

# Kondo Effect in Distorted Titanium Phthalocyanine Molecules Adsorbed on a Cu(110) Metallic Surface

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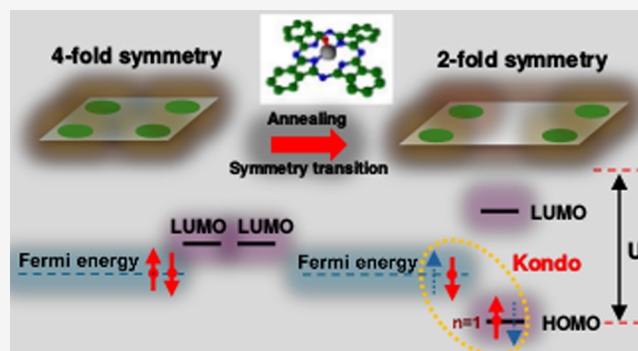


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**ABSTRACT:** In this work, we study the quantum transition taking place when titanium phthalocyanine molecules are adsorbed on a copper's surface. Submitted to thermal annealing, depending on the way in which the molecule is adsorbed, this system can be characterized by a Kondo ground state, giving rise to a zero bias peak in the differential conductance. To clarify this new property, derived from the annealing process, we propose a model Hamiltonian that describes the essential physics involved. We show that the Kondo ground state appears as a consequence of the broken symmetry introduced by the annealing. It is not due to an increase of the molecule–substrate interactions but to the modification of the intermolecular lobe orbital matrix elements. This rearrangement rules the entrance of charge into the molecule and provides the conditions for the establishment of the Kondo state. Our results for the differential conductance, corresponding to the electronic current between a STM tip and one of the molecular lobes, agree with the experimental differential conductance measurements. It presents an Abrikosov–Suhl–Kondo resonance at the Fermi level for the configuration where the molecule is distorted. The results obtained within the model we propose, when compared with the experiments, give quantitative support to our interpretation.



## INTRODUCTION

In 1964, Jun Kondo proposed a theory that explained an experimental observation dated from more than 30 years before, consisting of a minimum value observed in the resistivity, as the temperature is lowered, in some metallic compounds doped with magnetic impurities.<sup>1,2</sup> Kondo assigned this behavior to the interaction of the localized spins at the magnetic atoms with the spins of the conduction electrons of the host metal. It turns out that this Kondo effect takes place in an energy scale known as Kondo temperature  $T_K$ , which precisely corresponds to the energy associated with the antiferromagnetic interaction between the impurity and the conduction spins. The solution of this challenging problem came years later when Wilson proved that at low temperatures, close to zero and well below  $T_K$ , the spins of the conduction electrons completely screen the spin of the magnetic impurity.<sup>3</sup>

Albeit during almost 60 years, the Kondo effect has been a hallmark for checking the performance of a variety of theoretical techniques developed to treat many-body problems.<sup>4</sup> From an experimental point of view, the study was restricted to the case of magnetic impurities in nonmagnetic metals. This scenario started to change due to the progress achieved in nanotechnology that made it possible to build up and study a large variety of nanostructures and devices. This was possible due to the development of lithographic methods and to the high accuracy attained by scanning tunneling

microscopy (STM) and the scanning tunneling spectroscopy (STS).<sup>5,6</sup> These techniques allow us to scan, with atomic resolution, very small structures, as a molecule adsorbed on a metallic surface, and to obtain either the current through the molecule or the local density of states (LDOS) in determined sites of its structure. Experiments have been carried out, either on magnetic atoms<sup>7–9</sup> or molecules,<sup>10–16</sup> mostly organic molecules containing magnetic atoms<sup>17–19</sup> adsorbed on metallic surfaces.

