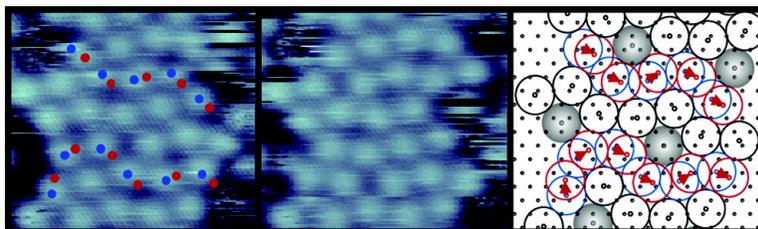


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J. Am. Chem. Soc., **2004**, 126 (34), 10787-10793 • DOI: 10.1021/ja049113z • Publication Date (Web): 05 August 2004

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Benzene on Au{111} at 4 K: Monolayer Growth and Tip-Induced Molecular Cascades

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Abstract: Low-temperature scanning tunneling microscopy has been used to characterize the various structures of submonolayer and near-monolayer coverages of benzene (C_6H_6) on Au{111} at 4 K. At low coverage, benzene is found to adsorb preferentially at the top of the Au monatomic steps and is weakly adsorbed on the terraces. At near-monolayer coverage, benzene was found to form several long-range commensurate overlayer structures that depend on the regions of the reconstructed Au{111} surface, namely a $(\sqrt{52} \times \sqrt{52})R13.9^\circ$ structure over the hcp regions and a $(\sqrt{133} \times \sqrt{133})R17.5^\circ$ "pinwheel" structure over the fcc regions. Time-lapse imaging revealed concerted cascade motion of the benzene molecules in the $(\sqrt{133} \times \sqrt{133})R17.5^\circ$ pinwheel overlayer. We demonstrate that the observed cascade motion is a result of concerted molecular motion and not independent random motion.

Introduction

A fundamental understanding of overlayer growth and molecular dynamics on clean ordered surfaces is a major requirement toward understanding the mechanism of applied heterogeneous catalytic systems. These systems lower the activation energy of the target reactions by providing sites for accumulation of reactants and facilitate the transport of the reactant molecules toward catalytically active sites. Scanning probes have become an established technique for obtaining information on the local environment of surface systems, as well as a means of linking the fundamental and applied aspects of these systems. Recently, scanning tunneling microscopy (STM) has been used to investigate the various aspects of catalytic systems ranging from structural, to spectroscopic, to correlation with molecular dynamics characterization.^{1–6} In this article, we characterize the growth of benzene monolayers (ML) and observe transport mechanisms in the benzene overlayer.

Recently, Heinrich et al. constructed a system designed to exhibit controlled molecular cascades.⁷ In their system, CO molecules on Cu{111} were manipulated by the STM tip and arranged in specific metastable "chevron" configurations, which decay into the more stable $(\sqrt{3} \times \sqrt{3})$ configuration. By aligning several chevron structures, a molecular cascade was constructed and observed with time-lapse STM imaging.

However, the system studied in ref 7 relies on a low coverage of CO molecules in order to retain control of the structure of the cascades. To our knowledge, the observation of concerted molecular motion in molecular overlayers has not been reported to date.

Here, we report the STM characterization of benzene molecules adsorbed on Au{111} at 4 K, as well as the first time observation of tip-induced molecular cascades at near-monolayer coverage through the use of time-lapse STM imaging. In this study, we show how the characteristic herringbone reconstruction of Au{111} has a strong influence on the overlayer structure of the adsorbate. Moreover, we show that the long-range commensuration of the benzene overlayer with the Au{111} atomic lattice creates the possibility of cascade motions. The observation of these benzene cascades might shed light on aspects of surface reactions, such as the transport of reactants or intermediates to the reaction sites of heterogeneous catalysts.

Experimental Section

The experiments were performed in ultrahigh vacuum at 4 K, using a custom-built low-temperature STM, which has been described elsewhere.^{8,9} All images were scanned in constant-current mode using a mechanically cut Pt/Ir tip. All bias voltages are reported as applied to the sample, except where indicated otherwise. An ordered Au surface was obtained through repeated sputter and anneal cycles (1 keV Ar⁺ sputtering at ~800 K, annealing at ~800 K). Benzene (purchased as 99.9% from Sigma Aldrich) was purified by freeze/pump/thaw cycles prior to use and was introduced into the UHV chamber via a leak valve.

