Collective Concerted Motion in a Molecular Adlayer Visualized through the Surface Diffusion of Isolated Vacancies

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We have measured STM movies to study the diffusion of individual vacancies in a self-assembled layer of a tetrathiafulvalene derivative (exTTF) on Au(111) at room temperature. The diffusion is anisotropic, being faster along the compact direction of the molecular lattice. A detailed analysis of the anisotropic displacement distribution of the single vacancies shows that the relative abundance of double jumps (that is, the collective motion of molecular dimers) with respect to single jumps is rather large, the number of double jumps being more than 20% of the diffusion events. We conjecture that the relative abundances of long jumps might be related to the strength of the intermolecular bonding and the misfit of the molecular overlayer with the substrate lattice.

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INTRODUCTION

Vacancy diffusion is one of the most important atomistic processes involved in mass transport through solids. The formation of solid alloys, the aging of conducting wires due to electromigration processes, the electrical conductivity of ionic conductors or the ductility and malleability of metals are only some of the physical properties of materials that ultimately depend on the mobility of individual vacancies through the crystal lattice. However, obtaining direct information about the diffusion of individual vacancies is not at all straightforward. Most of the experimental methods are sensitive to the motion of the atoms that jump into the vacancies, i.e. the so-called tracer atoms, and not of the vacancies themselves. Scanning Tunneling Microscopy is one of the few techniques that allows a direct observation of individual vacancies. It has actually been applied to the investigation of the surface diffusion of individual vacancies in semiconductors, metal oxides and metal surfaces. The number of available studies is however scarce, and most of the studies in metals have used a tracer-atom approach and no studies have been carried out for molecular solids.

In this letter we report a STM study of the room temperature diffusion of single vacancies in a self-assembled monolayer of 2-[9-(1,3-dithiol-2-ylidene)anthracen-10(9H)-ylidene]-1,3-dithiole (exTTF, see Figure 1b) on the Au(111) surface. We will show that the diffusion events, especially along the close-packed direction, occur very often through long jumps, i.e. diffusion events in which the initial and final positions of the vacancy are separated by more than one lattice site. The long jump events for vacancy diffusion result from the correlated motion of groups of exTTF molecules adjacent to the initial vacancy site. We speculate that the relative abundance of long jumps could be related to the bonding strength between molecules and to the misfit between the molecular layer and the substrate lattice.

II. EXPERIMENTAL DETAILS

The growth of the molecular films and the STM measurements were carried out in a UHV chamber with a base pressure of < 2 × 10⁻¹⁰ Torr. Atomically flat, crystalline Au(111) surfaces were prepared by standard sputter/anneal procedures (sputter with 1 kV Ar⁺ ions for 15 min followed by annealing to 800 K for another 15 min). The molecules were deposited from a low temperature Knudsen cell, heated at 400 K, onto the clean Au(111) substrate,
that was held at room temperature. The diffusion of the vacancies was studied by acquiring time-resolved STM movies with an Aarhus-type variable-temperature fast scanning STM purchased from SPECS. Tunnelling conditions were chosen so as not to disturb individual molecules ($V_b > 1$ V, $I < 100$-$500$ pA). The time required to acquire a frame is about 16 s.

III. RESULTS AND DISCUSSION

The adsorption and self-assembly of exTTF on Au(111) surfaces\(^7\) and coadsorbed with other molecular species\(^8\) has recently been described. For large enough coverages exTTF molecules self-assemble to form a well-ordered structure. The unit cell is rhombohedral, with sides 7.8 and 10.7 \AA long and an angle of 114.8° (see Figure 1). In the following we will designate the close-packed direction as $\mathbf{a}$ and the other direction in the unit cell as $\mathbf{b}$. We will also find useful to name the short diagonal of the unit cell as $\mathbf{c}$, since the intermolecular distances along $\mathbf{b}$ and $\mathbf{c}$ (10.3 \AA) turn out to be very similar (see Figure 1c).

