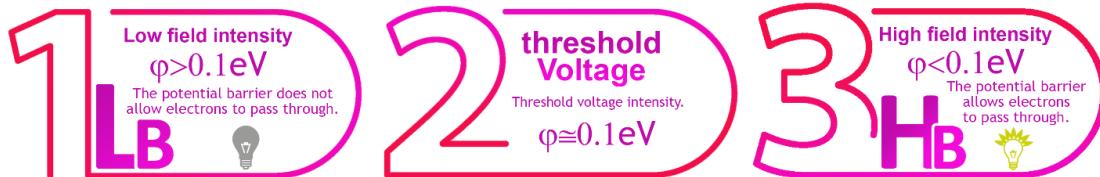


Fig. 2 Amplitude of external electric field intensity applied (ON/OFF range).

Results and Discussion

First, in order to investigate the electronic properties of the studied molecular switch, Figure (1), the effect of the electric field on the frontier molecular orbitals (HOMO/LUMO) and the gap between them (HLG) in state of the isolated molecular switch (M) was investigated, (figure 3).

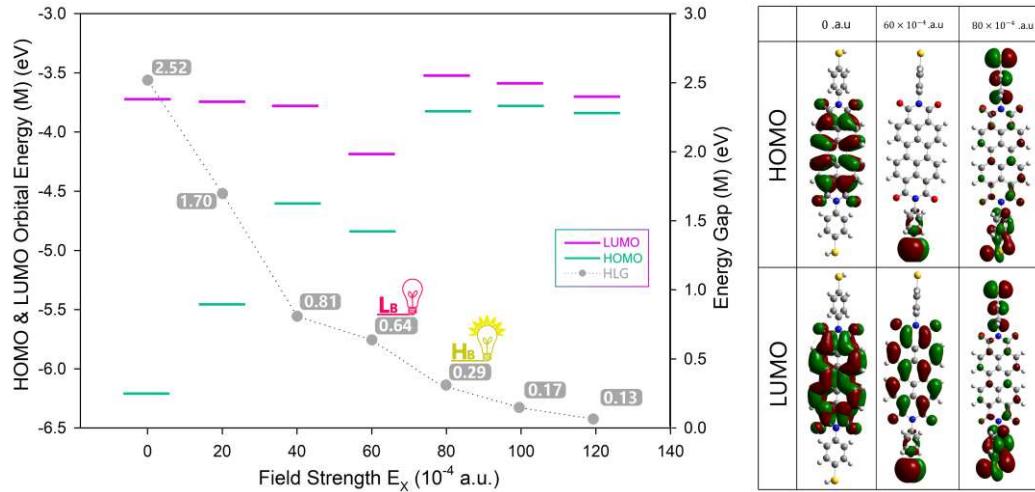


Fig. 3 Graph of changes in energy levels of frontier molecular orbitals (HOMO, LUMO, in terms of eV) and energy gap for the isolated molecular switch (M) studied in the intensity of different fields effect.

Usually, the reduction of energy gap values between frontier molecular orbitals indicates a shortening of the potential barrier [51]. According to Figure (2), the energy of the frontier molecular orbitals depends on the intensity of the External electric field effects. This property indicates the measurable response of the studied molecular switch to the field effect. In addition, the External electric field effects (EF) on this molecular switch (M) caused the separation of positive and negative charge centers in its structure. Therefore, the change in polarizability, dipole moment, and electrical moment as the molecule's response (molecular switch) to the field effects were investigated, Figure (4). According to the obtained results, the total dipole moment increases with the increasing electric field, Figure (4).

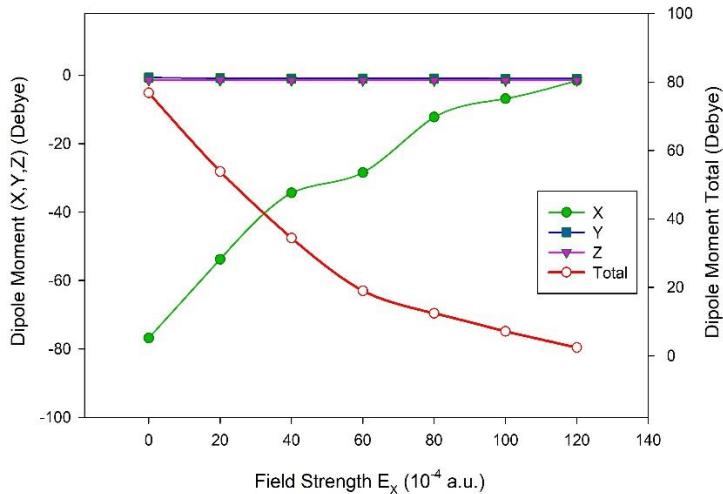


Fig. 4 Changes in the molecular electric dipole moments, at different electric field intensities, of the isolated molecular switch (M) studied in this work.

The results show the total dipole moment increases (Due to the displacement of π -conjugated bond along the molecule) with increasing electric field, (Figure 4). The external electric field effects showed that in addition to the electronic properties (molecular density of state, DOS), the vibrational properties of this

molecular switch (such as vibrational frequencies, IR) show a significant response to the field-effect Figures (5 and 6).