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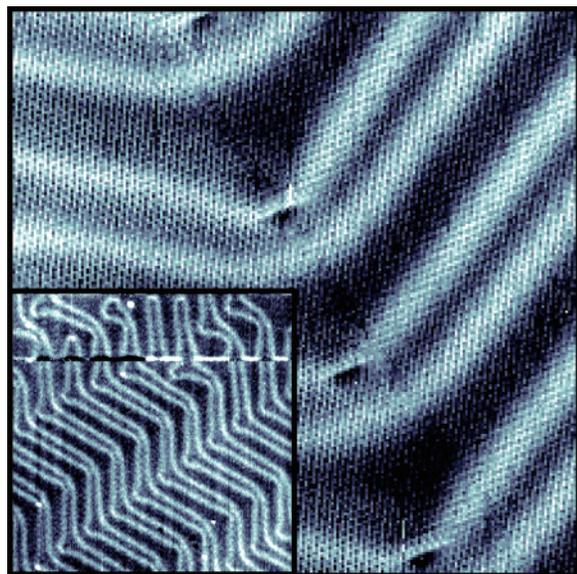


Figure 1. Atomically resolved STM image of the clean reconstructed Au{111}-($23 \times \sqrt{3}$) surface ($200 \text{ \AA} \times 200 \text{ \AA}$, $V_{\text{sample}} = -0.05 \text{ V}$, $I_t = 200 \text{ pA}$) showing the fcc and hcp regions separated by the soliton walls of the herringbone reconstruction. The inset shows an STM image of the clean Au{111}-($23 \times \sqrt{3}$) surface ($660 \text{ \AA} \times 660 \text{ \AA}$, $V_{\text{sample}} = 0.1 \text{ V}$, $I_t = 100 \text{ pA}$). This image shows one atomic step edge as well as the herringbone reconstruction.

The purity of benzene was verified in situ by mass spectrometry to be $\geq 98\%$ pure and was deposited on a Au{111} substrate at 4 K with line-of-sight dosing by back-filling the UHV chamber.⁹

Results and Discussion

Clean Au{111} Substrate. Figure 1 shows two typical images of the clean gold surface at 4 K before benzene deposition. The ($23 \times \sqrt{3}$) herringbone reconstruction is observed as pairs of periodically bent corrugation lines across terraces and monatomic step edges.¹⁰ The soliton walls of the herringbone reconstruction, which appear as 0.3 \AA protrusions in the STM images, correspond to the transitional regions where the topmost layer of gold atoms are partially dislocated with respect to both face-centered cubic (fcc) and hexagonal close-packed (hcp) hollow sites of the bulk layers. The wider depressions between soliton walls are regions where the topmost layer of gold atoms are stacked on top of the second layer fcc hollow sites, whereas the surface gold atoms in the narrower depressions between soliton walls are stacked on top of the hcp second layer hollow sites. The 120° bend of the soliton wall pairs delimits the boundaries between rotational domains of the ($23 \times \sqrt{3}$) structure. Terraces that are 500 \AA wide were routinely found and single-atom defects were observed in concentrations of less than 1 per 1000 surface atoms.

Low Coverage. At 0.3 ML coverage, benzene molecules decorate the top of the Au{111} atomic step edges in the form of a two-dimensional (2D) solid, very similar to benzene on Cu{111} at 77 K observed by Stranick et al.¹¹ Figure 2, parts A and B, shows STM images of the same area taken without and with a benzene molecule on the probe tip apex, respectively. Figure 2A shows an STM image acquired with a nominally bare Pt/Ir tip. In this image, benzene molecules are observed as protrusions lined up at the step edge. The average distance