At room temperature the diffusivity of isolated exTTF molecules is very high. The edges of the islands are very mobile, since molecules are continuously attaching to or detaching from the island edges, a process which facilitates the formation of single vacancies which then diffuse within the island. Vacancies are easily found within the molecular lattice (see Figure 1a). At RT they are observed to diffuse in the time scale of the STM scanning (see Figure 2), and these diffusion events are found to be independent of the scanning direction. However, they cannot be observed when the images are recorded at 77 K, even when rather harsh tunnelling conditions ($V_{Bias} < 0.2$ V, $I_t > 1$nA) are used. We thus conclude that the observed diffusive processes are thermally induced: although the presence of the STM tip might have some minor effect on the absolute values of the diffusion rates (see below), it is not the main factor determining the observed vacancy mobility.

Figure 2a, b and c show three consecutive STM images, taken at room temperature, of the same area of the exTTF overlayer. (The images were taken inside a large molecular island and, to minimize edge effects, at least 100 \AA away from any island edge).\(^10\) Two of the vacancies, marked by white circles, do not move during the time-span covered by the three frames. Every other vacancy undergoes one or two diffusion events in the three frames shown in Figure 2. In order to better identify and characterize the diffusion events we also show the difference images in panels d and e. In a difference image, a diffusion event in
which a vacancy changes location appears as a red area-black area pair over a background of locations with negligible changes. Examining the difference images in Figure 2d and e, it becomes apparent that indeed red and black areas always appear in pairs, and the direction and size of the jumps can easily be extracted.

Some examples of different diffusion events are marked by ovals of various colors in the different panels of Figure 2. Most of the diffusion events correspond to displacements to nearest neighbors along the close-packed $a$ direction (blue oval). It is however not infrequent that the displacements take place in a different direction (pink oval) or correspond to displacements longer than one lattice spacing (green oval).

The observed long displacements might arise either from a single jump over two or more lattice parameters (long jump), or alternatively might be the result of multiple single jumps taking place during the time span needed to record one image. A quantification of the relative abundances of these alternatives can be obtained by a careful analysis of the displacement distribution.\(^\text{11}\) (Contrary to the motion of isolated molecules on a surface, in this case the displacements are described with respect to the molecular lattice, not with respect to the substrate). In order to exclude vacancy-vacancy interaction effects, only diffusion events in which the vacancies were isolated (with no other vacancy in the next or next-nearest neighbour sites), both in the starting and final position, were taken into account in the analysis. Vacancies which initial or final positions were uncertain or out of the scope of the image were also excluded. The resulting final displacement distribution, for a total of 966 events (a number large enough to obtain a meaningful statistics),\(^\text{9}\) is shown in a color scale in Figure 3a and in a histogram plot in Figure 4 (black bars). Notice that the diffusion is anisotropic, being more than twice faster along the close-packed $a$ direction of the molecular lattice than along the other two directions.

In order to analyze this set of data, we start by assuming that an isolated vacancy can diffuse exclusively by single jumps along the directions $a$, $b$ and $c$ (the intermolecular distance along $c$ is almost the same as along $b$). If the single jump rates along the $a$, $b$ and $c$ direction are $\alpha$, $\gamma$, and $\beta$, respectively, then the probability $p_{x,y}$ that the vacancy is found at the coordinates $(x,y)$ at the time $t$ knowing that it was at $(0,0)$ in $t = 0$, is given by\(^\text{11}\)

$$\frac{dp_{x,y}}{dt} = \alpha(p_{x+1,y} + p_{x-1,y}) + \beta(p_{x+1,y+1} + p_{x-1,y-1})$$
where $x$ and $y$ are measured in nearest-neighbor distance units along the directions $a$ and $b$, respectively. The solution of this equation is

\[ p_{x,y}(t) = \exp[-2(\alpha + \beta + \gamma)t] \times \sum_i I_{x-i}(2\alpha t)I_i(2\beta t)I_{y-i}(2\gamma t), \] (2)

