STM Image Simulation: Effect of the Number of Tunneling States and the Isosurface Value

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ABSTRACT

In this work, Scanning Tunneling Microscopy (STM) images were simulated for the organic molecule 3,4,9,10 perylenetetracarboxylic dianhydride (PTCDA) to study the effect of the number of tunneling states and the integrated Local Density of States (LDOS) isosurface value. Local Density Approximation of Density Functional Theory (DFT-LDA) calculations were performed to achieve the simulated images under the Tersoff and Hamann approximation. The number of tunneling states has a strong effect on the image appearance of the patterns. Intermediate isosurface values for the integrated LDOS produce good resolution and matching in relation to the experimental STM image. Both parameters seem to be of significant importance for STM image simulation.

INTRODUCTION

Since the s-wave-tip model [1] was established, an STM pattern can be interpreted as reflecting properties from the sample without strong influence of the probe tip. Using this model, a simulated constant current STM image can be made with a number of LDOS isosurface values integrated over an energy range near the Fermi level [2]. By matching the simulated image with the experimental one, the validity of the model is checked. Although it is known that the tunneling current and the applied bias voltage between the sample and the tip modulate the STM image ([3], [4]), it has not been explicitly pointed out how both variables affect the image appearance. The bias voltage and the tunneling current are closely related to the number of tunneling states and the integrated LDOS. In this work, we analyse the effect of the number of tunneling states and the integrated LDOS isosurface value in the simulation of STM images with Tersoff-Hamann approximation for the organic semiconductor PTCDA (see figure 1), which is supposedly weakly adsorbed onto a conducting substrate.

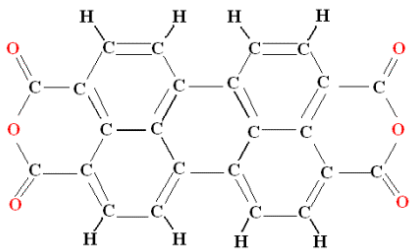

Figure 1. 3,4,9,10 perylenetetracarboxylic dianhydride (PTCDA).

METHODOLOGY

If a constant current STM experiment is assumed to image a molecule weakly adsorbed onto a substrate, and the Tersoff and Hamann approximation [1] is ruling, it is apparent that the STM patterns produced for a molecule will depend mainly on its electronic structure and both the applied bias voltage and the tunneling current used in the experiment. In simulating STM images main contributions come from local densities of states near the Fermi energy, so by extending the Tersoff and Hamann [1] expression the tunneling current is obtained as follows:

$$I_t = (const) \int_{E_F}^{E_F+eV} \rho(\mathbf{r}, E) dE \tag{1}$$

where

$$\rho(\mathbf{r}, E) = \sum_i |\psi_i(\mathbf{r})|^2 \delta(E - E_i) \tag{2}$$

is the local density of states, ψ_i the sample eigenvector with energy E_i, E_F the Fermi energy, V the applied bias voltage and e the charge of the electron.

By integration, (1) becomes

$$I_t = (const) \sum_{i=1}^{n} |\psi_i(\mathbf{r}_0)|^2 , \tag{3}$$

where $\mathbf{r}_o$ labels the center of curvature of the tip, n is the number of tunneling states which fulfills the condition:

$$(\varepsilon_n - E_F) \leq eV , \tag{4}$$

ε_n being the eigenvalue for the n^{th} state.

In the expression (3), i = 1 corresponds to the Highest Occupied Molecular Orbital (HOMO) for filled states, or the Lowest Unoccupied Molecular Orbital (LUMO) for empty states. The summation of the n terms represent the integrated LDOS which can be written:

$$Integrated LDOS = \sum_{i=1}^{n} |\psi_i(\mathbf{r}_0)|^2 . \tag{5}$$

In this work the organic semiconductor PTCDA was used to simulate its STM patterns based on equation (3) and study the effect of both the number of tunneling states (n) and the isosurface value of the integrated LDOS. Electronic structure and geometry optimization calculations for the isolated molecule were made with the program *Gaussian 98* [5], performing the method DFT-LDA/6-31G**, from which the Density of States (DOS) and the integrated LDOS were plotted. The visualization of the integrated LDOS isosurfaces were performed with the program *Insight II* [6].