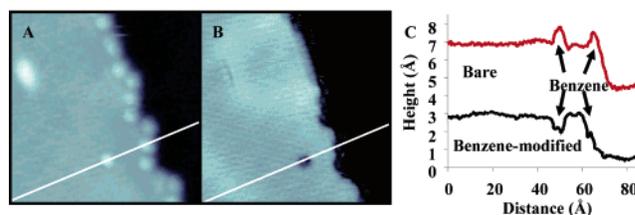


Figure 2. (A) STM image ($120 \text{ \AA} \times 120 \text{ \AA}$, $V_{\text{sample}} = -1.1 \text{ V}$, $I_t = 10 \text{ pA}$) of 0.3 ML of benzene on Au{111} taken with a bare Pt/Ir tip. Benzene molecules are aligned on top of the atomic step edge. Two features are present on the top terrace, namely a point dislocation at the elbow of the herringbone reconstruction and a single benzene molecule adsorbed on a single-atom defect. The coverage for this image is estimated based on dosing conditions, assuming a sticking coefficient of unity. (B) STM image ($120 \text{ \AA} \times 120 \text{ \AA}$, $V_{\text{sample}} = -1.1 \text{ V}$, $I_t = 10 \text{ pA}$) of the same area taken with a benzene molecule attached to the Pt/Ir tip. The Au{111} substrate is atomically resolved over the terrace, where both the herringbone reconstruction and the point dislocation can be clearly distinguished. (C) The white line in each image denotes the apparent height recorded with the nominally bare Pt/Ir tip (red) and the benzene modified tip (black). The apparent heights of the benzene molecules at the single-atomic defect and at the step edge are measured to be $0.9 \pm 0.1 \text{ \AA}$ and $0.6 \pm 0.1 \text{ \AA}$, respectively. The two height traces are offset by 4 \AA for clarity.

between molecules is measured to be $7.1 \pm 0.1 \text{ \AA}$. Two other features over the upper terrace are observed, namely a point dislocation at an elbow of the herringbone reconstruction¹⁰ as well as a single benzene molecule adsorbed on a single-atom defect, both imaged as protrusions (shown as bright). It should be noted that atomic resolution in Figure 2A is not observed because of the high gap impedance (-1.10 V sample bias voltage, 10 pA).

The images shown in Figure 2, parts A and B, are taken over the same area with the same tunneling conditions. Comparison of these two figures reveals two phenomena; first, the contrast reversal caused by imaging with a benzene molecule modified STM tip, and second, the enhanced resolution of the topographic image.^{12–15} In Figure 2B, benzene molecules adsorbed at the step edge and on top of the single atomic defect appear as depressions compared to the Au{111} substrate, whereas the herringbone reconstruction and a point dislocation at the herringbone reconstruction elbow are atomically resolved. From these observations, we postulate that prior to the imaging process for Figure 2B, a benzene molecule was picked up by the STM tip, with the positively charged tip apex interacting with its electron rich π -ring system, thus decreasing the apparent height of the benzene molecules observed in the image. This type of image contrast reversal caused by a molecule modified tip has been observed previously in other systems such as CO on Cu{111}.^{13,14} The atomic resolution of the image in Figure 2B is attributed to the spatially localized molecular orbitals of the benzene molecule attached to the tip apex, overlapping with the electronic states at the surface.^{12,15,16} The red and black traces on the right of Figure 2 represent the topographic height, indicated by the white lines in the STM images with and without a benzene-modified tip, respectively. When imaged by a nominally bare tip, the apparent height of benzene molecules at the single-atomic defect and at the step edge are measured to be $0.9 \pm 0.1 \text{ \AA}$ and $0.6 \pm 0.1 \text{ \AA}$, respectively. Because a

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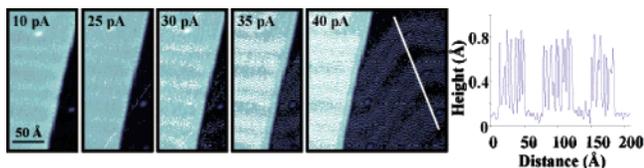


Figure 3. Series of STM images ($230 \text{ \AA} \times 130 \text{ \AA}$, $V_{\text{sample}} = -1.2 \text{ V}$) of 0.3 ML of benzene on Au{111} taken at increasing tunneling current. As the distance between the surface and the tip is reduced from image to image, areas of the noisy pattern become larger due to increasing tip-adsorbate interactions, indicating the increased presence of weakly adsorbed benzene molecules on the terraces. The white line on the rightmost image denotes the location of the height trace. The average height of the noise peaks is measured to be $0.6 \pm 0.1 \text{ \AA}$, which is comparable to the apparent height of benzene measured in Figure 2. Benzene molecules at the step edge are imaged as protrusions, indicating that these images are recorded with a nominally bare Pt/Ir tip.

