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Theoretical study of Di-Amino-Triazine adsorption on Cu(110) and Au(111) surfaces.

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Abstract

The diffusion of adatoms or molecules on metal surfaces is the lifeblood of many phenomena as growth. Various microscopic experiences realized by STM (Scanning Tunneling Microscopy) or by AFM (Atomic Force Microscopy) techniques at CEMES center show that the determination of some variables is very necessary to overcome many experimental difficulties. In this paper, MM_4 (Molecular Mechanics (2003)) method and ASED+ codes have been used to determine the position of the Lander molecule equipped with dual Di-Amino-Triazine (DAT, $C_{64}H_{68}N_{10}$), 1,4-bis(4-(2,4-diaminotriazine)phenyl)-2,3,5,6-tetrakis(4-*tert*-butyl phenyl) benzene on the Cu(110) and Au(111) surfaces. The same tools have estimated the rotation and the diffusion barriers on the substrates. The ESQC (Elastic Scattering Quantum Chemistry) program has been developed to calculate the image and to describe the adsorbed molecule form. The adsorption of energies, geometries, diffusion and rotation barriers are very well described by this new semi-empirical technique of calculation; opening the way of optimizing larger conjugated molecule on the surface.

Keywords: Lander molecule, DAT, Adsorption, Cu(110), Au(111), MM4, ASED+, ESQC, PM6.

1. Introduction

The first STM experiments performed are concerned in some lateral manipulations on metal surfaces such as moving atoms [1], molecules [2], unities and making connections that could not be achieved by a direct input of materials or by self-assembly. In the case studied the adsorbate does not leave the surface during operations (to ensure the stability of atoms and molecules manipulated) as it cannot be performed under conditions of high vacuum and low temperature. It is now known that the use of the STM tip helps to "push", "pull" or "drag" a single atom or molecule on a surface with an accuracy better than 0.01nm [3, 4].

Molecular Landers are a class of compounds in which an aromatic backboard (the π system) is decoupled from the underlying, which substrates via bulky spacer groups (e.g., tert-butyl moieties, C_4H_9). These Molecular systems are required because the functional organic molecules arranged on the surface. Those are playing an important role in the rapidly growing field of nanotechnology, particularly in areas as molecular electronics and molecular recognition [3-7]. Molecular Landers studies have recently attracted much attention because of its highly efficient charge transfer along the dorsal Molecular [8, 9]. Most strikingly, Landers molecules can behave as molecular molds thanks to their capacity of capturing and assembling metal atoms in well-defined metal nanostructures in their cavity and their attractive interaction with aromatic metal atoms. Many studies have been reported in literature concerning molecular Lander effects, taking as example Nanostructuring Cu surfaces using custom-designed molecular molds [10] and trapping metal atoms in the cavity under the aromatic board [7].

In 2009, the CEMES group has extended these previous studies by investigating a novel Lander-type molecule,1,4-bis(4-(2,4-diaminotriazine)phenyl)-2,3,5,6-tetrakis(4-*tert*-butylphenyl)benzene(DAT, $C_{64}H_{68}N_{10}$), which consists of a hexaphenyl benzene core with four *tert*-butyl groups as spacer legs and two diaminotriazine functional groups positioned at opposite sides of the molecular board [8]. The compound is specifically designed for studies into organization of Lander compounds by intermolecular hydrogen bonding interactions, which are enabled by the peripheral diamino triazine groups. Particularly interesting potential application to create heteromolecular, one-dimensional chains by co-adsorption of DAT with other Lander-type compounds equipped with functional moieties that are complementary to the diamino triazine groups [11].

The first aim of the present work is to perform a theoretical study of Di-Amino-Triazine adsorption on Cu(110) and Au(111) surfaces in order to optimize the adsorbate molecule structure and find the rotation and the diffusion barriers [12-14]. For this reason, MM4 (2003) code based on molecular mechanics [15] and the semi-empirical atom superposition electronic delocalization molecular orbital ASED-MO code [16] have been used to explain theoretically the adsorption of DAT, ND molecules on the surface. In the second aim we want to calculate STM images on the surfaces by using extended Hückel molecular orbital-elastic-scattering quantum chemistry (EHMO-ESQC) and to confirm the experiments results obtained by iNANO group [11,17].