where $I_i$ is the modified Bessel function of the first kind of order $i$. By fitting the experimental results with this expression, taking $\alpha$, $\beta$, and $\gamma$ as free parameters, we obtain $\alpha = 0.0086(3)$ s$^{-1}$, $\beta = 0.0036(3)$ s$^{-1}$, and $\gamma = 0.0032(3)$ s$^{-1}$. The distribution calculated using these values is plotted in Figure 3b and Figure 4 (light-grey bars). Notice that the quality of the fit is not very satisfactory. It overestimates the expected probability values for short displacements (single jumps), but underestimates the probability values for longer ones, which is a well known artifact resulting from the attempt to fit the experimental distribution without considering the existence of long jumps.$^{11}$ The goodness of the fit can be quantified by the quadratic standard deviation $\sigma^2$ between the expected values and the experimentally determined ones, which in this case is 19.2.

The fit can be improved by allowing longer jumps of different lengths in the different lattice directions. The simplest attempt is to include the possibility of jumps to second neighbors (with a rate $\delta$) in the close-packed direction $a$ (for which the single jump is the highest). Then, equation 1 becomes$^{11}$

\[
\frac{dp_{x,y}}{dt} = \alpha(p_{x+1,y} + p_{x-1,y}) + \beta(p_{x+1,y+1} + p_{x-1,y-1}) + \gamma(p_{x,y+1} + p_{x,y-1}) + \delta(p_{x+2,y} + p_{x-2,y}) - p_{x,y}(2\alpha + 2\beta + 2\gamma + 2\delta),
\] (3)

and the corresponding solution is

\[ p_{x,y}(t) = \exp[-2(\alpha + \beta + \gamma + \delta)t] \times \sum_{l,i} I_{x-l}(2\alpha t)I_{i}(2\beta t)I_l(2\gamma t)I_{y-i}(2\delta t), \] (4)
where \( m = x - y + l - 2i \) and \( n = y - l \). The results of this fit give \( \alpha = 0.0076(2) \text{ s}^{-1} \), \( \beta = 0.0032(2) \text{ s}^{-1} \), \( \gamma = 0.0028(2) \text{ s}^{-1} \), and \( \delta = 0.0019(2) \), and the calculated probability distributions are shown in Figure 3c and Figure 4 (middle-grey bars), where a significant improvement in the similarity with the experimental data can be observed: the variance is now \( \sigma^2 = 8.3 \), noticeably smaller than in the previous case. The results indicate that the contribution of double jumps to the room temperature diffusion is very important, with a rate \( \delta \) that is \( \sim 0.25 \) times the single-jump rate \( \alpha \), and \( \sim 0.6 - 0.7 \) times the single-jump rates in the two other directions.

The inclusion of double jumps along the other two main directions is less important, but still relevant. For example, while the inclusion of double jumps exclusively along \( b \) results in \( \sigma^2 = 14.6 \), and along \( c \) in \( \sigma^2 = 13.2 \), when double jumps are allowed simultaneously in the three directions, the fit is noticeably improved. In this case,

\[
\frac{dp_{x,y}}{dt} = \alpha(p_{x+1,y} + p_{x-1,y}) + \beta(p_{x+1,y+1} + p_{x-1,y-1}) + \gamma(p_{x,y+1} + p_{x,y-1}) + \delta(p_{x+2,y} + p_{x-2,y}) + \epsilon(p_{x+2,y+2} + p_{x-2,y-2}) + \phi(p_{x,y+2} + p_{x,y-2}) - p_{x,y}(2\alpha + 2\beta + 2\gamma + 2\delta + 2\epsilon + 2\phi),
\]