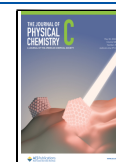
Ultraviolet photoemission spectroscopy (UPS), conjugated to the STM and STS methods, was used to investigate the Kondo state that emerges in a metal-free phthalocyanine 2Hpc adsorbed on the silver Ag(111) surface due to the screening of an unpaired spin acquired by the adsorbed molecule.<sup>11</sup> Also, in a system composed by CuPc molecules adsorbed on Cu(110)-(2 × 1)O, Maughan et al.<sup>20</sup> observed a change in the interfacial electronic structure that was associated with a transition in the film structure.<sup>21</sup> These authors, using STS techniques, were

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able to study, at the atomic level, the physical process taking place at the molecule–substrate interfaces of adsorbed molecules. The physics related to the interface interactions of the phthalocyanine molecule (TiOPc) adsorbed on a Cu(110) surface was studied using STM.<sup>22</sup> It was concluded that these interactions determine important properties of this system as its adsorption configuration, i.e., the molecular orientation with respect to the metal and the nature of the molecular self-assembled structure. Indeed, the authors observed the formation of a one-dimensional self-assembled nanostructure in the film growth that depends on the adsorption configuration and that was associated with the Cu(110) surface anisotropy. In fact, these nanostructures are composed by molecules with their oxygen atoms pointing toward the metal surface, the “O-down” configuration, and observed on the step edge of the substrate. On the other hand, the molecules adsorbed with the oxygen atom pointing toward vacuum, in the “O-up” adsorption configuration, are observed on the planar regions of the substrate. In these systems, the signature of the Kondo effect appears in the conductance measurements, either as an Abrikosov–Suhl–Kondo (ASK) resonance or as a Fano dip,<sup>23</sup> depending upon the molecule and its adsorption configuration.<sup>24,25</sup>

Among the organic molecules most widely studied are the phthalocyanines<sup>26–29</sup> and the porphyrins.<sup>27,30–32</sup> It was shown that the Kondo temperature can be modified by distorting the molecule,<sup>24</sup> or by changing the number of neighboring molecules,<sup>33,34</sup> or the metallic surface on which it is adsorbed.<sup>35</sup> In addition, long-range ferromagnetic order, mediated by Ruderman–Kittel–Kasuya–Yosida (RKKY) interactions, was observed by Girovsky et al.<sup>36</sup> in supra-molecular Kondo lattices. They were composed by hexadeca-fluorinated iron and manganese phthalocyanines (FeFPc and MnPc) adsorbed on Au(111) substrates and coassembled in a checkerboard pattern. Also, in recent works, FePc molecules adsorbed on a Au(111) surface were presented as a platform where a topological quantum phase transition takes place.<sup>37,38</sup> A generalization of the theory proposed by these authors was studied by Žitko et al.<sup>39</sup> The FePc molecule, used as an experimental materialization of this problem, possesses three orbitals near the Fermi level, which introduces important difficulties to solve a model that incorporate them.<sup>40</sup> Recently, considering a three-channel model, using the mean field slave boson approximation, Aligia<sup>41</sup> was able to study this system as a function of the splitting between the orbitals. These are only a few examples of a very vast literature on the subject.

In this work, we propose a model to describe the TiOPc molecular system experimentally studied by Maughan et al.,<sup>22,42,43</sup> considering a class of molecules that present coplanar adsorption on the metallic substrate, with the oxygen atom pointing toward the vacuum. This “O-up” molecular adsorption originally preserves a 4-fold symmetry configuration (FSC) observed through constant current STM images. In the experiments, it was also observed that the molecules on the “O-down” adsorbed configuration, with the oxygen pointing toward the substrate plane. This configuration is not analyzed in this paper since its quantum state is not modified by thermal treatment. Conversely, the “O-up” molecules are affected by the annealing process, which gives rise to Kondo properties, whose origin was suggested to be related to the increase of the molecule–substrate interaction due to the molecular distortion produced by the annealing.<sup>42</sup> The main goal of this paper is to clarify this question by analyzing the physical mechanism