The calculations of the molecular conformation on the Cu(110) and Au(111) surfaces were performed by using the semi-empirical atom superposition and electronic delocalization molecular orbital (ASED-MO) [16], this method is based on the extended Hückel molecular orbital theory; it is a powerful numerical tool which describe the behavior of large molecules [18]. Note that a description of Van der Waals forces based on the MM4 force-field [19] is added with the ASED+ version [20]. Standard parameters for carbon, hydrogen and nitrogen were used [21]. Moreover, ASED+ results have already shown a very good agreement with DFT results [20].

The calculations of STM images were performed using extended Hückel molecular orbital-elastic-scattering quantum chemistry code (EHMO-ESQC) [22, 23]. This method has already demonstrated its ability to accurately calculate STM images of several physical systems, ranging from atoms to large molecules adsorbed on metallic, semiconducting, and thin insulating films as well. Most of these examples demonstrate that method has to describe the electronic structure to reproduce the experimental results. Another important point is the determination of a molecular conformation inside the STM junction after relaxing the molecule on the surface with ASED+ and MM4(2003) codes [20]. This force field is well-adapted for such a system as the molecule physisorbed on the gold surface [10, 24, 25].

1. Results and discussion

1.1- Molecular conformations of DAT and ND adsorbed on Cu(110) and Au(111) surafces

In the gas phase, the DAT molecule is about 22 Å long and 15 Å wide and it consists of a central benzene ring connected to six phenyl groups by σ-bonds and four *tert*-butyl groups and two diamino-triazine attached to a phenyl ring. The last one is perpendicular to the DAT group due to the interaction between the nitrogen atoms of the triazine and the hydrogen atoms of the phenyl which fixes the plane of the DAT orthogonally to the plane of the phenyl. Once, the DAT molecule adsorbed, the "leg" spacer groups guide the final conformation and so their phenyl rings interact with the phenyl connecting to the DAT groups and this phenyl is no longer perpendicular to the surface plane. As the DAT group seems to rotate quite easily with respect to the phenyl ring, it does not lie parallel to the surface in consequence and instead assumes the orientation shown in Figure 1 (a) and (b). Several geometrical orientations of this molecule were examined at each site by performing rotations from 0 to 360 degrees around z axis perpendicular on the surface.

A variation of the potential energy of an adsorbed DAT ($C_{64}H_{68}N_{10}$) molecule on Cu(110) substrate has been studied and presented in Figure 2(a). The labels T, B and H refer to adsorption sites as defined in Figure 2. denoted to top site, bridged site and hollow site respectively. Several rotation barriers of the DAT molecule on Cu(110) surface have been calculated. The results obtained were 378 meV for hollow site, 641 meV for the bridge site and 479 meV for the top site. The diffusion barrier is estimated to be equal to 650 meV and the adsorption energies obtained by these calculations are between 3.41 eV and 3.47 eV.

It can be observed that the top site is the most stable with θ=0 degree and the long axis of the molecular board (melamine-melamine) is oriented along the [001] direction, and that the difference relative to the hollow and bridge sites is 20 meV and 30 meV, respectively This gives an adsorption distance of 4.35 Å between the central benzene ring of the molecule and the Cu(110) surface on a top site (Figure 1(a).).