similar apparent height change is observed for the benzene molecules at both adsorption sites, we conclude that benzene adsorbs at the top of the Au{111} atomic step edge. This observation is explained by the charge transfer at metal atomic step edges, the Smoluchowski effect, which enhances the empty local density of states (LDOS) at the top of the step, and the filled LDOS at the bottom of the step edge.¹⁷ With the presence of this strong electronic perturbation, the nucleophilic π -ring system of the benzene molecules will interact preferentially with the top of the step edge, as observed on other metal surfaces.^{11,18,19}

Figure 3 shows a series of STM images acquired at increasing tunneling current (decreasing tip–surface separation). As the tip–surface distance is reduced, the STM images show increasing noise over the soliton walls of the $(23 \times \sqrt{3})$ reconstruction. This noise is attributed to tip-induced motion of the benzene molecules transiently adsorbed on the terraces.²⁰ Benzene molecules adsorbed on top of the step edge are imaged as protrusions throughout the current increase, indicating no benzene molecule is permanently attached to the tip apex. The white line on the bottom image shows the location of the height trace over the herringbone-modulated noise pattern on the Au{111} terrace. The average height of the noise peaks is measured to be $0.6 \pm 0.1 \text{ \AA}$, which is comparable to the apparent height of a benzene molecule imaged with a nominally bare tip (Figure 2). Therefore, benzene molecules over the terraces are moving in and out of the tunneling junction faster than the imaging time scale, thus causing the “noise” in the STM image. The modulation of the noise reflects tip-adsorbate interaction of the benzene molecules over the herringbone reconstruction at low coverage. At negative sample bias, the attractive interaction between the π -ring system of the benzene molecules and the tip yields noise over regions where the substrate–adsorbate interactions are the weakest, namely over the soliton walls.²¹ This agrees with previous observation of CS_2 on Au{111}, where the appearance of the noisy patterns also takes place at negative sample bias.²⁰ Under these tunneling conditions, the tip-adsorbate interaction is repulsive between the tip and the electrophilic carbon center of the CS_2 molecule. As the distance between the tip and the substrate is reduced by

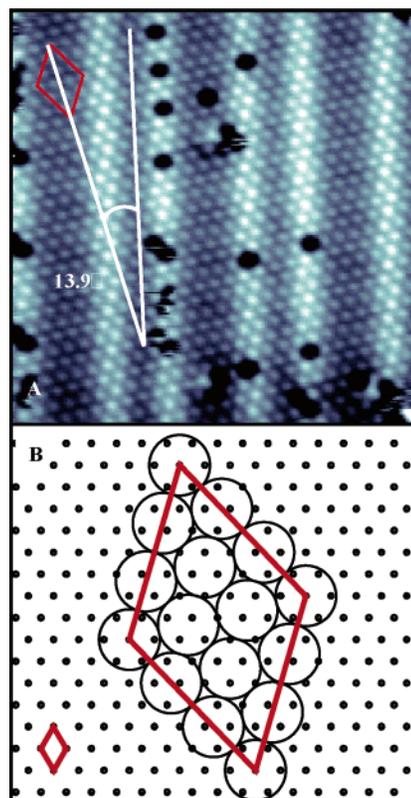


Figure 4. (A) STM image ($190 \text{ \AA} \times 190 \text{ \AA}$, $V_{\text{sample}} = -1 \text{ V}$, $I_t = 10 \text{ pA}$) of 0.99 ML of benzene on Au{111}. The benzene overlayer structure over the terrace at this coverage is $(\sqrt{52} \times \sqrt{52})R13.9^\circ$, the same structure as over the hcp region at 0.9 ML coverage. Most of the missing molecules are located on the soliton walls. (B) A schematic of the $(\sqrt{52} \times \sqrt{52})R13.9^\circ$ structure of the benzene overlayer over the hcp region of Au{111}. The unit cell of the structure is shown by the large red rhombus. The nearest neighbor distance between two benzene molecules is 6.95 \AA for this proposed structure.

decreasing the sample voltage, the noisy patterns appear in regions of high local electron density, where the interactions between the electrophilic carbon center and the surface electrons are strongest.²⁰

In summary, benzene on Au{111} at low coverage adsorbs preferentially at the top of the Au{111} step edges. Molecules adsorbed on the terraces are weakly physisorbed and are easily displaced by the scanning STM tip either through adsorption onto the tip apex or through tip-induced motion and therefore cannot be imaged at low benzene coverage.