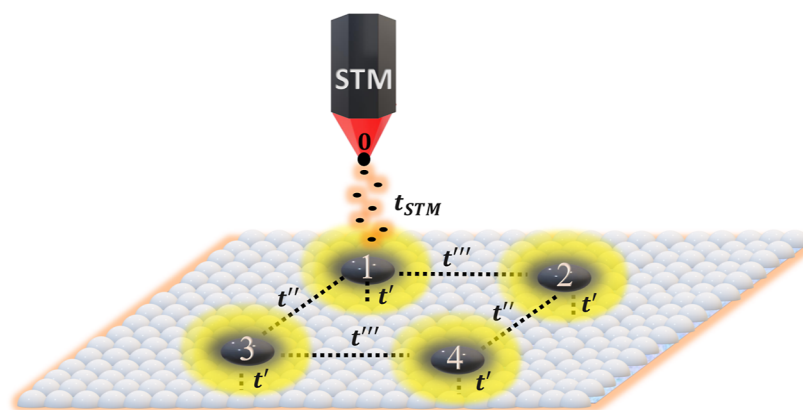
behind the annealing process responsible for the appearance of a Kondo ground state in the system. We show that the energy changes of the molecular orbitals with respect to the Fermi level due to the break of its original FSC result in the main mechanism, governing the entrance of charge in the molecule and, therefore, underpinning the observed Kondo physics.

The second section is dedicated to the discussion of the model Hamiltonian proposed to study molecules adsorbed on the metallic surface. The third section presents the results and the fourth the conclusions.

## MODEL

The isolated TiOPc molecule is a complete-shell compound, without any magnetic property,<sup>44</sup> but the adsorption on the Cu(110) surface changes its structure. The isolated molecule consists of a central Ti atom, surrounded by four symmetrically arranged lobes mainly formed by carbon atoms. The adsorption is carried out with the molecules disposed in “O-up” and “O-down” configurations. Both possess their own properties, considering the interactions involved and, particularly, the physics governing its adsorption. The molecules on the “O-down” configuration, for instance, are predominantly observed in nonplanar substrate regions, as in the edges formed by Cu layers. The “O-up” molecules, in contrast, accumulate mainly on the Cu terraces, which are the planar regions of the substrate. Preserving a very well-determined FSC, these molecules present a flat adsorption, which results from identical interactions between the lobes and to the substrate [Cu(110) surface].<sup>22,42</sup> The molecular adsorption generally changes the energy of the HOMO due to the charge transfer from the metal to the molecule.<sup>35</sup> We consider this for the case of TiOPc. Specifically, LUMOs of the isolated molecule, with energy well below the Fermi level of the metal surface and mostly Ti–O character, become doubly occupied. Also, the molecule possesses double degenerate LUMOs, with energy above the Fermi level that results from its FSC.

In this paper, we study the physics associated with the break of the FSC due to thermal annealing and the appearance of an Abrikosov–Suhl–Kondo peak at the Fermi level for the molecule in the “O-up” configuration. This resonance is observed in the differential conductance (DC) between a STM tip and one of the molecular lobes.<sup>42</sup> We model the system in a simple scenario capable of capturing its essential features. The isolated molecule presents HOMO and LUMO separated by an energy gap of  $\sim 1.2$  eV. The lower energy LUMOs have a predominantly  $\pi$  symmetry and a high Ti–O character. However, energetic LUMOs have a very low Ti–O character. When the molecule is adsorbed on the Cu(110) surface, a charge transfer to the molecule occurs that stabilizes the system. This charge transfer takes place mainly to the lowest energy LUMO orbital with high Ti–O character, which becomes double occupied because its energy results in being below the Fermi level of the metal by an amount greater than the local Coulomb interaction. This is the HOMO of the adsorbed molecule. Next above the Fermi level, the LUMO of the adsorbed molecule has low Ti–O character and  $\pi$  symmetry and has a predominant role in the transport properties across the molecule. For the “O-up” configuration, a FSC is experimentally observed with no central feature in the molecular lobe structure, reflecting a flat adsorption geometry on the Cu surface, with all the lobes placed at the same distance from it.<sup>42</sup> We analyze this configuration, considering its transition from a FSC to a 2-fold symmetry configuration



**Figure 1.** Four high interacting lobes' model for the “O-up” titanyl phthalocyanine molecules TiOPc adsorbed on Cu(110).

(TSC) and the consequent emergence of Kondo physics, when the system is submitted to an annealing process.