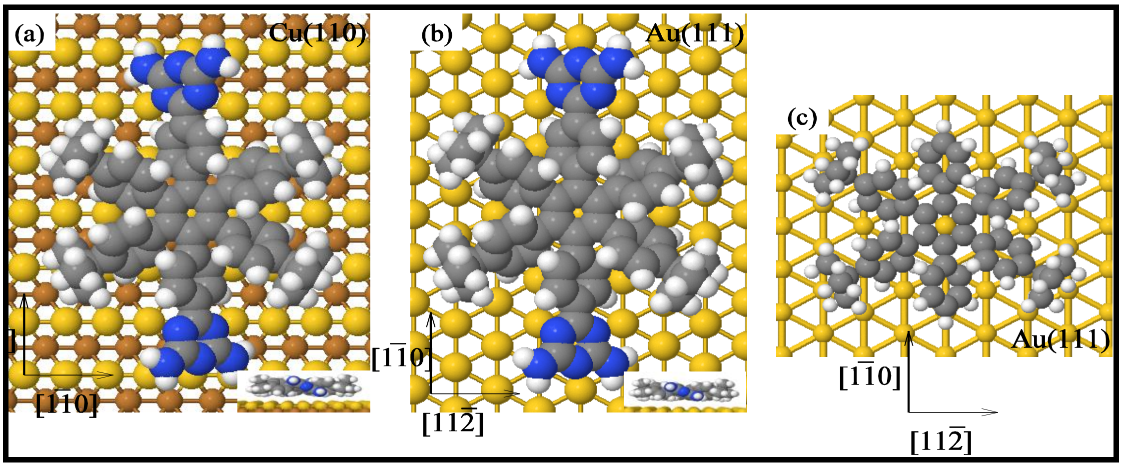

Figure 1: (a) Space-filling model of DAT molecule, (1,4-bis (4-(2,4-diaminotriazine)phenyl)-2,3,5,6-tetrakis(4-tert-butyl-phenyl)benzene ($C_{64}H_{68}N_{10}$)) consisting of a central benzene core connected through phenyl groups to four tert-butyl and two diamino-triazine groups, adsorbed on the C(110) surface. (b) Space-filling model of DAT molecule adsorbed on the Au(111) surface. (c) Space-filling model of Lander-ND molecule ($C_{58}H_{62}$) on the Au(111) surface. Where the white, blue and grey spheres present Hydrogen, Nitrogen and Carbon atoms respectively, and all other spheres describe the surface atoms.

A variation of the potential energy of an adsorbed DAT ($C_{64}H_{68}N_{10}$) molecule on Au(111) substrate has been studied for each site T (top), H (hollow) and B (bridge) has been determined. This is considered in Figure 2(b). The curves describe the adsorption energy variation for the three sites by considering a relaxed molecule with all the degrees of freedom free to relax for each rotation. The most favourable position is above the top site (about 42 meV) with the long axis of the molecular board (melamine-melamine) orientated along a [110] direction of the Au(111) substrate (Figure 1(b)). Figure 2(b) shows also that there is not much variation in adsorption energy between different configurations of the DAT molecule adsorbed on Au(111) surface. Therefore the potential governing the interaction between the DAT molecule and the Au(111) surface is a potential of planar molecule able to perform high rotations and translations over a flat surface with a diffusion barrier equal to 228 meV Figure 2 (b). Quantitatively, the distances $h_{DAT\text{-}Au(111)}$ have the same order of magnitude (4.55 Å), with a simple relationship between distance and adsorption energy.

While the difference of diffusin barriers (650 meV Cu(110) and 228 meV Au(111)) is relatively large. This difference can be explained by the structure of the Au(111), Cu(110) surfaces and the DAT molecule. These rotation and diffusion barriers are in qualitative agreement with the experimental study obtained for DAT adsorbed on Cu(110) surface at low temperature [11].

To understand the role played by functional groups (diamino-triazine) in the manipulation of the DAT molecule on the surface, Lander ND ($C_{58}H_{62}$) has been used, because it is considered as a derivative of the DAT molecule, for comparison. The ND molecule has the same structure of the Lander DAT except that the diamino-triazine groups are missing as shown in Figure 1 (c). The Figure 2 (c) shows that the variation of the potential energy of ND molecule ($C_{58}H_{62}$) on Au(111) substrate. ND Lander is adsorbed on a top site with a distance closest to the surface $h_{ND\text{-}Au(111)}$=4.45 Å and instead of 4.50 Å when it is in others sites. This can be explained by repulsive interaction between the surface and the molecule, and it has almost the same characteristics of adsorption of the DAT molecule. The Comparison between the diffusion energy in DAT (228 meV) and in ND (266 meV) molecules adsorbed on the Au(111) surface demonstrate that the melamine groups and the sigma bond phenyl-melamine offer more freedom inclination and rotation, accordingly to facilitate the manipulation of the DAT molecule on the surface. These results are in perfect agreement with the experiment's results obtained by our group [11,14].