RESULTS

Effect of the number of tunneling states

Table I shows some eigenvalues close to the Fermi level for filled and empty states of PTCDA obtained with the DFT-LDA method and *Gaussian 98* [5].

Table I. Eigenvalues close to the Fermi level of PTCDA. The number of tunneling states (n) are written in **bold** characters for filled states and in *cursive* ones for empty states.

MOLECULAR ORBITAL	EIGENVALUE (eV)	NUMBER OF TUNNELING STATES (n)
HOMO –10	-8.7	**11**
HOMO –9	-8.6	**10**
HOMO –8	-8.1	**9**
HOMO –7	-8.1	**8**
HOMO –6	-8.1	**7**
HOMO –5	-7.9	**6**
HOMO –4	-7.8	**5**
HOMO –3	-7.8	**4**
HOMO –2	-7.2	**3**
HOMO –1	-7.2	**2**
HOMO	-6.6	**1**
LUMO	-5.1	*1*
LUMO +1	-3.7	*2*
LUMO +2	-3.7	*3*
LUMO +3	-3.2	*4*
LUMO +4	-2.7	*5*
LUMO +5	-2.6	*6*
LUMO +6	-2.3	*7*

Figure 2 plots the Density of States (DOS) of PTCDA with the number of tunneling states (*n*) appearing over each peak. Note that *n* is a cumulative value and includes all the states up to the considered peak.

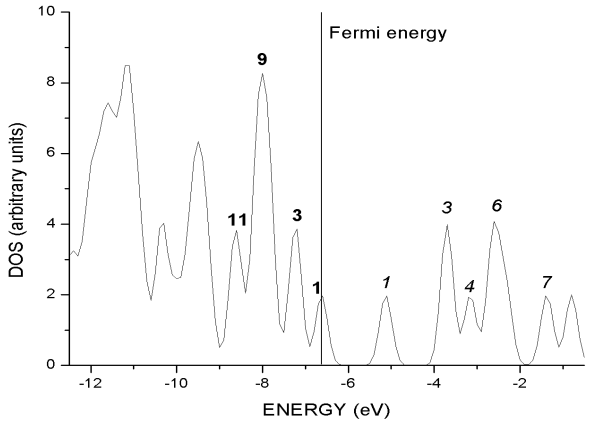

Figure 2. Density of States (DOS) vs. Energy for PTCDA, with appropriate *n* values.

Figure 3 shows the simulated STM patterns obtained for PTCDA from its filled and empty states close to the Fermi level, taking into account different number of tunneling states (n) with the isosurface value of the integrated LDOS held constant (K= 0.001).

