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Tunneling Mechanism Implications from an STM Study of H$_3$C(CH$_2$)$_{15}$HC=C=CH(CH$_2$)$_{15}$CH$_3$ on Graphite and C$_{14}$H$_{29}$OH on MoS$_2$

Christopher L. Claypool, Francesco Faglioni, William A. Goddard, III,* and Nathan S. Lewis*

Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125

The observations reported herein confirm that the bright spots in high-resolution STM images of adsorbed alkanes and alkanols are predominantly due to the electronic and topographic structure of the molecule, and not predominantly due to the substrate. STM images of a monolayer of 17,18-pentatriacontadiene, H$_3$C(CH$_2$)$_{15}$-HC=C=CH(CH$_2$)$_{15}$CH$_3$, adsorbed on graphite were obtained to evaluate whether changes in the orientation of the exposed methylene hydrogen atoms relative to the STM tip produced changes in the observed pattern of bright spots in a STM image. STM images of this system showed a pattern of bright spots within individual molecules that appears to change on either side of the allene −C=C=C− functionality. STM images were also obtained for tetradecanol overlayers on graphite and MoS$_2$ surfaces. The angles and distances observed in the images of tetradecanol on MoS$_2$ were nearly identical to those measured previously in our laboratories for alkanol and alkane monolayers on graphite despite that fact that the separation between bright spots in an STM image of graphite is 2.46 Å, while the separation between bright spots in STM images of MoS$_2$ is 3.16 Å.

Although various laboratories have now reported scanning tunneling microscopy (STM) images that appear to reveal the internal structure of molecules,[1−5] there is still a need to understand the fundamental mechanisms that produce the tunneling current contrast in such images.[1−5] A particularly attractive system for the investigation of these questions involves imaging alkanes or alkanols adsorbed onto highly ordered pyrolytic graphite (HOPG) surfaces.[5] These species produce ordered overlayers that allow resolution of various atomic and functional group features with a STM.[5] In addition, systematic changes in the topographic and electronic structure of these molecules can be correlated with changes in the observed STM images.[1,5g−j]

In prior work in this laboratory,[1] high-resolution STM images of alkanes and alcohols were shown to produce distances and angles between bright spots (i.e., between points of high tunneling probability relative to the reference alkane chain regions) that closely corresponded to the locations of the methylene hydrogen atoms that point toward the tip, in an adsorbate structure for which the carbon−carbon skeleton of the alkane or alkanol is oriented parallel to the graphite surface plane (Figure 1).[1] This assignment was confirmed by the molecular packing observed in the adsorbate overlayer, which displayed intermolecular angles that were consistent with the sterically favored packing arrangement for alkanes or alkanols that have their carbon−carbon skeletons oriented parallel to the surface plane. Although the distances between bright spots observed in these high-resolution STM images are statistically distinguishable from the distances between alternating carbon atoms in the graphite substrate (Table 1), the distances between the observed spots are sufficiently close to those of the underlying graphite (2.46 Å) that additional experiments are desirable to deduce conclusively that the positions of these spots

are dominated by the features of the molecular adsorbate, and not by the electronic and geometric structure of the underlying graphite lattice.

Two sets of experiments have been performed to address this issue. In one set of experiments, images of these adsorbate overlayers have been obtained on MoS$_2$, which has a significantly different lattice spacing than HOPG. In the second set of experiments, images of an allene have been obtained on HOPG, to evaluate whether changes in the orientation of the exposed methylene hydrogen atoms relative to the STM tip produce changes in the observed STM bright spot patterns.

STM data were obtained at constant current in the variable height mode using a Pt/Ir tip and a Nanoscope III STM (Digital Instruments, Santa Barbara, CA), under sample preparation and imaging conditions similar to those reported previously.[1] The images were filtered primarily to enhance the visual presentation of the printed images, but the filtering was performed in such a way that it did not distort any of the primary metrics evident in the original data nor did the filtering procedure introduce any new spot patterns or new topographic features into an image. H$_3$C(CH$_2$)$_{15}$HC=C=CH(CH$_2$)$_{15}$CH$_3$ was synthesized from stearone following literature procedures.[6] All images were collected at room temperature under equilibrium conditions with the tip immersed in a phenyloctane solution that contained a saturated amount of either H$_3$C(CH$_2$)$_{15}$HC=C=CH(CH$_2$)$_{15}$CH$_3$ or tetradecanol.