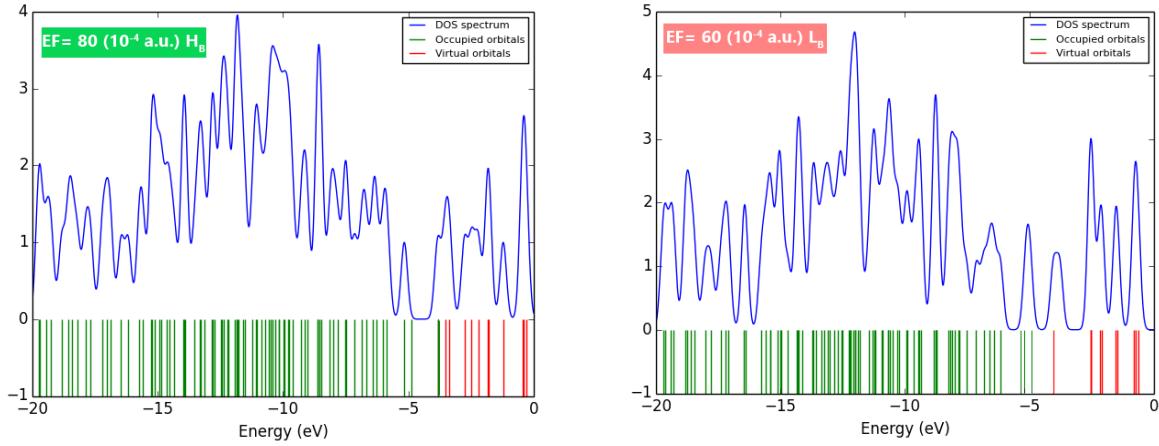


Fig. 5 External EF effect on molecular density of state (DOS) of the molecular switch M studied in this work (at low Bias/OFF field state and at High Bias/ON field state)..

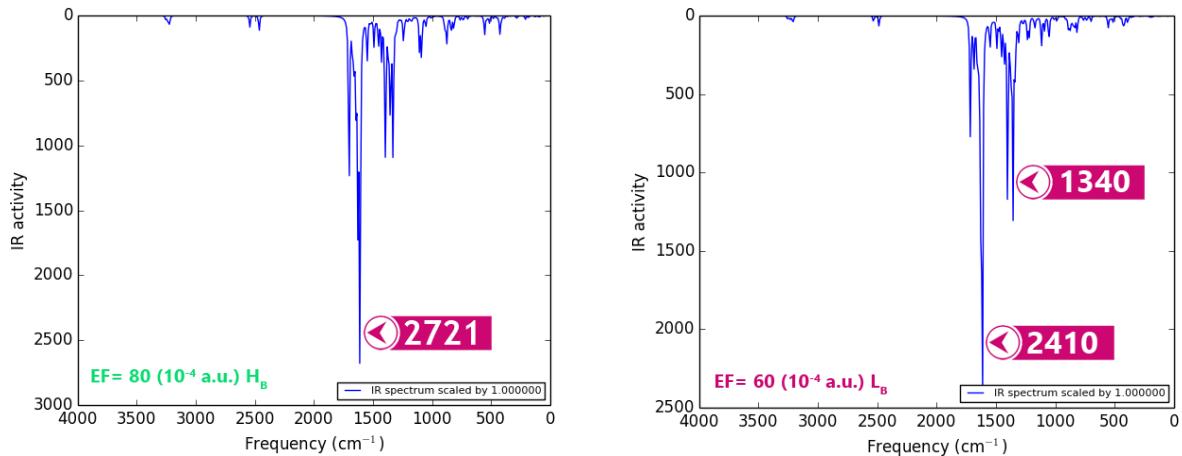


Fig. 6 External EF effect on molecular vibrational frequencies of the isolated molecular switch (M) studied in this work; (in both low Bias/OFF field and high Bias/ON field states).

External electric field effects (EF) to the molecular switch study can cause the intramolecular distribution of its charge and energy. The study of intramolecular charge/energy exchange helps predict the efficiency of components in nanocircuits [52]. Therefore, using the quantum theory of atoms in molecules (AIM), the electron wave function obtained from the studied molecular switch structures (M) at any applied field intensity was quantum studied. Then, using AIM, some of the electronic properties of atomic basins of this molecular switch (such as electron density, Laplacian electron density, atomic charges, and energy of atomic basins) were calculated in Figures (7 and 8). Analysis of AIM results showed that the field-effect on important atomic basins such as oxygen (O), sulfur (S), and carbon (C) in this molecular switch (M) showed that the response of sulfur atomic basins is higher than other atomic basins, such as oxygen and carbon, Figure (7). The results show that sulfur atomic basins are the primary charge site and intramolecular

energy exchange in this molecular switch (M). Also, the electric field effect on some studied properties (Electron density ($\rho(r)$), Laplacian electron density ($\nabla^2\rho(r)$), Electron kinetic energy ($K(r)$) showed that the electric field effect higher than 80 on changes in charge and energy is more prominent. Some of the results below were reported, Figures (8-10) and Tables (1 and 2).

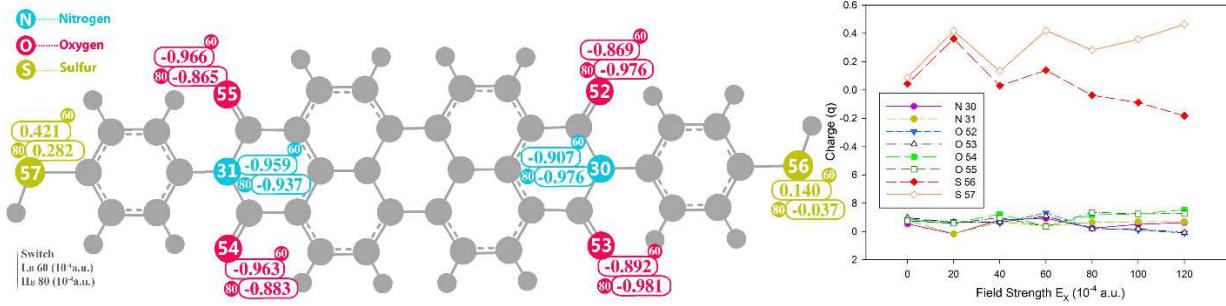


Fig. 7 External field effect (EF) on the electronic atomic charges, of some atomic basins of the isolated molecular switch (M).