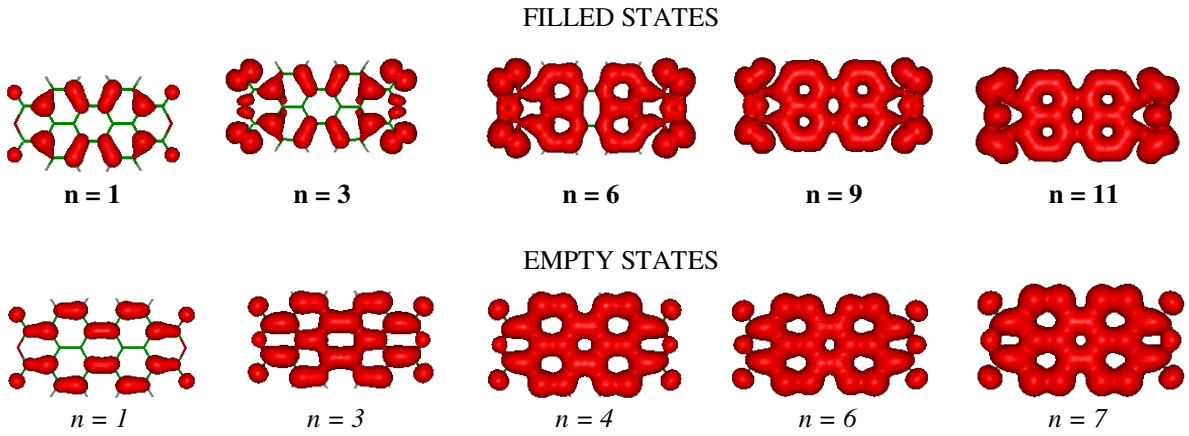

Figure 3. Simulated STM patterns for PTCDA as a function of the number of tunneling states (n) with an integrated LDOS isosurface value (K) of 0.001.

As it can clearly be observed the simulated STM patterns are significantly modulated by varying the number of tunneling states. Considering higher number of tunneling states results in more complex appearance of the simulated image. Once this number is high enough (n higher than **6**, or n higher than *4*) the image appearance converges to a topology in which four closed circular structures are formed.

Effect of the integrated LDOS isosurface value

Taking into account equation (5) the tunneling current (I_t) can be obtained from equation (3) written as follows:

$$I_t = (const)(Integrated\ LDOS), \tag{6}$$

where

$$const = 32\pi^3\hbar^{-1}e^2V\phi^2D_t(E_F)R^2\kappa^{-4}\exp(2\kappa R), \tag{7}$$

according to the s-wave tip model [1]. V is the applied voltage, ϕ the sample work function, D_t the density of states per unit volume of the probe tip, R the radius of curvature for the tip, $\kappa = (2\pi/h)(2m\phi)^{1/2}$.

Then for a fixed number of tunneling states (n), i.e. the bias voltage held constant, the tunneling current is proportional to the *Integrated LDOS*, as it can be observed in equation (6). By varying the integrated LDOS isosurface value the tunneling current is proportionally changed, whenever the sample workfunction and the tip properties do not change.

Different isosurface values of the integrated LDOS have been considered to make the simulated STM patterns for PTCDA shown in figure 4. Three tunneling states were held constant either for filled and empty states.