Figure 2 depicts the STM images of a monolayer of the allene 17,18-pentatriacontadiene, H$_3$C(CH$_2$)$_{15}$HC=C=CH(CH$_2$)$_{15}$CH$_3$, adsorbed on HOPG. This molecule was chosen because the orthogonal *pi* systems in the double bonds of the allene functionality should induce an ≈90° twist in the orientation of carbon−carbon skeletons on either side of the allene group. In Figure 2, the individual molecules are clearly resolved, and the mean molecular length of 46 ± 0.5 Å corresponds well with the length of 45.1 Å that is calculated for the all trans-

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TABLE 1. Values of the Distances (Å) and Angles Associated with the Experimental STM Images[a]

	$C_{14}H_{29}OH$ on graphite	$C_{14}H_{29}OH$ on MoS_2	$H_3C(CH_2)_{15}HC=C=CH(CH_2)_{15}CH_3$ on graphite
ab ($\approx$)	2.57 ± 0.02 (2.56)	2.55 ± 0.05 (2.56)	2.56 ± 0.05 (2.56)
bc ($\approx$)	2.36 ± 0.02 (2.51)	2.35 ± 0.05 (2.51)	2.36 ± 0.05 (2.51)
ac ($\approx$)	2.36 ± 0.02 (2.51)	2.35 ± 0.05 (2.51)	2.36 ± 0.05 (2.51)
cd ($\approx$)	2.72 ± 0.02	2.75 ± 0.02	
de ($\approx$)			2.56 ± 0.05 (2.56)
ef ($\approx$)			1.57 ± 0.05 (1.57)
$\angle$acb	61° (61.3°)	61° (61.3°)	61° (61.3°)
$\angle$def			89° (90°)
θ	25° (26°)	25° (26°)	0° (0°)
l (Å)	19.9 ± 0.1 (19.2)	19.8 ± 0.1 (19.2)	46.3 ± 0.5 (45.1)

[a] Values in parentheses are the expected values based on molecular modeling. The angle θ is predicted using a steric argument and the measured molecular distances (see text). The lattice constants of graphite and MoS_2 are 2.46 and 3.16 Å, respectively.