In contrast with the CoPc system of ref 45, the Ti atom is a rather passive element. The main physical process, associated with the entrance of charge into the molecule due to thermal annealing, occurs by the predominant participation of the molecular lobes levels. Then, it is possible to model the “O-up” TiOPc molecule adsorbed on the surface by four orbitals with local strong Coulomb interaction  $U$ . These orbitals are mutually coupled through hopping parameters in an FSC and TSC. The interaction of the molecule with the Cu(110) surface is introduced by the hopping parameters between the lobes and the metal,  $t'$ , as presented in Figure 1, which also shows a STM tip placed over one of the molecular lobes and through which the current circulates. This STM tip is incorporated into the model through the hopping parameter  $t_{STM}$  which couples the tip to one of the molecular lobes.

In the context discussed above, the molecule is described by a four-orbital Anderson Hamiltonian of the type

$$\begin{aligned} \hat{H}_m = & \sum_{i=1,\sigma}^4 (\epsilon_0 + V_g) \hat{n}_{i\sigma} + U \sum_{i=1}^4 \hat{n}_{i\uparrow} \hat{n}_{i\downarrow} \\ & + \sum_{\sigma} (t'' [\hat{c}_{1\sigma}^\dagger \hat{c}_{3\sigma} + \hat{c}_{2\sigma}^\dagger \hat{c}_{4\sigma} + \text{H. c.}] \\ & + t''' [\hat{c}_{1\sigma}^\dagger \hat{c}_{2\sigma} + \hat{c}_{3\sigma}^\dagger \hat{c}_{4\sigma} + \text{H. c.}]) \end{aligned} \quad (1)$$

where the operator  $\hat{c}_{i\sigma}^\dagger (\hat{c}_{i\sigma})$  creates (annihilates) an electron of spin  $\sigma$  at the orbital  $i$ , with  $i = 1, 2, 3$ , and  $4$ ,  $\hat{n}_{i\sigma} = \hat{c}_{i\sigma}^\dagger \hat{c}_{i\sigma}$  represents the spin  $\sigma$  electron occupation operator of orbital  $i$ . The Coulomb interaction at the molecular lobes is given by the parameter  $U$ . The  $i$  orbitals possess a local energy value  $\epsilon_0$  that can be tuned by a gate voltage  $V_g$  and are mutually coupled by the hopping matrix elements  $t''$  and  $t'''$ . These parameters are written in terms of an asymmetry quantity  $\Delta t$ , being  $t'' = t + \Delta t$  and  $t''' = t - \Delta t$ . If  $\Delta t = 0$ , the molecule presents an FSC, corresponding to its configuration before the thermal annealing. For  $\Delta t \neq 0$ , the molecule undergoes a transition to a TSC that, considering the interaction of its orbitals to the Cu substrate through the hopping  $t'$ , corresponds to the molecular configuration after the annealing process, as reported in ref 42.

The total Hamiltonian of the system, not including the STM tip and its interaction with the molecule, is given by

$$\hat{H}_T = \hat{H}_m + \hat{H}_s + \hat{H}_{ms} \quad (2)$$

where the metal is described by the tight-binding Hamiltonian

$$\hat{H}_s = \sum_{\sigma,\alpha,\beta} t_{\alpha,\beta} (\hat{c}_{\alpha\sigma}^\dagger \hat{c}_{\beta\sigma} + \text{H. c.}) \quad (3)$$

The parameter  $t_{\alpha,\beta}$  corresponds to the hopping matrix element between site  $\alpha$  and  $\beta$  of the metallic substrate, while the Hamiltonian representing the interaction between the four molecular lobes and their nearest metallic sites can be written as

$$\hat{H}_{ms} = \sum_{\sigma,\alpha,i=1}^4 t' (\hat{c}_{i,\sigma}^\dagger \hat{c}_{\alpha,\sigma} + \text{H. c.}) \quad (4)$$