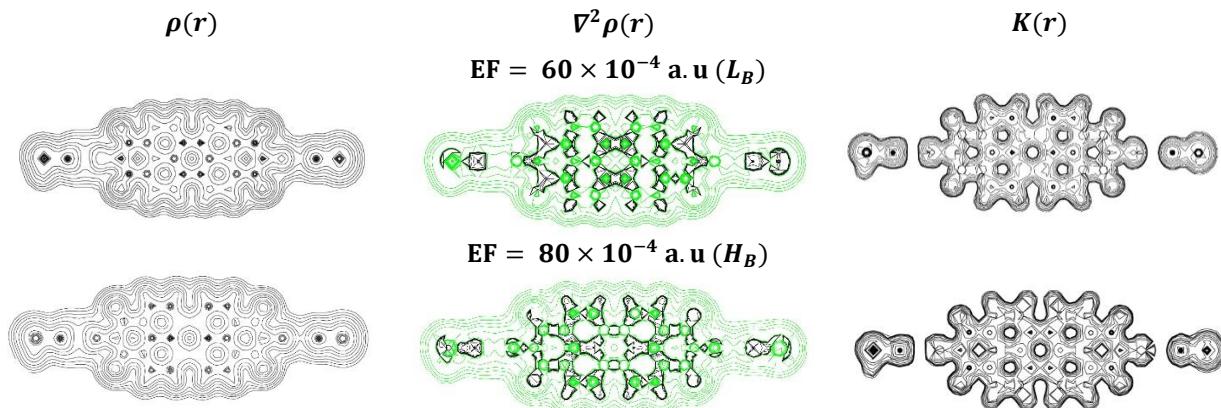


Fig. 8 External EF effect on contour/local map of electron density ($\rho(r)$), Laplacian electron density ($\nabla^2\rho(r)$) and electronic kinetic energy ($K(r)$) of the the isolated molecular switch (M) is studied in this work, are calculated using QTAIM.

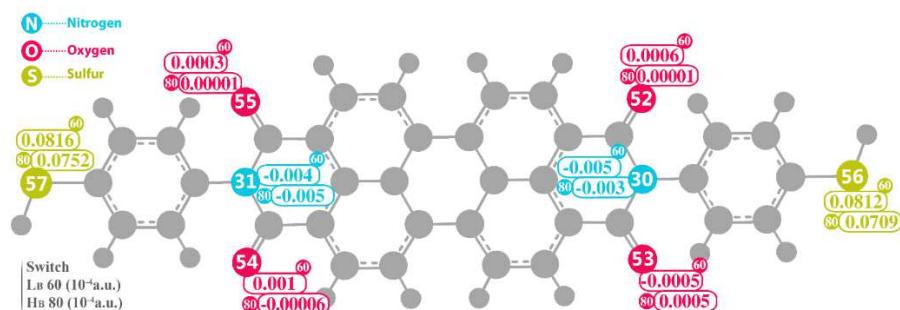


Fig. 9 External EF effect on the Laplacian ($\nabla^2 \rho(\mathbf{r})$) of some atomic basins studied of the isolated molecular switch (M).

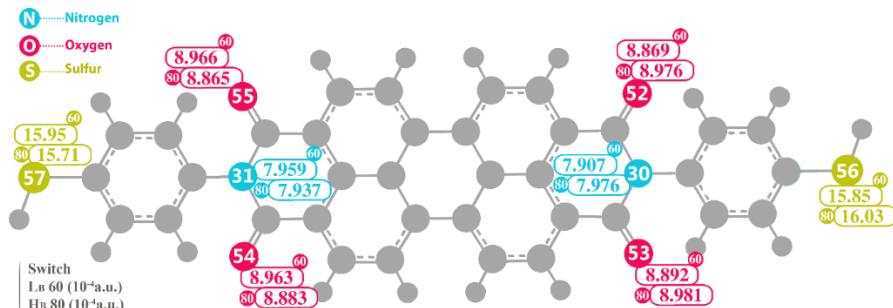


Fig. 10 External EF effect on the electron density ($\rho(\mathbf{r})$) of some atomic basins of the molecular isolation switch (M) studied.

Table 1 External field effect (EF) on the viral energy/potential ($v(r)$), of some atomic basins of the isolated molecular switch (M), (low field/ L_B state and high field/ H_B state).

Switch	field	$v(r)$							
		S57	S56	N30	N31	O52	O53	O54	O55
L_B	60	795.0	794.8	109.9	110.0	150.35	150.39	150.46	150.47
H_B	80	794.8	794.9	110.0	109.9	150.45	150.46	150.38	150.35

Table 2 External field effect (EF) on the electronic kinetic energy ($K(r)$), of some atomic basins of the isolated molecular switch (M), (low field/ L_B state and high field/ H_B state).

Switch	field	$K(r)$							
		S57	S56	N30	N31	O52	O53	O54	O55
L_B	60	397.54	397.47	54.95	55.01	75.17	75.19	75.23	75.23
H_B	80	397.46	397.53	55.02	54.99	75.22	75.23	75.19	75.17

The results obtained from Figures (9-10) and Tables (1,2) showed that the studied molecular system into electron-acceptor/donor (n-like and p-like) Were can divide. Therefore, we can investigate the role of each part in the mechanism of charge transfer and intramolecular energy. This intramolecular classification is possible using AIM theory based on the summation of atomic properties ($A_{\text{Molecule}} = \sum_{\Omega}^{\text{All Atoms}} A(\Omega)$).