(5)

where \( \epsilon \) and \( \phi \) are the rates for double jumps along the \( c \) and \( b \) directions, respectively. The solution of this equation is

\[
p_{x,y}(t) = \exp[-2(\alpha + \beta + \gamma + \delta + \epsilon + \phi)t] \times \sum_{i,j,k,l} I_m(2\alpha t)I_n(2\beta t)I_l(2\gamma t)I_i(2\delta t)I_j(2\epsilon t)I_k(2\phi t),
\]

(6)

where \( m = x - y + l - 2i + 2k \) and \( n = y - l - 2j - 2k \). The results of the fit in this case yield \( \alpha = 0.0074(2) \text{ s}^{-1} \), \( \beta = 0.0028(2) \text{ s}^{-1} \), \( \gamma = 0.0024(2) \text{ s}^{-1} \), \( \delta = 0.0015(2) \), \( \epsilon = 0.0006(2) \), and \( \phi = 0.0008(2) \). The best-fit distribution is shown in Figure 3d and Figure 4 (dark-grey bars). The variance in this case has reduced to \( \sigma^2 = 4.6 \). (Note that, due to the low number of long displacements in \( b \) and \( c \), the relative error of \( \epsilon \) and \( \phi \) is relatively large). Of course,
Considering jumps of even longer length always improves the fit, but the reduction in $\sigma^2$ is not significant.

In either case, these results indicate that the contribution of double jumps to the room temperature diffusion is very important, with a rate that is close to $\sim 0.25$ times the single jump rate. We thus conclude that almost once every four times the diffusion occurs by displacing the vacancy two or more lattice sites, and therefore that long jumps must be considered as a very important mechanism contributing to the mobility of vacancies in a self-assembled molecular monolayer.

Long jumps in vacancy diffusion are conceptually different than the well-studied long jumps in adsorbate diffusion.$^{11-14}$ While the latter are related to weak dissipative effects during the adsorbate diffusion,$^{15}$ the former implies the correlated detachment of a molecular cluster from one side of the vacancy and the attachment to the other side (see Figure 5). Thus, a double vacancy jump corresponds to the correlated diffusion of a molecular dimer, a triple jump to that of a molecular trimer and so on.

It is tempting to relate the relative abundance of double jumps to the concerted motion of isolated dimers or small clusters (either atomic or molecular) on a solid surface.$^{25}$ It has been shown that, in certain cases, the activation barrier for dimer diffusion may be equal or even smaller than the barrier for monomer diffusion.$^{19-23}$ This has been explained as due to a combination of a strong bond between the molecules (or atoms) and the misfit of the ideal molecular lattice with the substrate,$^{22,24,25}$ (although entropy effects have also been claimed to play a role).$^{21}$ The misfit has a double effect: before the diffusion event, it would prevent both molecules from bonding to the substrate in the optimal geometry; during the diffusion, it makes that both molecules do not follow the same potential surface: as one molecule moves through a region where the potential is increasing, the lattice potential of the other molecule may be decreasing.$^{26}$ Both effects contribute to reduce the diffusion barrier.

In our case the situation is slightly different. It is true that the interaction between the molecules is rather strong, especially in the $\mathbf{a}$ direction ($E_b \sim 0.4 \text{ eV}$), due to the combination of a shorter separation and to the existence of a molecular dipole.$^7,27$ However, the molecules are not isolated on the surface, but they form part of a molecular overlayer, and the effect of the misfit would be more complicated to evaluate. Nevertheless, an experimental observation that points to the importance of the misfit is schematically depicted in Figure 6. We have observed that when there are two single vacancies separated by a single molecule (as shown
It is almost four times more plausible for the vacancies to be farther apart (Figure 6b) than closer (Figure 6c) in the next diffusion stage. From the energetic point of view, this implies that configuration 6b is more stable than 6c; that is, the two molecules in the dimer in 6b must be in a different configuration than the rest of the molecules in the chain, a configuration with a lower energy. Since molecule-molecule interaction results in a weaker molecule-substrate bond,\textsuperscript{21,24} we can assume that the two molecules in the dimer are more strongly bound to the substrate than the rest of molecules in the chain, from where we deduce that the molecular layer is probably incommensurate with the substrate, and it is this misfit what makes configuration 6b to be more stable than 6c, and then it could also contribute to the relatively high rate of double jumps.