High Coverage. At near-monolayer coverages, benzene molecules can be imaged stably on the Au{111} terraces, where benzene forms an ordered overlayer that has a long-range commensurate structure with respect to the Au{111} substrate. Figure 4A shows an STM image of 0.99 ML of benzene on Au{111}. This image shows that the gold herringbone reconstruction is still present after the formation of an overlayer, again indicating that the substrate–adsorbate interactions are weak, contrary to other systems such as alkanethiols on Au{111} where the chemisorption of the adsorbate lifts the substrate reconstruction.²² The unit cell of the benzene overlayer is illustrated by the red rhombus in Figure 4A. The angle of the unit cell with respect to the soliton wall is measured to be $13.9 \pm 0.5^\circ$ and is indicated by the set of white lines. Figure 4B

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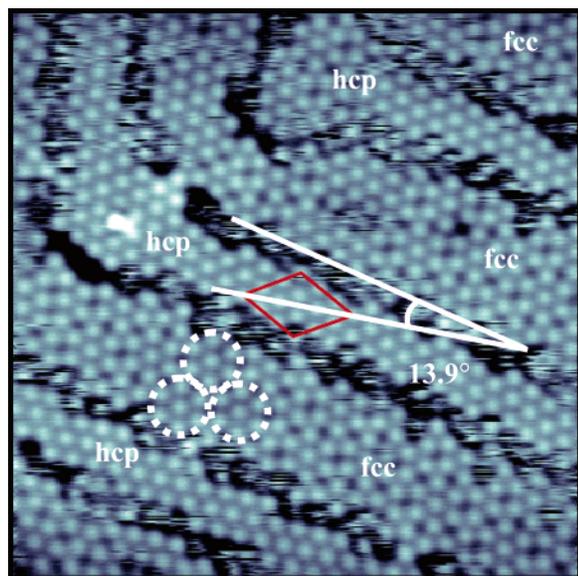


Figure 5. STM image ($190 \text{ \AA} \times 190 \text{ \AA}$, $V_{\text{sample}} = 0.2 \text{ V}$, $I_t = 10 \text{ pA}$) of 0.9 ML of benzene on Au{111}. The image shows that the benzene overlayer structure is different over the hcp and fcc areas of the terrace. Occasional mobility is observed over the soliton walls of the herringbone reconstruction.

shows the exact registry of the overlayer ($\sqrt{52} \times \sqrt{52}$)R13.9° structure, which is the long-range commensurate structure that most closely matches our observed benzene overlayer. Although the exact adsorption sites of the benzene molecules are unknown, our proposed structure suggests the presence of three types of adsorption sites, which include atop, 3-fold hollow and near bridge sites, all of which have been observed previously in systems such as benzene on Pt{111} and Rh{111}.^{18,23} It should be noted that most of the benzene vacancies are found over the soliton wall regions of Au{111}, where the benzene–Au bond strength is the weakest. This effect is attributed to the differences in electronic structure of the various substrate regions and is discussed in detail elsewhere.²¹

At a slightly lower coverage, the benzene overlayer on Au{111} exhibits definite structural variation over the different regions of the substrate. Figure 5 shows an STM image of a 0.9 ML of benzene adsorbed on Au{111}. In this image, different benzene overlayer structures are observed over the hcp, fcc, and soliton wall regions. Benzene molecules over the hcp areas have the same ($\sqrt{52} \times \sqrt{52}$)R13.9° structure, as is observed for the 0.99 ML coverage (Figure 4). The unit cell of this structure is highlighted by the red rhombus and the angle with respect to the soliton wall direction is marked once again by the white lines.