conformation of the molecule, using the standard bond length values and standard van der Waals radii for the terminal atoms. The pattern of bright spots within individual molecules appears to change on either side of the allene functionality that is located in the center of the molecule. On the left-hand side of the molecules as displayed in the image of Figure 2, the bright spots are separated by a mean distance of 2.56 ± 0.05 Å in the direction along the molecule (a to b), and the distance between these spots is 2.36 ± 0.05 Å (a to c and b to c). These values are in close agreement with those observed previously[1] (i.e., Figure 1) and with those expected for adsorbates whose carbon—carbon skeleton is oriented parallel to the graphite surface plane.[1]
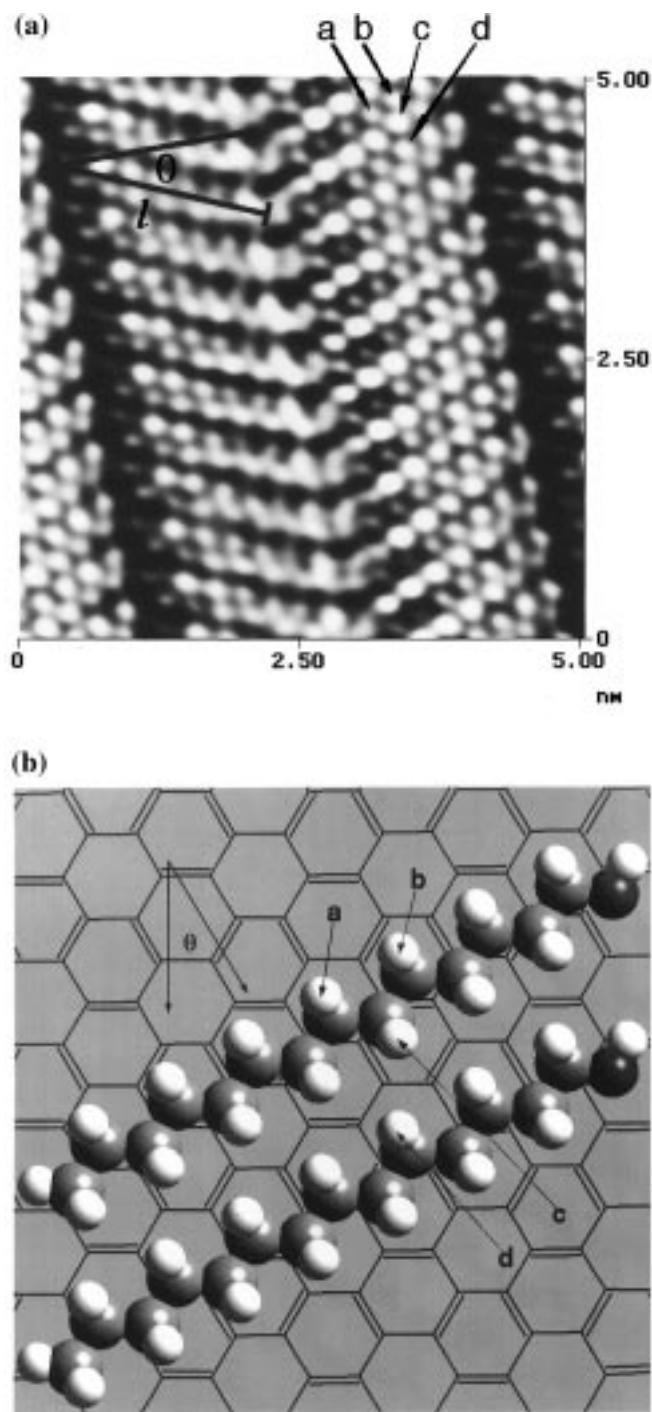
In contrast, on the right-hand side of the molecules in the image of Figure 2a, the bright spots are separated by a mean distance of 2.56 ± 0.05 Å in the direction along the molecule (d to e). The different spot pattern on each side of the molecule is expected based on the 90° twist in the orientation of the carbon—carbon skeleton relative to the graphite surface plane that should be imposed by the presence of the allene functionality. These data also are in accord with the hypothesis that a rectangular-type spot pattern observed for alkane overlayers on graphite results from the positions of the methylene hydrogens closest to the STM tip when the alkane molecules are trapped in an unfavored orientation in which their carbon—carbon skeletons are perpendicular to the graphite surface plane.[7] In addition, they confirm the assignments of bright spots in STM images of liquid crystals on graphite, in which the regions of high tunneling current have been associated with the positions of the methylene hydrogens of the hydrocarbon chains in the adsorbed monolayer.[8]

Figure 2, parts B and C, shows the computed constant current STM images of an alkane adsorbed with its carbon—carbon skeleton oriented parallel, and perpendicular, respectively, to the graphite surface plane.[9] Calculations were performed using the equations and methods described previously in the literature.[9] In each case, the calculated images show high tunneling probability contours (i.e., bright spots) that correspond closely to the positions of the hydrogen atoms that are located closest to the tip.[1,9] In the constant current simulation of Figure 2b, for molecules with their carbon—carbon skeleton oriented parallel to the graphite surface plane, the average calculated distance between spots along the direction of the molecule is 2.56 Å and the average distance between subsequent spots along the alkane chain is 2.61 Å. In Figure 2c, for molecules having their carbon—carbon skeleton oriented perpendicular to the graphite surface plane, the average calculated distance between spots is 2.59 Å along the backbone and is 1.57 Å between nearest neighbors. These calculated images are clearly in excellent agreement with the experimental images represented by Figure 2a.