I-V diagram and switching mechanism

In this study, Landauer's theory was used to calculate (predict) the electrical conductivity of a molecular switch in two isolated (M) and electrode-conjugated (Au-M-Au & Au4-M-Au4) states. This study showed that by increasing the intensity of the electrical field effect to 80×10^{-4} a.u. Currents in the isolated system (M) increased significantly. In this case, it is expected that the molecular switch would be in the ON state.

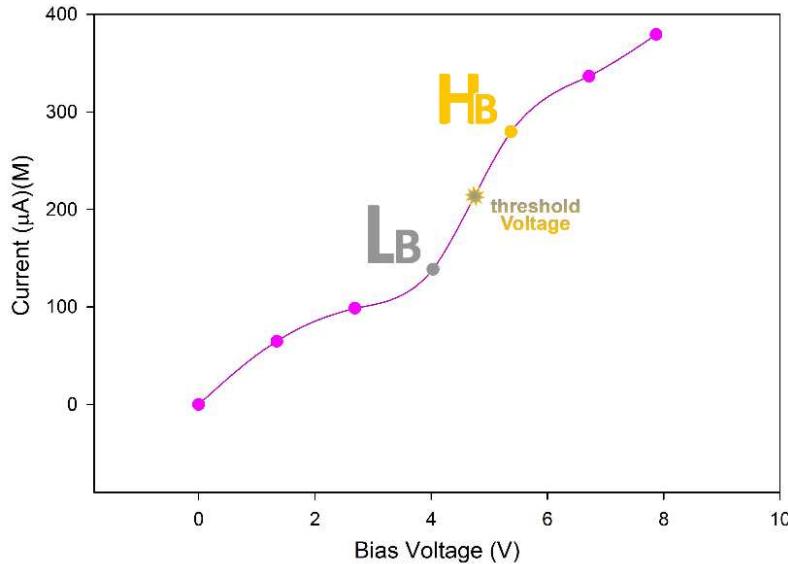


Fig. 11 Current-voltage diagram of the isolated molecular switch (M) is studied in this work (low bias/L_B and high bias/H_B state).

According to Figures (3-11), increasing the intensity of the electrical field (especially in the H_B region) has a more significant effect on the electronic properties. It is predicted that this molecular switch's (M) switching function takes place between oxygen and nitrogen after the effect of an external electric field by transferring π -conjugated electrons (Figures 11,12).

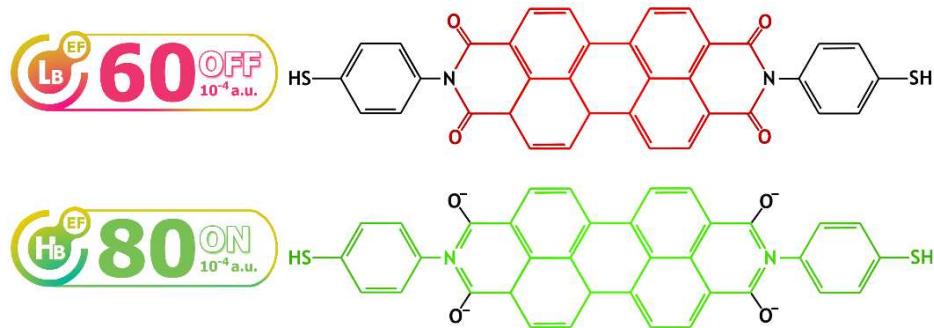


Fig. 12 How to transfer the π -conjugate bond in the intensity of electric fields 80×10^{-4} a.u. and 60×10^{-4} a.u in the isolated molecular switch (M).

The results show that at fields with intensities less than 60×10^{-4} a.u., the electrical resistance of the molecular system is significant. This factor causes the molecular switch (M) to be in the off state. Also, with increasing the intensity of the electric field (electrical fields above 60×10^{-4} a.u.), the electric current of the system increases significantly. In this case, the molecular switch (M) is in the ON position (Figure 12).

Electrode effect

To investigate the effect of the electrode, we conjugated the molecular system (M) to the gold nanoelectrodes (Au-M-Au & Au4-M-Au4), (Figure 13). Then, this molecular switch (Au-M-Au) was

studied (ab initio) using AIM and DFT theory (at the theoretical level of UB3LYP/6-311G*) and the LANL2DZ model. For example, analysis of the results obtained from AIM showed that thiol groups (S-H) are the primary site of charge and energy exchange in this structure (Figure 7). Therefore, these groups we can select as the Main location connection of gold nanoelectrodes. This work investigated the effect of an external electric field on this molecular switch after connection to the electrode (Au-M-Au and Au₄-M-Au₄). The results showed that with increasing field strength (electric fields with intensities more significant than 60×10^{-4} a.u.), the electric current increases significantly, and the molecular switch turned ON, Figure (14). In addition, the effect of the electrode changes the electronic and vibration properties of this molecular switch. These changes can also be due to the participation of free electrons of gold atoms in the mechanism of charge and energy transfer in the studied molecular switch.