The proposed Hamiltonian takes into account the essential features of the complex molecular structure of phthalocyanines and porphyrins.<sup>45–47</sup> It adequately describes the physics of the system including the Kondo properties that appear when the molecule is distorted. Analyzing the molecular model in its most simple noninteracting and symmetric version, where  $t'' = t''' = t$  and  $U = V_g = t' = 0$ , we identify four energy levels, namely,  $\epsilon_1 = -2t + \epsilon_0$ ,  $\epsilon_2 = \epsilon_3 = \epsilon_0$  and  $\epsilon_4 = 2t + \epsilon_0$ . Thus, considering the molecule adsorbed in the FSC, the level initially at  $\epsilon_1$ , for the isolated molecule, is filled, given a complete-shell configuration. The doublet  $\epsilon_2 = \epsilon_3$ , next to the Fermi energy, remains empty above this level, as occur with the level of energy  $\epsilon_4$ .

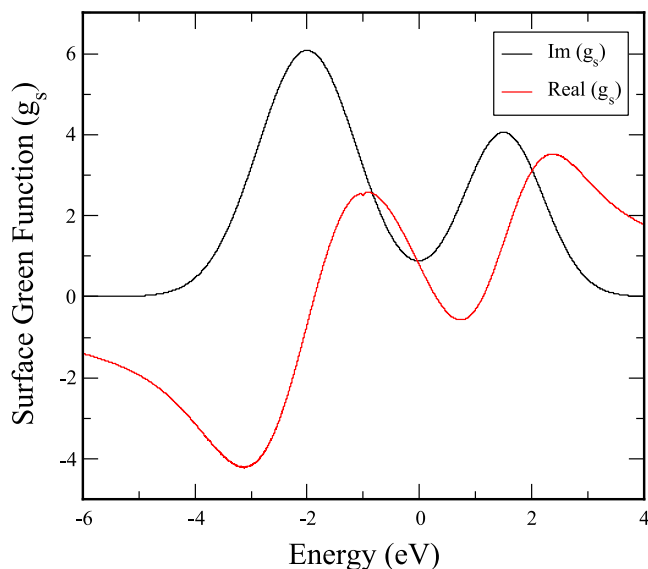
With the addition of the other terms of the Hamiltonian, we then take this scenario as representative of the adsorbed molecule on the metal surface in the FSC. This configuration can be modified to the TSC by considering finite values for the parameter  $\Delta t$  ( $\Delta t \neq 0$ ) that quantifies the molecular distortion introduced by the annealing. This distortion lifts the degeneracy of the LUMOs by changing the hopping matrix elements  $t''$  and  $t'''$ .

The local density of states (LDOS) at the molecular lobe  $i$ ,  $\rho_i(E)$ , is calculated by the equation

$$\rho_i(E) = \frac{1}{2\pi} i [G_i^{(r)}(E) - G_i^{(a)}(E)] \quad (5)$$

where the retarded and advanced Green functions,  $G_i^{(r)}$  and  $G_i^{(a)}$ , respectively, are obtained using the equation of motion method.<sup>48</sup> The coupling with the metal is considered by incorporating the Green function  $g_s(E)$  of the metal substrate in the equation of motion of the Green functions. The

imaginary part of  $g_s(E)$  is numerically calculated from the LDOS of the Cu(110) surface, qualitatively estimated from ref 49. It is represented by the black curve of Figure 2. Additionally, the real component of  $g_s(E)$ , the red curve presented in Figure 2, is obtained by taking the Hilbert transformation of the imaginary component of this function.