Additional support for the correlation of the bright spots with the properties of the adsorbate structure was obtained by investigation of the behavior of alkanols adsorbed on MoS_2 substrates. Although images of dotriacontane ($C_{32}H_{66}$) on MoS_2 have been reported previously,[2] the resolution was not sufficient to allow identification of the bright spot pattern within individual molecules. Figure 3 displays an image obtained in our laboratories of tetradecanol molecules ($C_{14}H_{29}OH$) adsorbed on MoS_2. The average molecular length in Figure 3 of 19.8 ± 0.1 Å is in good agreement with the molecular length of 19.2 Å obtained from molecular modeling using a DreidingII force field[2] for the all trans- conformation of the molecule. Similar to the high-resolution images of tetradecanol on HOPG (Figure 1), a series of alternating bright spots was observed within features assigned to individual $C_{14}H_{29}OH$ molecules. The bright spots are separated by a mean distance of 2.55 ± 0.05 Å in the direction along the molecule (a to b) and the distance between these spots is 2.35 ± 0.05 Å (a to c and b to c). The distance between alternating spots in adjacent molecules is 2.75 ± 0.05 Å. Images that showed the alternating bright spots within an individual molecule were observed much less frequently on MoS_2 than on HOPG, but many such images were obtained over several imaging sessions.
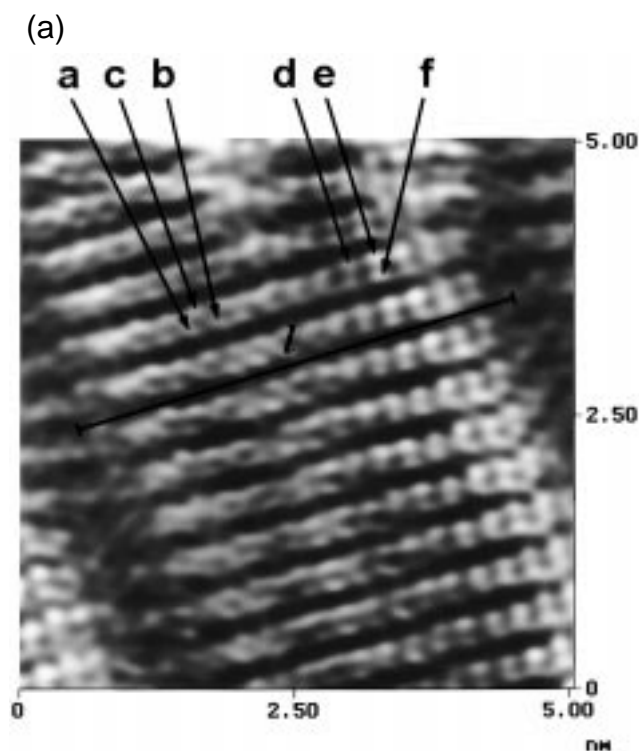
These data are nearly identical to those measured previously for alkanol and alkane monolayers on HOPG (Table 1),[1] despite that fact that the separation between bright spots in an STM image of HOPG is 2.46 Å, while the separation between bright spots in STM images of MoS_2 is 3.16 Å.[2,3,10] These observations therefore confirm that the bright spots in high-resolution STM images of alkanol overlayers are predominantly due to the electronic and topographic structure of the molecule, and not predominantly due to the substrate. The high-resolution bright spot patterns of Figure 3 also confirm that tetradecanol molecules are oriented with their carbon—carbon skeleton parallel to the surface plane of the MoS_2 substrate, as expected for an overlayer structure that maximizes hydrogen bonding between adjacent alkanols while minimizing steric repulsion between methylene groups on adjacent molecules.[1] This conclusion is also consistent with the packing angle θ of 25° that is observed for this system on both HOPG[1] and MoS_2 substrates (Figure 3).

In summary, experiments that have varied both the molecular orientation of the molecules in the overlayer and the lattice constants of the substrate have shown that the spot patterns observed in high-resolution STM images of alkane and alkanol overlayers arise predominantly from topographic and electronic properties of the molecule as opposed to being dominated by the properties of the substrate. Additionally, the bright spot patterns for the methylene groups in alkane chains seem to be
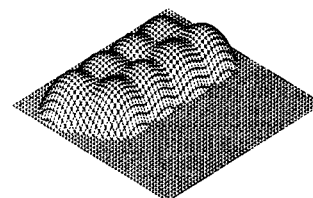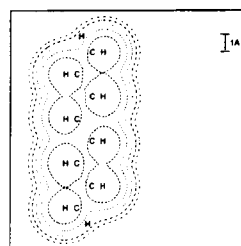
(a)

(a)