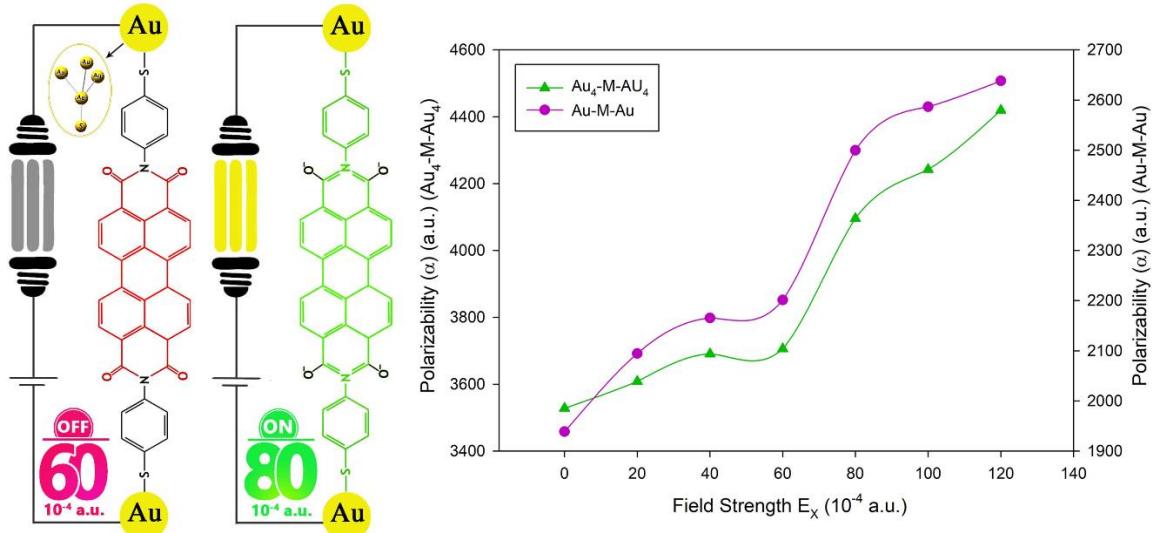


Fig. 13 How to place the molecular switch in the proposed circuit (left) and external EF effect on polarizability (right) of the molecular switch conjuncted to the electrode (Au₄-M-Au₄/Au-M-Au).

As can be seen from Figure (13), the effect of the electric field on the total polarizability (as a symbol of the molecular switch response to the field-effect) is more significant for the Molecular system Au₄-M-Au₄ more than for other molecular systems Au-M-Au.

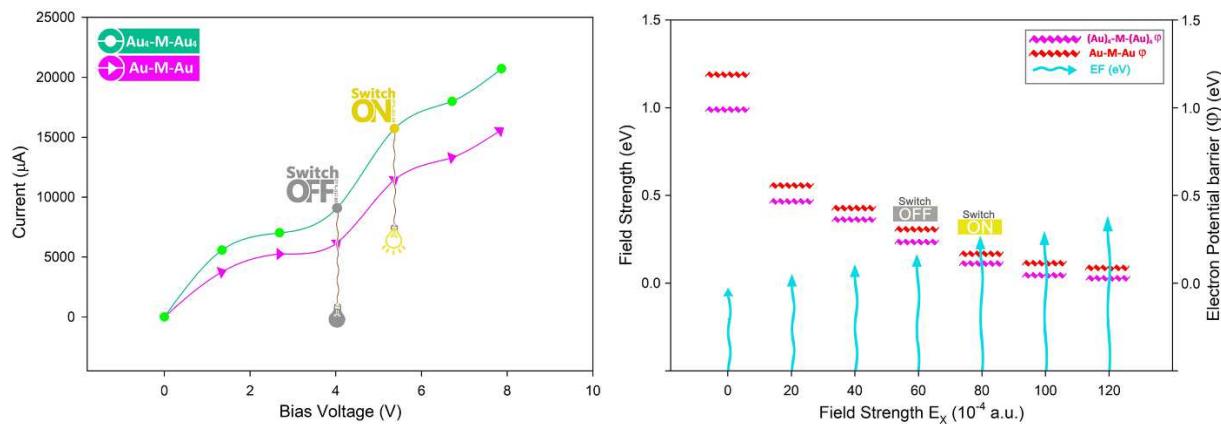


Fig. 14 Current-voltage diagram (left) and electron potential barrier (right) of the molecular switch $\text{Au}_4\text{-M-Au}_4$ & $\text{Au}\text{-M-Au}$, are studied in this work.

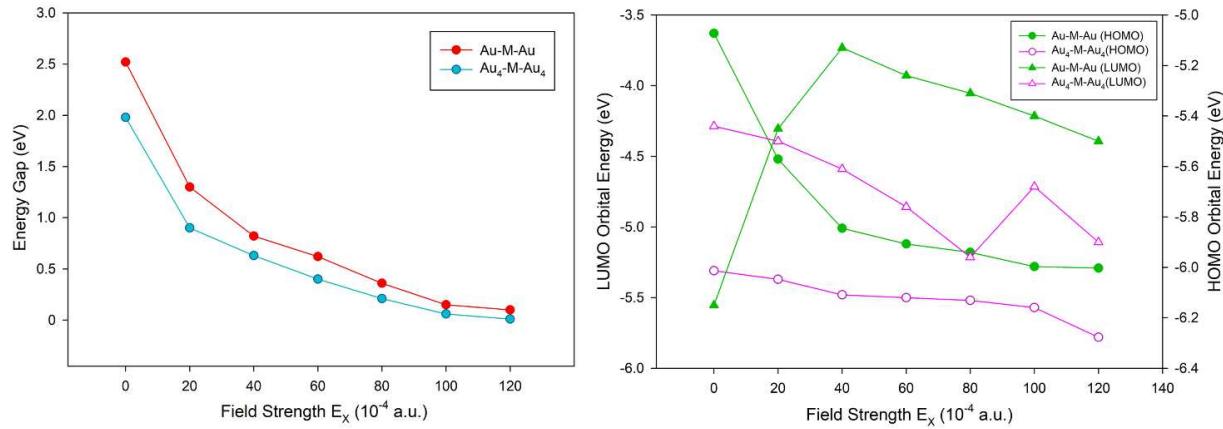


Fig. 15 Graph of changes in HOMO and LUMO frontier molecular orbitals (right) and energy gap (HLG) (left) of the molecular switch $\text{Au}_4\text{-M-Au}_4$ & $\text{Au}\text{-M-Au}$.