The overlayer structure is less densely packed over the fcc regions. This structure is composed of “pinwheels” of 7 close-packed benzene molecules, highlighted in Figure 5 by dotted circles. Figure 6 shows the proposed ($\sqrt{133} \times \sqrt{133}$)R17.5° structure for the fcc area, which most closely matches our observed overlayer. The large circles represent the benzene molecules as imaged by STM, with the pinwheel centers labeled in gray. The proposed overlayer structure has long-range commensuration, in which pinwheel centers are defined as molecules adsorbed on either atop or 3-fold hollow sites. Each benzene molecule forming the wheel around each pin is located

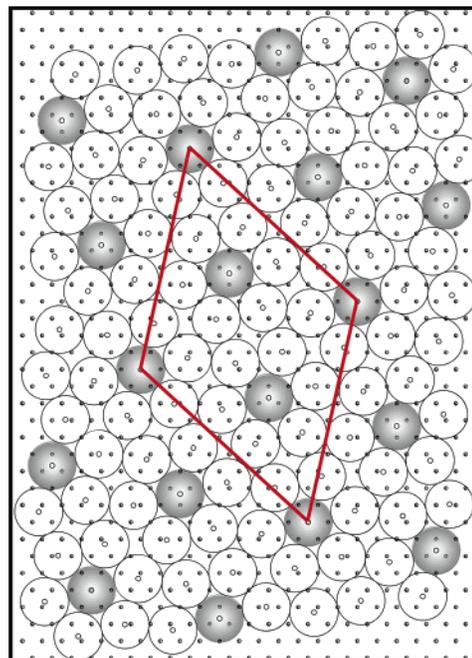


Figure 6. Schematic of the ($\sqrt{133} \times \sqrt{133}$)R17.5° pinwheel structure of the benzene overlayer over the fcc region of Au{111}. The large circles represent the apparent circumference of benzene molecules. The small circles represent the center of each benzene molecule. The black dots are the location of the surface Au atoms. The unit cell of the structure is shown by the red rhombus. Benzene molecules shown in gray are the centers of each pinwheel. Our proposed structure places every pinwheel center at atop or 3-fold hollow sites. The nearest neighbor distance between two benzene molecules is 7.07 Å for this proposed structure.

on equivalent, near atop sites. The unit cell for this structure is marked by the red rhombus in Figure 6. This pinwheel structure is similar to that of N₂O on the basal plane of graphite observed by Leinböck et al.²⁴ in which two adsorption geometries were observed over the same monolayer, namely the pin N₂O molecules were predicted to adsorb with the molecular axis perpendicular to the surface plane, whereas the surrounding wheel N₂O molecules lay flat. It should be noted that this N₂O pinwheel structure is also commensurate with the graphite atomic lattice through its pinwheel centers. These observations suggest that different adsorption energies for the pin and wheel molecules are a possibility. Further evidence for this argument will be presented in the next section. It should be noted that unlike the N₂O monolayer, the central pin benzene molecule does not stand up.

Over the soliton walls, benzene molecules are not stably adsorbed for STM imaging at this coverage, these vacancy rows in the benzene overlayer appear as depressions. However, the transient adsorption of benzene molecules over the soliton walls is evident from the streaky noise in the image over the depressions. Therefore, at 0.9 ML coverage, benzene forms a 2D gas over the soliton walls that coexists with two 2D solid phases over the hcp and the fcc areas.^{6,20,21,25} The difference in the overlayer structures is explained by the region specific substrate electronic structure and is discussed in detail in ref 21.

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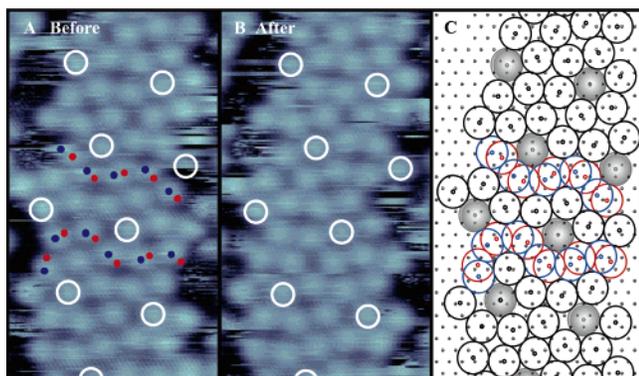


Figure 7. (A) STM image ($40 \text{ \AA} \times 81 \text{ \AA}$, $V_{\text{sample}} = 1 \text{ V}$, $I_t = 20 \text{ pA}$) showing the benzene overlayer structure over the fcc region of Au{111} substrate before a cascade motion. The white circles indicate the benzene molecules assigned to be adsorbed on atop or 3-fold hollow sites. The blue dots indicate the location of specific benzene molecules in this image that will move to the location indicated by the red dots in the subsequent image. (B) STM image ($40 \text{ \AA} \times 81 \text{ \AA}$, $V_{\text{sample}} = 1 \text{ V}$, $I_t = 20 \text{ pA}$) of the same region after the cascade motion. (C) Representation of Figure 7A. The black dots show the location of the Au{111} substrate lattice. The large red circles indicate the end position of a cascade event.