**Figure 2.** Green function of the metallic surface. The Fermi level is taken at  $E_f = 0$ .

To solve the problem, the Coulomb interaction is considered within the Hubbard III<sup>50</sup> and the finite- $U$  mean field slave boson (finite- $U$  SBMFA)<sup>51,52</sup> approximations. The first approximation describes the system out-of-the Kondo regime,  $T > T_k$ , and is used to solve the Hamiltonian of eq 1 using the alloy analogy formulation described in ref 50. Each lobe is considered as an impurity with energy  $\epsilon_0 + V_g$  or  $\epsilon_0 + V_g + U$ , associated, respectively, to the probabilities  $1 - n_{i\bar{\sigma}}$  and  $n_{i\bar{\sigma}}$ , being  $n_{i\sigma} = n_{i\bar{\sigma}} = n_i$  the electronic occupation per spin of the  $i$ -th lobe, a quantity that is spin independent. The Green functions are then obtained for the system, supposing that lobe  $i$  assumes energy values of  $\epsilon_0 + V_g$  or  $\epsilon_0 + V_g + U$  with probabilities  $1 - n_i$  and  $n_i$ . This approximation does not access the Kondo physics but permits to obtain a good description of the system in the Coulomb blocked regime. Alternatively, the slave boson formalism provides results which are valid in the region close to Fermi energy  $E_f$ , corresponding to the low-temperature regime,  $T < T_k$ . It incorporates the physics of the Kondo regime through the renormalization of the couplings and of the energy  $\epsilon_0$  of the local state of the molecular lobes, leading to a noninteracting renormalized system. In this case, it is simple to calculate the LDOS and the occupation of the molecular lobes. We incorporate the STM tip, represented by a semi-infinite noninteracting chain, with its initial site  $n = 0$  interacting with the molecular lobe  $i$ , by the Hamiltonians

$$\hat{H}_{\text{tip}} = \sum_{m,n} t_{m,n} (\hat{d}_{m\sigma}^\dagger \hat{d}_{n\sigma} + \text{H. c.}) \quad (6)$$

and

$$\hat{H}_{\text{tip,M}} = t_{\text{STM}} (\hat{c}_{i\sigma}^\dagger \hat{d}_{0,\sigma} + \text{H. c.}) \quad (7)$$

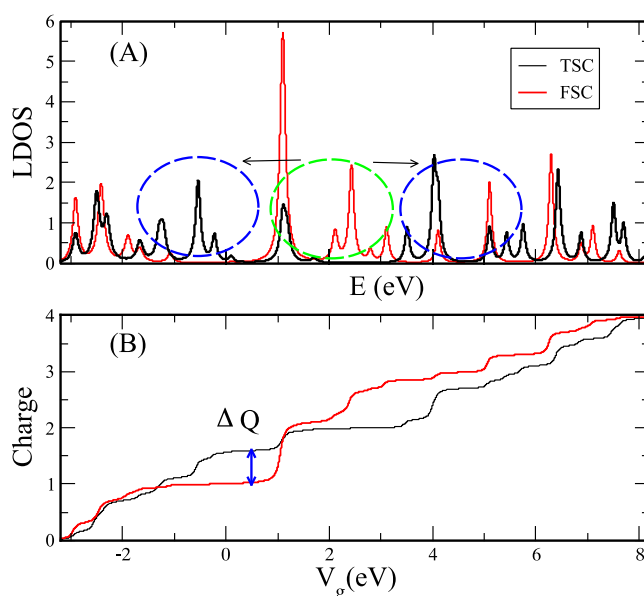
The DC between the STM tip and one of the molecular lobes can be obtained using the Keldysh formalism<sup>48,53</sup> (see Supporting Information)

$$\frac{dI}{dV} = 4\pi^2 t'^2 t_{\text{STM}}^2 \rho^{\text{STM}}(V) \rho^{\text{Cu}}(V) [|G_{11}(V)|^2 + |G_{12}(V)|^2 + |G_{13}(V)|^2 + |G_{14}(V)|^2] \quad (8)$$

In this expression,  $\rho^{\text{Cu}}$  and  $\rho^{\text{STM}}$  are the LDOS of the Cu substrate and the semi-infinity noninteracting linear chain that corresponds to the STM tip, respectively. The functions  $G_{ij}(V)$  are the equilibrium Green functions between lobes  $i$  and  $j$  of the molecule.