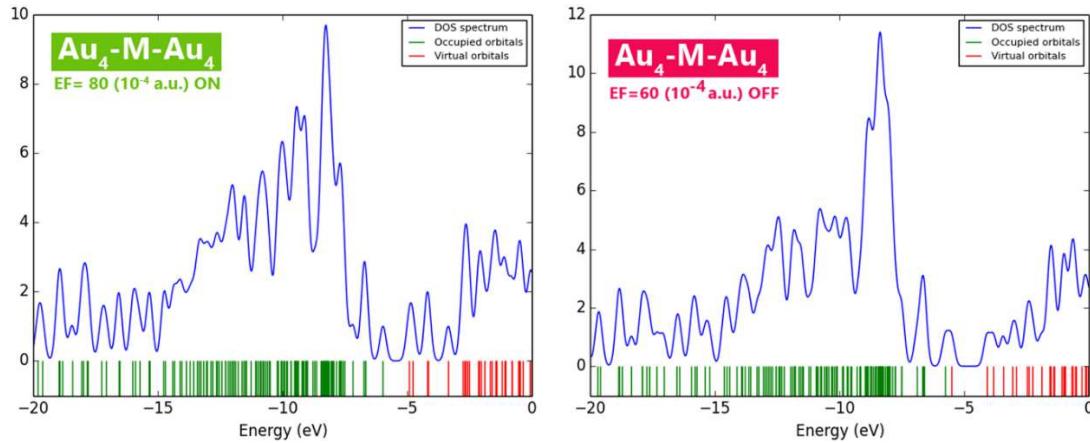


Fig. 16 External EF effect on molecular density of state (DOS) of the molecular switch $\text{Au}_4\text{-M-Au}_4$ is studied in this work (in OFF/ON states).

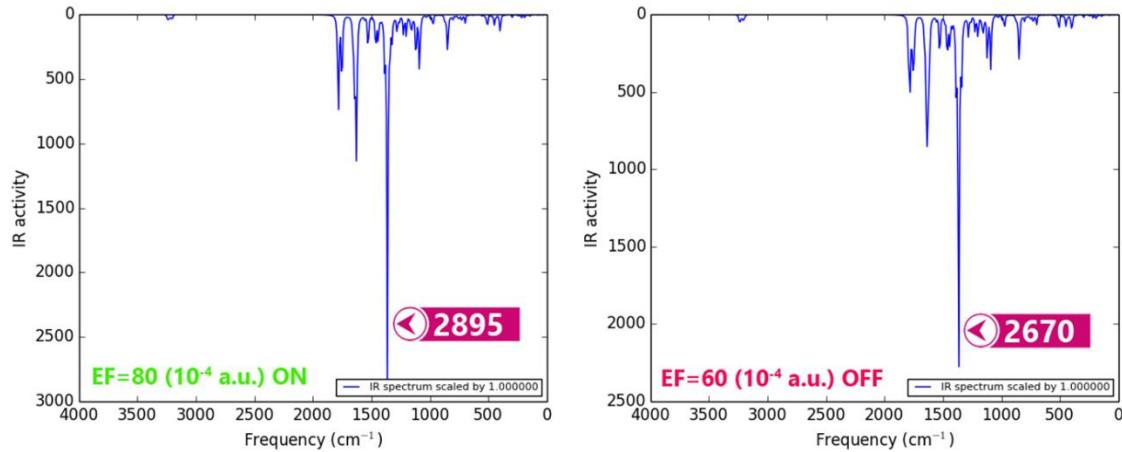


Fig. 17 External EF effect on molecular vibrational frequencies of the molecular switch $\text{Au}_4\text{-M-Au}_4$ is studied in this work (in OFF/ON states).

The stability of this molecular switch due to the electrical field effect was investigated using a viral theorem ($V_{elec}/K_{elec} = -2$) [53]. Establishing this theorem causes the electronic energy of the whole system to calculate by calculating the system's electronic kinetic energy. For this reason, the viral theory were investigated in the intensity range of the effect of the electric field. The results showed that minor deviations (negligible) were created in the calculated value (V_{elec}/K_{elec}) by increasing the electric field intensity (Figure 18).

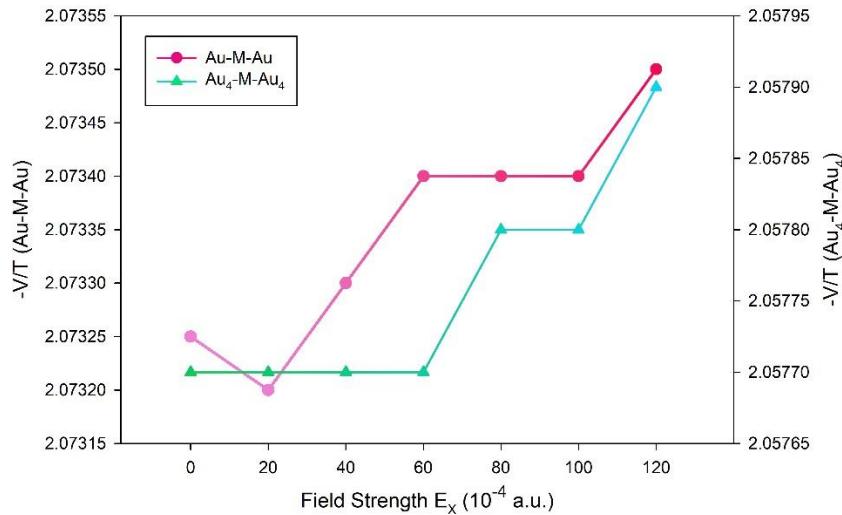


Fig. 18 virial theorem ($V_{elec}/K_{elec}=-2$) in the intensity of external electric fields of the $\text{Au}_4\text{-M-Au}_4$ and Au-M-Au systems.