Cascade Motion in the fcc Overlayer. Molecular motions in this system were investigated by analyzing a series of 600 time-lapse images acquired over 40 h. Each image is of a $88 \text{ \AA} \times 88 \text{ \AA}$ area, which encompasses the hcp, fcc and soliton wall regions. The acquisition time for each STM image was four minutes. The resulting movie can be viewed in the Supporting Information.²⁶ Each image was digitally processed to identify the location, the number of nearest neighbors and the motion for each of the benzene molecules. Three types of molecular motion are observed, namely (1) 2D evaporation and condensation of benzene molecules,²¹ (2) isolated single molecule motions of a few Ångströms, and (3) concerted cascade motions in which two or more adjacent molecules are each displaced by a few Ångströms. The latter two types of motion are characterized by each benzene molecule being displaced by $2.4 \pm 0.6 \text{ \AA}$. The following discussion focuses on the cascade motion over the fcc region of Au{111}.

For clarity, the term “cascade” is used in this article to describe a chain of adjacent benzene molecules observed to have moved together within or between two consecutive STM images. Due to the limited time-resolution of STM, only the initial and final locations of the cascade events are observed. On the basis of previous theoretical work, our observed average distance between the benzene molecules over the fcc region (7.07 \AA) suggests that the forces between benzene molecules are attractive.^{21,27}

Figure 7, parts A and B, shows two consecutive STM images taken from the time-lapse series before and after cascade motions. The white circles indicate the benzene molecules we have assigned to be “pin-molecules.” In Figure 7A, the blue dots indicate the starting position of molecules that will undergo cascade motion, whereas the red dots indicate the location of the molecules in the subsequent image. These markers are visual aids to help identify cascade movements. Figure 7C is a representation of the STM images in Figure 7, parts A and B, showing the location of the surface Au atoms (black dots). In this representation, the final positions of the benzene molecules

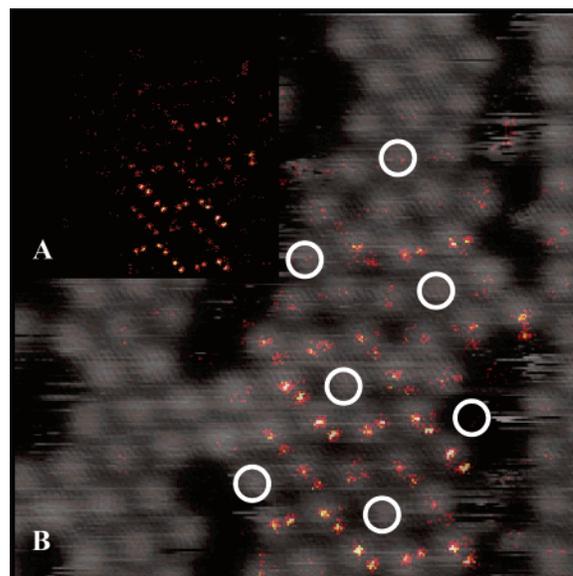


Figure 8. (A) Motion density map of all cascade events over the fcc region. Each molecule that underwent a cascade motion is labeled by a one-pixel colored dot. Bright spots on the map thus represent benzene molecules that are most prone to cascade motion. (B) The same motion density map as in (A), superimposed over the first STM image of the movie ($81 \text{ \AA} \times 81 \text{ \AA}$, $V_{\text{sample}} = 1 \text{ V}$, $I_t = 20 \text{ pA}$). The molecules marked by the white circles rarely moved throughout the movie and therefore are assigned to be adsorbed on either atop or 3-fold hollow sites. The lateral size of the dots is due both to tip drift during the movie, and error in identifying the center of each benzene molecule.

after the cascade events are indicated by large red circles. It should be noted that unlike Figure 6, the wheel molecules are not adsorbed on equivalent, near atop sites. Figure 6 is an ideal representation of the $(\sqrt{133} \times \sqrt{133})R17.5^\circ$ structure over the fcc regions, whereas Figure 7 is an observation of the real system between cascade movements. Focusing on the cascade events, several molecules are adsorbed on atop or 3-fold hollow sites in their initial positions, whereas all of the final positions are on near atop sites. The majority of cascade events starts and ends at the fcc/soliton wall interface. Although the structure of the benzene overlayer possesses a 3-fold symmetry, the net direction of most cascade events is almost parallel with the $[\bar{1}10]$ direction of the substrate. It appears that cascade events are reversible; a cascade in one direction is often followed by a cascade in the opposite direction.