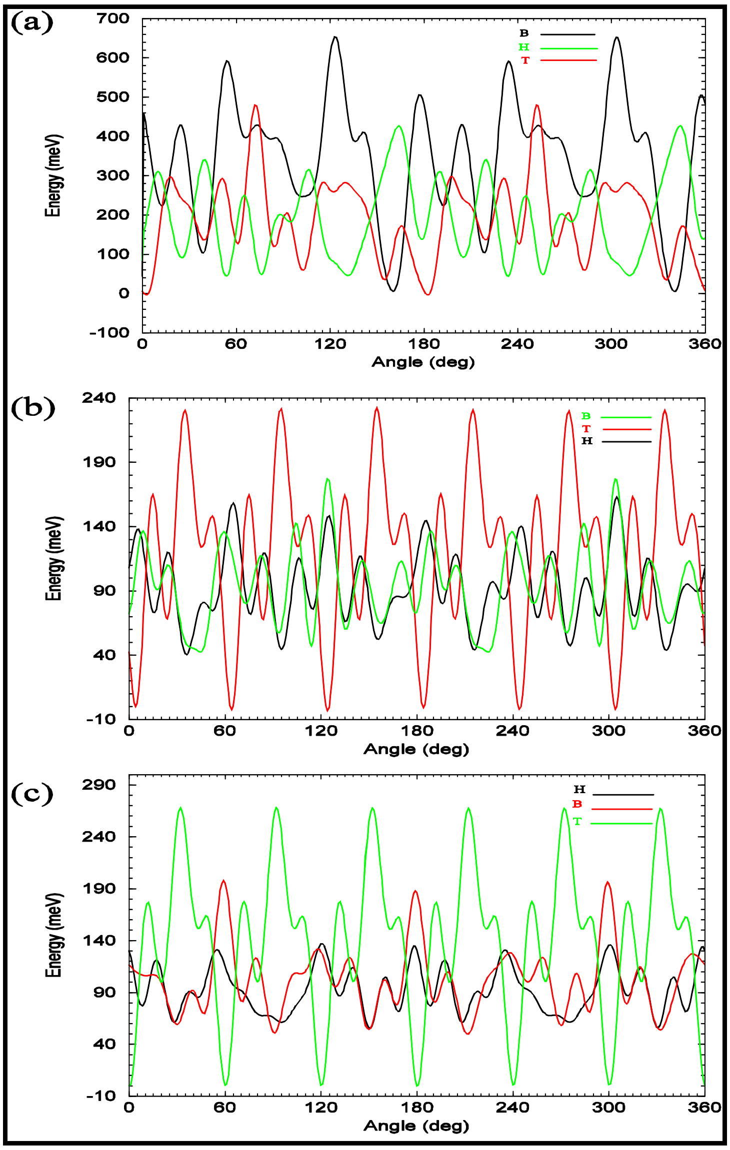

Figure 2: (a) Variation of the potential energy of an adsorbed DAT ($C_{64}H_{68}N_{10}$) molecule on Cu(110) substrate. (b) Variation of the potential energy of an adsorbed DAT ($C_{64}H_{68}N_{10}$) molecule on Au(111) substrate. The two minima are separated by $2\pi/6=60°$ and correspond to the symmetry of the molecule and the surface. (c) Variation of the potential energy of ND molecule ($C_{58}H_{62}$) on Au(111) substrate, for different sites top (T), bridge (B) and hollow (H) according to the relative orientation. The zero of the energy axis is based on the lowest energy found by calculation.

1.2- Theoretical simulation of STM images by ESQC method

The ESQC (Electron Scattering Quantum Chemistry) method [22,23] fully describes the molecular junction, particularly, molecule-metal interface by its geometry and chemical composition without a priori assumption of the shapes and the values of the metal-molecule coupling. The hamiltonian of the junction is constructed from the molecular orbital method of extended Hückel approximation. The success of the ESQC method has previously been demonstrated [26-29]. The contrast of colors reflects the third dimension, namely z position of atoms, like our partners experimenters we‘ve estimated the height of the tip scans along lines of the system studied on Cu(110) [11]. Height of the peak in fact corresponds to the height required to follow a particular route.

Figure 3 (a) presents the theoretical image of the DAT molecule on Cu(110) surface, this figure is characterized by a rectangular shape from four light lobes (12.0 Å×7.0 Å) and some sub-protrusions in the center. The calculated image of the DAT molecule on the Au(111) substrate. Figure 4 (a) has almost the same characteristics as the image found on the Cu(110) surface. The rectangular shape from four light lobes (13.5 Å × 6.5 Å) are attributed to the four tert-butyl legs [7,10,30], the sub-protrusions are attributed to the hexa-phenyl rings which are connected to the central benzene core by σ bonds [31]. Interestingly, both surfaces were characterized by the absence of a signal for melamine groups, suggesting that these groups make only a minor contribution to the tunneling current. This is explained by the theoretical modeling studies elsewhere, which show that molecular orbitals with a preponderant weight on the terminal amino groups lie outside the range of bias voltages used. Furthermore, the simulated line scans Figure 3 (b), Fig 3 (c), Fig 4 (b) and Fig 4 (c) are also consistent with those experimental results [11,14].