IV. CONCLUSION

In summary, these results demonstrate the importance of vacancy long jumps, that is, the concerted movement of two or more molecules, in the surface diffusion of organic overlayers. Similar to the concerted motion of dimers or small clusters of atoms or molecules on a solid surface, this relative abundance of long jumps might be related to a strong bonding between molecules and the existence of misfit of the molecular overlayer with the substrate lattice. To what extent these results could be exported to the vacancy diffusion in other media remains to be studied further in depth.

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REFERENCES


Density functional theory (DFT) calculations performed for pairs of molecules in the experimental adsorption geometry estimate the bonding strength as 0.39 eV in the \textit{a} direction, 0.16 eV in the \textit{b} direction, and 0.05 eV in the \textit{c} direction. (The DFT calculations were
performed within the Generalized Gradient Approximation (GGA) using the DMol3 module from the Materials Studio software by BIOVIA Corp.)
FIG. 1. a) STM image (4.0 × 4.0 nm², \( V_{Bias} = 1.24 \) V, \( I_t = 1 \) nA) of exTTF molecules self-assembled on Au(111). The molecular lattice is marked by the blue lines, as well as the high symmetry directions denoted by \( a \), \( b \) and \( c \). Notice that the intermolecular distances along \( b \) and \( c \) are practically identical. The presence of a vacancy can be observed at the lower left corner. b) Schematic structure of the exTTF molecule. c) Molecular model for the adsorption and organization of exTTF molecules an a Au(111) surface, based on STM and X-ray Photoelectron Spectroscopy (XPS) experiments together with Density Functional Theory (DFT) calculations (see Ref. 7). The red lines indicate the high symmetry directions of the Au(111) surface.
FIG. 2. a), b) and c) Consecutive STM images of the same area of $(15 \times 9 \text{ nm}^2$, $V_{\text{Bias}} = 1.2V$, $I_t = 1\text{nA}$) of a self-assembled monolayer of exTTF deposited on Au(111). Two vacancies (white circles) remain in the same position that they occupied in the first frame. Some examples of vacancy diffusion events are marked by blue ovals (single displacement along the a direction), pink ovals (single displacement along b or green ovals (double displacement along a. d) and e) show the difference between consecutive images, in which the diffusion events can be easily identified. The time interval between the two images is 16 seconds.
FIG. 3. a) Experimental displacement distribution, in units of the unit cell vectors in the molecular lattice, for the diffusion of an isolated vacancy in an exTTF overlayer on Au(111). b) Best fit to the experimental data assuming only single jumps. c) Best fit to the experimental data allowing double jumps only in the compact a direction. d) Best fit to the experimental data allowing double jumps in the three main directions, a, b and c.
FIG. 4. Histograms showing the 1D jump distributions along the directions a (top), b (middle) and c (bottom) extracted from the 2D distributions shown in Figure 3. The experimental data are plotted in black. The grey bars are the results of the different fits mentioned in the text: assuming only single jumps (light gray), including also double jumps in the a direction (middle-grey), and allowing double jumps in the three directions (dark grey).
FIG. 5. a) and b) show schematic representations of the single and double vacancy jump processes. Notice that double jumps are equivalent to the diffusion of pairs of molecules in the chain. For the strictly 1D case the energy barrier for single and double jumps should be the same (and equal to the energy cost of breaking one bond to the chain).

FIG. 6. Starting from the initial configuration a), the final configuration shown in b) is almost four times more probable than the one shown in c).
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a) experimental map

b) single jumps

c) double jumps, a
d) double jumps, a, b, c
experiment
single jumps
double jumps, a
double jumps, a, b, c

total number of observations

number of observations

displacement, $\Delta x$