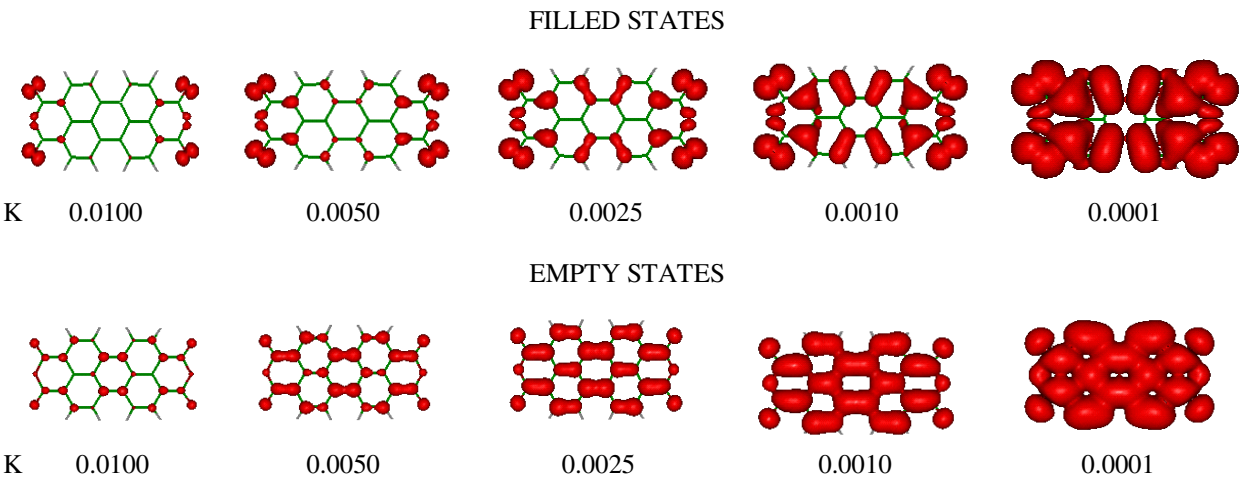

Figure 4. Simulated STM patterns for PTCDA molecule with the first three tunneling states (n = 3) for different integrated LDOS isosurface values (K).

As noticed, the appearance of the simulated STM images also depends on the integrated LDOS isosurface value (K). At the lowest values it is obvious a lack of resolution for the image. For the higher values contribution of the molecular orbitals may be very small and not useful for comparison with experimental data.

DISCUSSION

1. The tunneling current (I_t) and the bias voltage (V) values are the main variables to be controlled in an STM experiment. They both are closely related to the number of tunneling states (n) and the integrated local density of states (LDOS), used in this work to simulate STM images. This relationship can be assessed mathematically through the equations (3)-(5).

2. When a bias voltage is applied lower energy electrons are allowed to tunnel. By increasing the bias voltage results in more of the PTCDA states participating in tunneling and contributing to enrich details of the STM image. In this work we found that use of the higher number of tunneling states leads to more complex appearance of the simulated image. However, after certain number of tunneling states, the image appearance converges to a topology in which four closed circular structures are formed.

3. In order to obtain simulated STM images with all details at the highest possible resolution, we also found that an intermediate isosurface value of the integrated LDOS is required. In our simulations at number of tunneling states (n) held constant, the integrated LDOS isosurface value (K) was varied from 0.0001 to 0.01. A significant impact on the image appearance was noticed. At high values not all the possible details are observed and at lower ones the simulated images render a pattern of poor resolution.

4. In order to verify our simulation approach, the obtained theoretical images were compared with an experimental STM image of the PTCDA molecule in a highly ordered arrangement on the iodine modified Au(111) surface. According to previous work of Kunitake et al [7], who found the iodine modified surface to be less reactive than the clean Au(111) towards the organic molecules, one could suppose that PTCDA is weakly adsorbed. This assumption gives us a possibility to compare the obtained experimental image with our simulated data. The high resolution image of the PTCDA array was obtained in our laboratory using electrochemical preparation (see figure 5).

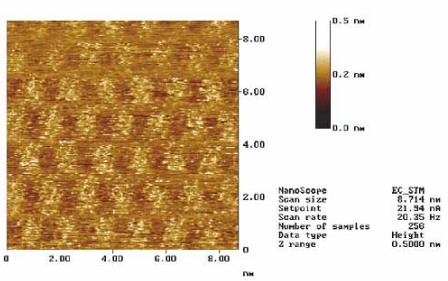

Figure 5. Experimental STM pattern for the PTCDA molecular array adsorbed onto iodine modified Au(111) substrate under electrochemical conditions, in 0.1 M $HClO_4$. $E_{substrate}$ = -0.154 V, E_{tip} = -1.18 V vs Pt reference electrode.

Although detail comparison between the experimental image and our simulated patterns did not lead to a straight conclusion, it seems that optimum description is achieved by using the simulated image for the first three empty states (LUMO, LUMO+1and LUMO+2), n = 3, of PTCDA with K = 0.001. However, to get an in detail interpretation of such high resolution STM image, more experiments involving imaging at constant voltage or constant current are required.

CONCLUSIONS

The number of tunneling states has a strong effect in the simulation of STM images with Tersoff-Hamann approximation, and the image qualitative topology converges for a certain number of them. In order to achieve an optimum resolution in the simulated images one should carefully define intermediate isosurface values for the integrated Local Density of States (LDOS). The tunneling current is proportional to the integrated LDOS isosurface value.

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