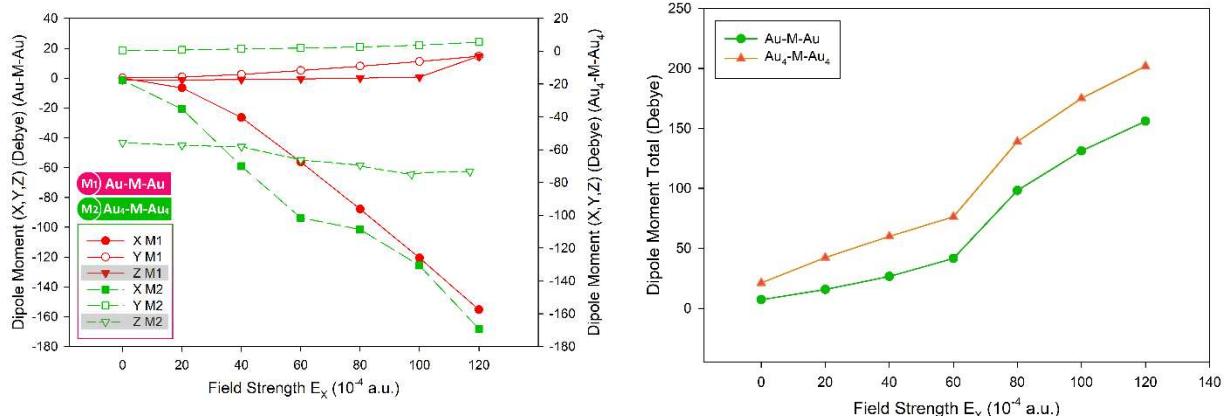


Fig. 19 External EF effect on electric dipole moment (left) and total electric dipole moment tensors (right) of the molecular systems Au_4 -M-Au₄ & Au-M-Au, are studied in this work.

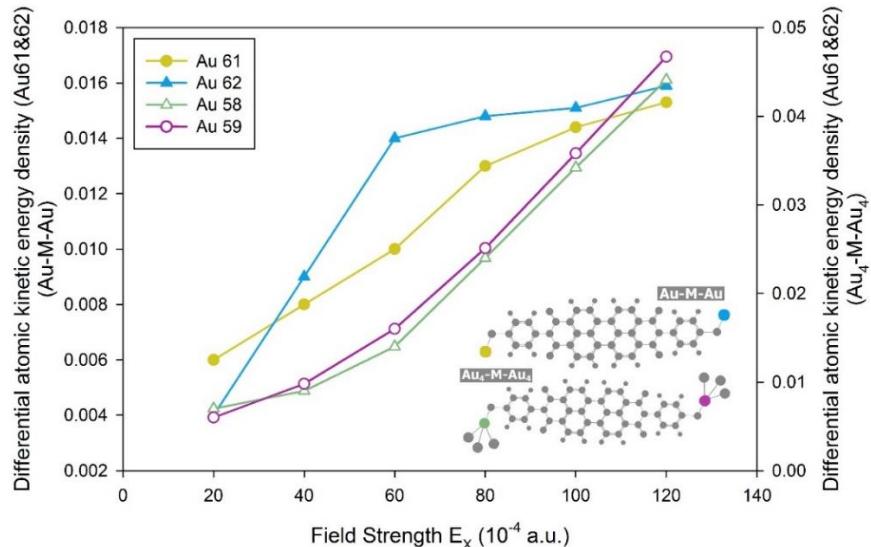


Fig. 20 Differential atomic kinetic energy , $\Delta K(\Omega, \varepsilon) = K(\Omega, \varepsilon) - K(\Omega, 0)$, of the Au atomic basins of the molecular switch (Au_4 -M-Au₄ & Au-M-Au).

Recently, attempts have been created to understand nanosize and molecular nanoelectronic systems' thermal (thermoelectric) effects [54,55]. We have introduced and described the thermoelectric and thermoelectric-like effects basically for the gaseous, metallic, and semiconductor systems, based on the charge and energy transfers.

Furthermore, research shows that the Seebeck, S, and asymmetrical, Π , coefficients are inter-related via $\Pi=TS$, and thus it is sufficient to calculate only one of them. In this work, the contributions of electrons and phonons (vibrational degrees of freedom) in the energy/heat transported between n-like and p-like intramolecular sections were studied. Studies show that temperature changes occur due to symmetry and asymmetry when an external electric field-effect a molecular system. The proposed molecular system for calculating the intramolecular heat/electricity coefficient was divided into two parts (left and right) (Figure

21). intramolecular heat/electricity properties (based on changes in electron energy in atomic fields) Checked by the quantum theory of atoms in molecules (QTAIM) [56].

The local symmetrical heating (Q^J) and the asymmetrical (Q^P), and the overall heating/ cooling (Q) of different IMTLSs of a molecular device can be defined similarly as:

$$\begin{cases} Q^J = \frac{Q^f + Q^r}{2} \\ Q^P = \frac{Q^f - Q^r}{2} \end{cases}; Q = Q^J + Q^P \quad (8)$$

The superscripts f and r correspond, respectively, to the forward and reverse biases. These definitions make it possible to discriminate between symmetrical and asymmetrical heat flow contributions to the IMTLCs [57].