## RESULTS AND DISCUSSION

We start by presenting, in Figure 3, the LDOS corresponding to the molecular lobes (panel (A)) and the molecular charge



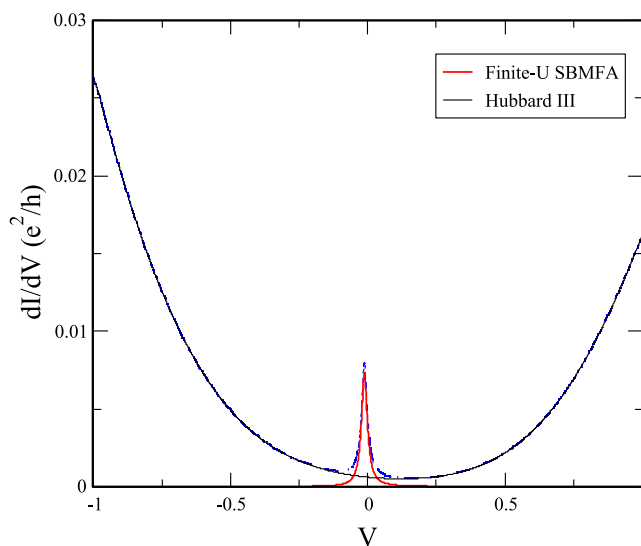
**Figure 3.** Figure presents in panel (A) the LDOS calculated at the lobes of the adsorbed molecule for the system with the Fermi energy  $E_f = 0$ . In panel (B), we show the molecular charge per spin as a function of gate potential  $V_g$ . The results of both panels were obtained within the Hubbard III approach and considering the system before (red line) and after (black line) the thermal treatment.

per spin (panel (B)) as a function of a gate potential  $V_g$ , which, applied to these lobes, tunes the local energy level  $\epsilon_0$  and, as a consequence, its charge. These LDOS results were obtained within the Hubbard III approximation that provides a reliable charge evaluation of the molecular orbitals, although it does not describe the low energy properties of the system, not capturing, thus, the Kondo physics reported in ref 42. The LDOS was obtained assuming the local energy levels at the lobes to be  $\epsilon_0 = 1.1$ , a Coulomb interaction  $U = 3.0$ , and a coupling to the substrate matrix element of magnitude  $t' = 0.06$ , all of them measured in eV. Also, for the FSC configuration, the couplings between the lobes are  $t'' = t''' = 2$ , while, for the TSC, these couplings are  $t'' = 0.8$  and  $t''' = 3.2$ , with an asymmetry parameter  $\Delta t = 1.2$ . The values of the parameters were taken to reproduce the experimental results of ref 42. Specially, the parameter  $\Delta t$  is related to the distances between the molecular lobes of the distorted molecules, which can be estimated from Figure 2 of this reference. The value of

these parameters can be modified without changing the physical mechanism behind Kondo physics. In both panels of Figure 3, red curves represent the FSC and black curves the TSC. Also, the Fermi level of the metal substrate was supposed to be  $E_f = 0$ . As we can see in this figure, for the FSC (red curve), the LDOS presents a structure composed of two resonances below the Fermi energy, in a region around  $E \approx -2.5$ . It indicates the double occupation of the orbital HOMO, the energy difference between these resonances being derived from the local Coulomb interaction  $U$  in the lobes. Additionally, the LDOS presents a strong resonance right above the Fermi level at  $E \approx 1.1$  (green circle). This resonance comes from the two degenerated orbitals already present in the isolated molecule at  $E = \epsilon_0$ . These orbitals are empty because their energy is above the metal Fermi level in the FSC and, therefore, the molecule does not possess magnetic properties in this configuration. The other resonance structures are of less importance in relation to the physics we analyze, as they are localized at  $E \approx 2.5$ ,  $E \approx 4.4$ , and  $E \approx 6.0$ , far from the Fermi energy.

In fact, in the FSC configuration, assuming  $E_f = 0$ , the HOMO is completely filled, with one electron per spin, as can be seen from the red curve in panel (B) of the figure, for a region where  $V_g \approx 0$ . As a consequence, the total spin of the molecule equals to zero. The spectral weight above the Fermi energy, shown in the red curve of panel (B), is indicated in panel (A) by a green dashed circle. After the annealing process, the molecule undergoes a transition to the TSC, where the orbital energies are modified, producing a flow of charge into the molecule. In fact, in panel (B), we can see that the molecular charge in the TSC is larger than in the FSC by an amount  $\Delta Q$  which results from the degeneracy breaking of the LUMOs, described by the splitting of its associated spectral weight. In the LDOS represented by the black curve in panel (A), for the TSC, we can see, from the blue dashed circles, that nearly half of this spectral weight is pushed downward to an energy region below  $E_f$ , while the other half is pushed upward, above the Fermi energy. Also, the Coulomb repulsion plays a central role regarding the configuration of charge in the molecule since, due to its effect, the splitting produces the electronic charge to increase by only one electron. As a consequence, the molecule in TSC has an odd number of electrons and therefore a net spin. This is the main effect of the symmetry breaking induced by the annealing process: the molecule results in a partially filled shell and a total spin  $S_t = 1/2$ . Under these conditions, the system possesses a Kondo ground state that determines the transport properties across the molecule.