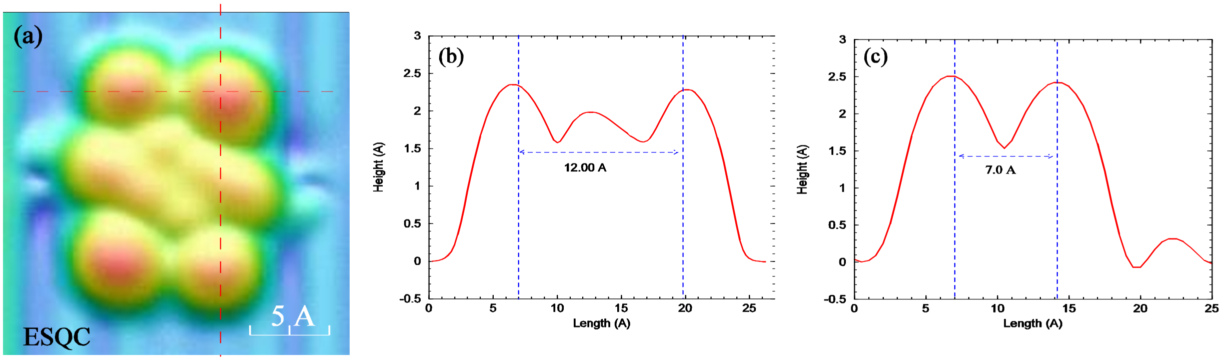

Figure 3: (a) ESQC image calculation of the DAT molecule on the Cu(110) substrate (V_t= -1.73 V; I_t=-0.66 nA). (b) and (c) Profiles showing the calculated apparent height of the DAT with respect to the Cu(110) surface (2.5 Å) and distances between the light lobes (12.0 Å×7.0 Å) respectively as showing in (a).

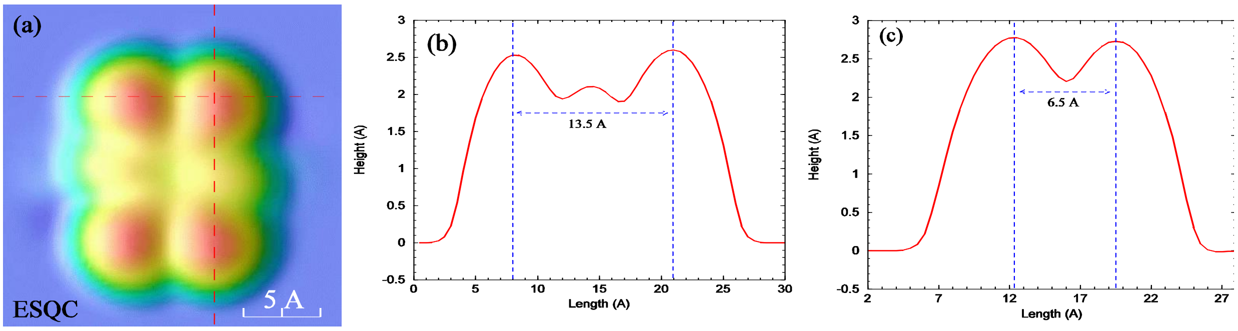

Figure 4: (a) ESQC image calculation of the DAT molecule deposited on the Au(111) substrate (V_t= 1.48 V; I_t=0.32 nA). (b) and (c) Profiles showing the calculated apparent height of the DAT with respect to the Au(111) surface (2.7 Å) and distances between the light lobes (13.5 Å×6.5 Å) respectively as showing in (a).

To describe the STM image calculations (Figure 4 (a) and Figure 3 (a)) and the reason why the DAT groups are not imaged, we have performed a molecular orbital analysis of the Lander-DAT molecule alone to track where the DAT molecular orbitals (MOs) are mainly located in energy. The analysis was performed using the PM6 method as implemented in MOPAC2009 code [32,33]. The calculated result, displayed in Figure 5, shows that in all cases we notice that the electron density of the molecular orbitals (MOs) of the DAT molecule is delocalized over the entire molecule and it is higher in both melamines groups for LUMO (Lowest Unoccupied Molecular Orbital) and LUMO+1 orbitals, for HOMO (Highest Occupied Molecular Orbital) the electron density is high on the central part and the feet (tert-butyl) and very low in both melamines groups while HOMO-1 is characterized by a high density on the core and on the feet (tert-butyl) and average over melamines groups. According to these results performed show the reason why the DAT groups are not imaged at low bias voltage. Where the bias voltage is lower than the highest occupied molecular orbital (HOMO)-lowest unoccupied molecular orbital (LUMO) gap of the molecule [14].