(B) Flat $CH_3(CH_2)_6CH_3$ at -1.0 eV Constant current

(C) Vertical $CH_3(CH_2)_7CH_3$ at -1.0 eV Constant current

Figure 1. (a) High-resolution STM image of tetradecanol adsorbed on graphite ($V = 1.127$ V, $I = 650$ pA). Individual tetradecanol molecules produce 14 bright spots in the STM image that correspond closely to the locations of the 14 hydrogen atoms nearest the tip. Values of the angles and distances labeled in the image are given in Table 1. (b) Schematic diagram of individual tetradecanol molecules adsorbed onto graphite.
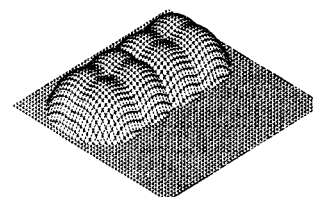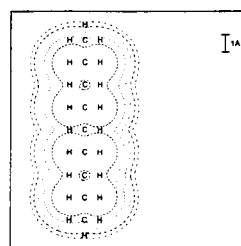
dominated by topographic constraints imposed by the location of hydrogen atoms that are closest to the STM tip, in accord with theoretical predictions of the STM image contrast of such systems. Further investigations of features that control the STM image contrast of simple monomolecular organic overlayers, including the interplay between topographic and electronic factors for an individual type of functional group that is located at sterically different positions on the alkane chain, are in progress.

Figure 2. (A) Constant current STM image of a monolayer of 17,-18-pentatriacontadiene, $H_3C(CH_2)_{15}C\!=\!C\!=\!C(CH_2)_{15}CH_3$, molecules adsorbed on a graphite surface ($V = 1.023$ V, $I = 500$ pA). The image is dominated by the topography of the adsorbate molecules, with the individual bright spots corresponding to the upward-facing hydrogen atoms in the alkyl chains on either side of the allene ($-C\!=\!C\!=\!C-$) functionality. On the left-hand side of the adsorbed molecules, the bright spots appear to alternate in a pattern and spacing similar to that of an alkane adsorbed in a flat orientation. On the right-hand side of the molecules, the bright spots are ordered in a rectangular pattern, and the alkyl chain on this side of the molecule appears to be adsorbed in a perpendicular orientation. Values of the angles and distances labeled in the image are given in Table 1. (B) Computed constant current STM images of an alkane molecule adsorbed onto the graphite surface in a flat and (C) vertical orientation. The contour levels are at 1/6, 2/6, 3/6, 4/6, and 5/6 of the maximum peak of each plot. 3-D plots are shown to the right of the contour plots.
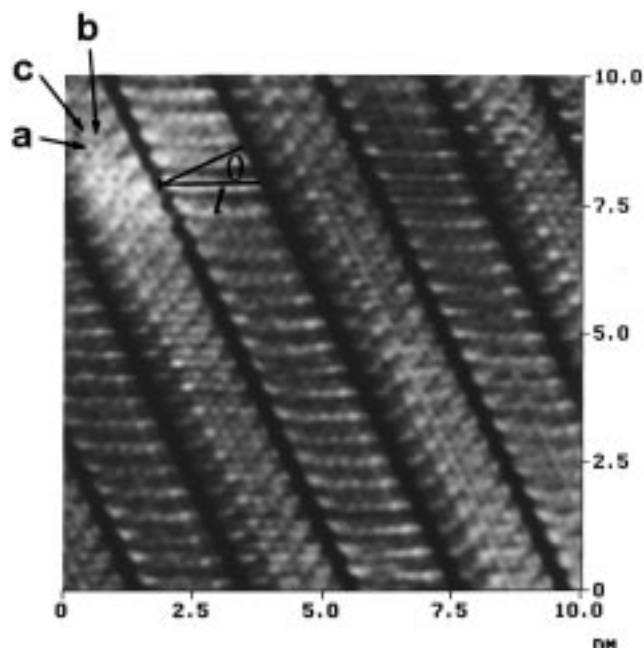
Figure 3. High-resolution STM image of tetradecanol molecules on MoS_2 ($V = 1.866$ V, $I = 300$ pA). Similar to the images observed for tetradecanol molecules on graphite, the individual tetradecanol molecules contain alternating bright spots whose positions correspond closely to the locations of the hydrogen atoms nearest the tip (Table 1).

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