In analogy with Eq. (8), the intramolecular symmetrical, $\Delta_{\gamma,q}^{sym}(\varepsilon)$, and intramolecular asymmetrical-like (asymmetric) heating, $\Delta_{\gamma,q}^{asym}(\varepsilon)$, for any pair of sections (S_L, S_R) corresponding to the coordinate q, can be defined as:

$$\begin{cases} \Delta_{\gamma,q}^{sym}(\varepsilon) = \frac{\Delta_{\gamma,q}^f(\varepsilon) + \Delta_{\gamma,q}^r(\varepsilon)}{2} \\ \Delta_{\gamma,q}^{asym}(\varepsilon) = \frac{\Delta_{\gamma,q}^f(\varepsilon) - \Delta_{\gamma,q}^r(\varepsilon)}{2} \end{cases}; q = x \text{ for } (S_L, S_R) \quad (9)$$

Also, using Eq $L^M = L_{elec}^M + L_{vib}^M$, the molecular system can be divided into two parts, symmetrical (L_{asym}^M) and asymmetrical (L_{sym}^M) IMTLCs, which describe the intramolecular symmetrical and asymmetrical (or asymmetrical -like) effects, respectively [58]. L_{elec}^M and L_{vib}^M corresponding, respectively, to the electronic and vibrational degrees of freedom. were can, therefore, write:

$$L_{sym}^M \equiv \frac{L^{M,f} + L^{M,r}}{2}, L_{asym}^M \equiv \frac{L^{M,f} - L^{M,r}}{2} \quad (10)$$

In which $L^{M,f}$ and $L^{M,r}$ are the overall IMTLC corresponding to the thermoelectric process with forward and reverse biases, respectively [59].

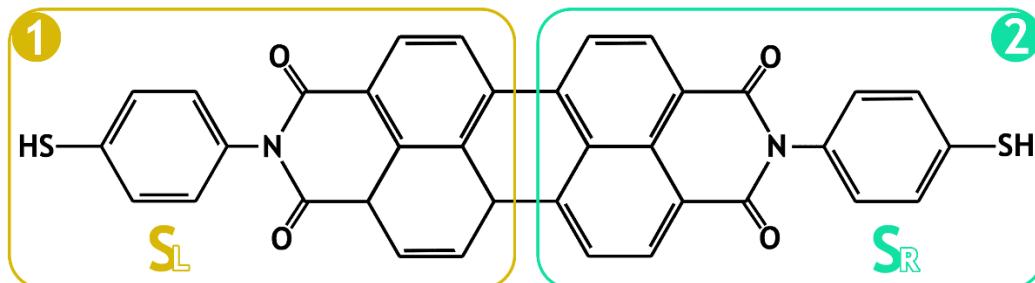


Fig. 21

As expected, symmetry is dependent on the electrical field-effect direction. The results show that symmetry is the primary heat transfer factor between different parts of the molecular system. Lsy/Lasy coefficients also decreased after the molecular system was attached to the electrode (Figure 22).

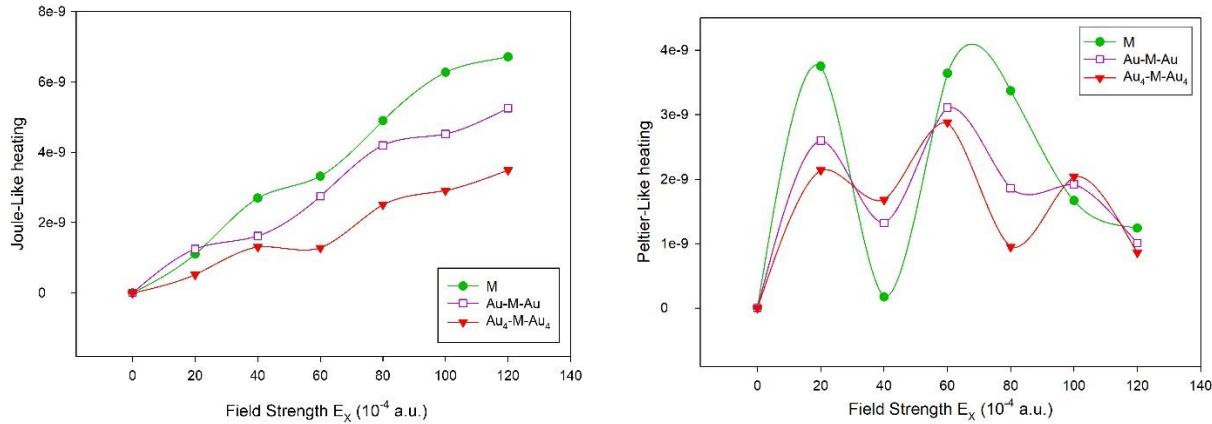


Fig. 22 The effect of symmetrical (Joule-Like) and asymmetrical (Peltier-Like) of the molecular switch conjoined to the electrode (Au₄-M-Au₄ & Au-M-Au).

Conclusion

In this study, the effect of electric field on the electronic/vibrational properties of a molecular switch in the field was studied using the method of theories and DFT and AIM and based on the computational method UB3LYP / 6-311G* and LANL2DZ. In this regard, using quantum information of the system (without using numerical methods such as Green's function methods, GF), this molecular switch's electrical conductivity behavior (Figure I-V) was predicted. The analysis of the obtained results showed that applying an external electric field could lead to the separation of atomic charges, and reduction of energy gap (HLG) and consequently increase the electrical conductivity of the studied molecular system. In addition, the analysis of the obtained results showed that the application of an external electric field could cause the exchange of charge and energy between different atomic basins and, consequently, changes in kinetic energy and potential (viral) energy of the studied molecular system. Also, the effect of electric field on the studied structure showed that in electric fields applied above 0.008 a.u. is due to the displacement of conjugated π -electrons along the molecule, in which case the molecular switch is in the ON state. The results showed that gold electrodes important role in the local distribution of charge and energy (Laplacian) within the molecule and, consequently, the I-V diagram of this molecular switch. Based on the results obtained in this study, it is predicted that this candidate field-effect molecular switch has acceptable performance in nanoelectronic circuits.

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*Code availability: No grant and code

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H. Hadi: Subject design, writing and calculations

R.Safari: Subject design, writing/ revising and analysis of results

H.R. Shamlouei: writing and editing

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