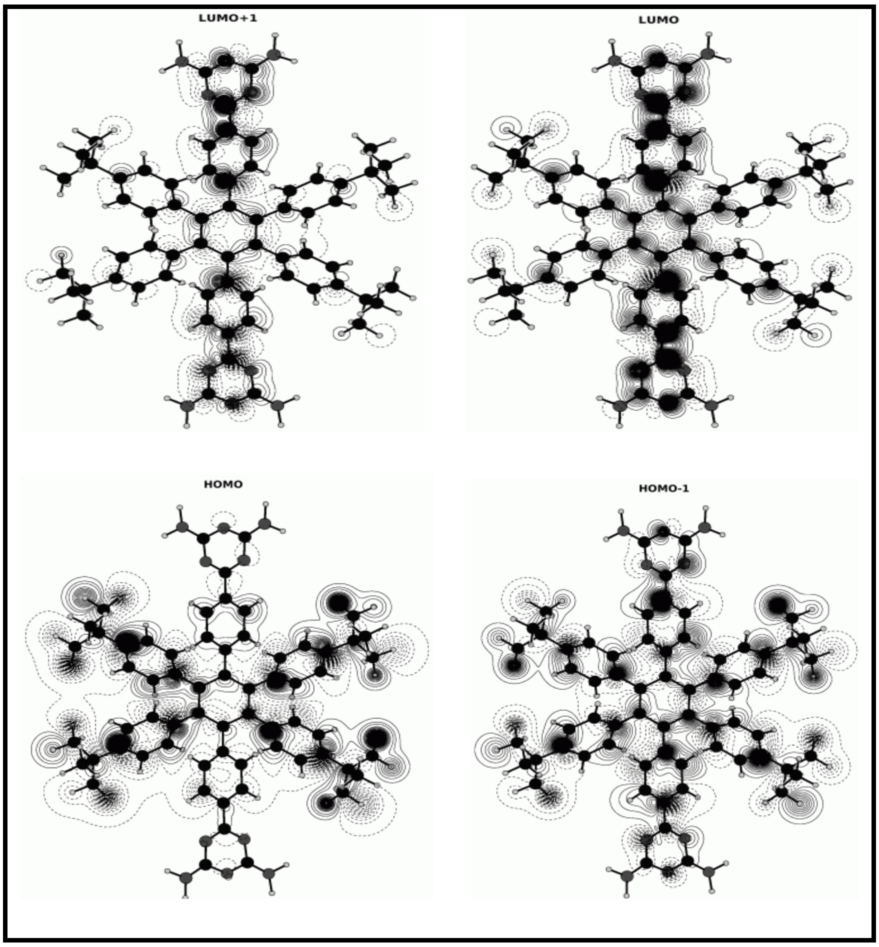

Figure 5: Calculated occupied and unoccupied molecular orbitals for DAT molecule in vacuum (HOMO-1, HOMO, LUMO and LUMO+1).

Conclusion

Overall, by means of MM4 method and ASED+ codes, we have studied the interaction of a specially designed Lander DAT molecule on Cu(110) and Au(111). On Cu(110), we find that the DAT-Cu(110) interaction is much stronger. However, on Au(111), the DAT molecule is facile to move away under STM manipulation. This comparison shows that the diffusion barrier of this DAT molecule is noticeable higher on Cu(110) as compared to Au(111). Considering that Au is the most inert metal, it is quite reasonable that the DAT-Au(111) interaction is much less stronger than the DAT-Cu(110) [11]. What is more important is the fact that the corrugation of the diffusion barrier on Au(111) surface is obvious small, in contrast of the Cu(110). Finally, ESQC method and Mopac2009 codes have been developed to calculate the image and to describe the adsorbed molecule geometry. The theoretical results obtained are in perfect agreement with the experimental ones, which are registered for the organic molecules adsorbed on metal substrates [7,10,34-36].

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