Now we analyze the emergence of the Kondo physics in the system, in the TSC, considering the structure of the DC measured in ref 42 as a function of the bias voltage  $V$ . To this end, considering the model we propose, we present two results for the DC, one obtained within the Hubbard III approach and another through the finite- $U$  SBMFA. The first, corresponding to the black curve in the Figure 4, does not describe the low energy physics of the system, not reproducing the Kondo resonance at zero bias reported in the experimental work. By contrast, it very well describes the DC for higher energies, quantitatively reproducing the experimental result in this energy. Conversely, the finite- $U$  SBMFA result, corresponding to the red curve in the figure, does not describe the system for higher energies but captures its low energy physics, in the region near



**Figure 4.** DC as a function of the bias voltage  $V$  calculated using the Hubbard III (black line) and the finite- $U$  SBMFA (red line). The parameters adopted are  $E_f = 0$ ,  $U = 3.0$ ,  $t' = 0.06$ ,  $t_{\text{STM}} = 0.01$ ,  $t'' = 2.0 - \Delta t$ , and  $t'' = 2.0 + \Delta t$ , with  $\Delta t = 1.2$ . The blue dashed curve is a simple superposition of the Hubbard III and finite- $U$  SBMFA, indicating the complementary character of these methods in reproducing the experimental results in all the energy range considered.

zero bias, where we can see the emergence of the Kondo resonance reproducing the result observed in the experimental work. The dashed blue curve in the figure is a simple superposition of the results obtained by the two methods and indicates its complementary character that is capable of describing the experimental result in all the energy ranges considered.<sup>42</sup>

The Kondo resonance observed at zero bias is produced by the spin fluctuation in the partially filled orbital HOMO of the molecule. In the transition from the FSC to TSC, the breaking of the degeneracy and the transformation of one of the LUMO into a single occupied HOMO do not depend upon any possible changes of the coupling between the molecule and the metal surface. As this process is responsible for the appearance of a Kondo ground state in the system after annealing, we conclude that the emergence of these properties, reported in ref 42, is not associated with any possible increase of the molecular interactions with the metal due to the distortion produced by the annealing.

## CONCLUSIONS

In this paper, we elucidate the physics underlying the emergence of Kondo state properties reported by Maughan et al.<sup>42</sup> in an ensemble of TiOPc molecules adsorbed on a Cu(110) surface when the system is submitted to thermal annealing. This is a treatment under which the TiOPc molecules adsorbed on the “O-up” configuration, initially possessing a FSC, characterized by the relative position of its four lobes, have their structures distorted. We show that although this distortion may in principle modify the interaction of the molecular lobes with the metal substrate, what really controls the new physics introduced by the annealing process is the displacement of the energy levels of the molecular orbitals, breaking the degeneracy of the two initially empty LUMO orbitals due to the thermal treatment. In fact, the

molecular distortion permits the entrance of one electron in the LUMO, which is pushed under the Fermi energy due to the breaking of the orbital degeneracy. With one unpaired spin, the molecule then becomes magnetic. The Kondo ground state emerges as a result of screening of the molecular spin by the metal surface itinerant electron spins.

## ■ ASSOCIATED CONTENT

### SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpcc.3c07751>.

Calculus of the differential conductance  $\frac{dI}{dV}$  between the STM tip and the molecular lobe 1 by the nonequilibrium Green function Keldysh formalism (PDF)

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### Notes

The authors declare no competing financial interest.

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