There are several geometries of cascade motion. Figure 7A shows the most commonly observed linear cascades. However, out of 600 frames scanned, 21 occurrences of multiple legs of a cascade joining/splitting are observed (see supplemental movie in ref 26). In addition, there are also 5 events where large groups of molecules move, usually in the hcp region.

When all of the locations of the cascade motion events in the time-lapse series are correlated, we can produce a motion density map showing where cascade events are the most probable throughout the entire time-lapse image series (Figure 8A). The motion of a single benzene molecule is represented by a pair of yellow dots that mark the initial and final positions of a cascade event. In the inset of Figure 8A, the intensity of the yellow dots represents the amount of motion. Areas that show no yellow dot pair denote areas where no molecular motion was observed. When the motion density map is superimposed on an STM image (Figure 8B), we observed that certain benzene molecules are less prone to molecular cascade

(26) See Supporting Information.

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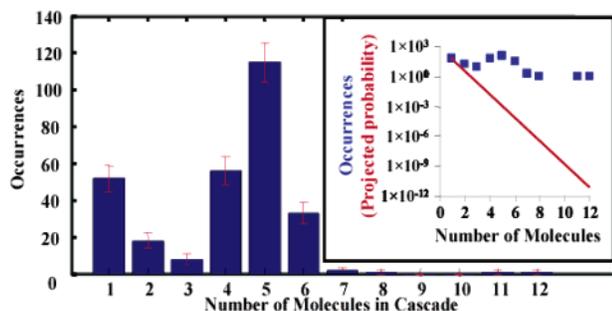


Figure 9. Graph showing the relationship between the occurrences of cascades event with the respective number of molecules per cascade. The inset shows a log scale plot of the same distribution. The red line in the inset shows the projected exponential decay of the occurrence for the case of independent random motion. The comparison of the two curves demonstrates that the observed cascade events do not result from independent random molecular motions.

motion; these are marked by white circles. When comparing the relative positions of these stable molecules with our proposed pinwheel structure, we find that these stable molecules correspond to the molecules we previously identified as pinwheel centers (highlighted as gray molecules in Figure 6). This observation also suggests a difference in adsorption energy between the pin- and the wheel-molecules, which is consistent with our assignment of these stable molecules as pin-molecules.

To determine if the cascade motion we observe is random or concerted motion, we calculated the probability of n adjacent molecules independently moving. If the mechanism of the cascade is independent random motion, we can then establish that the probability $P(n)$ of a cascade event involving n molecules is the product of the probability of individual molecular motion ρ , which leads to the relationship

$$P(n) = \rho^n \quad (1)$$

The probability ρ for the fcc region was calculated using the following equation

$$\rho = \frac{N_{\text{cascade, fcc}}}{N_{\text{total, fcc}}} \quad (2)$$

where $N_{\text{cascade, fcc}}$ is the total number of benzene molecules involved with cascade motion in the fcc region, and $N_{\text{total, fcc}}$ is the total number of benzene molecules counted over the fcc region. Our calculation yields $\rho = 0.061 \pm 0.001$.²⁸

To investigate the relationship stated by eq 1, we recorded the number of cascade events with the respective number of molecules in each cascade event from the time-lapse STM images. Only those cascades with STM images showing the initial and final benzene molecule positions were taken into account. We have discarded any cascade event whose number of benzene molecules involved was indiscernible. Out of a total of 385 cascade events observed, 98 events were discarded. The red dots in Figure 9 show the plot of occurrence of a cascade event with the number of molecules in that cascade. The

predominance of cascade events involving 4, 5, and 6 molecules can be explained by the morphology of the fcc region of the Au{111} substrate, which is confined in the $[\bar{1}10]$ direction by the soliton walls. This means that the width of the fcc region would restrict the cascade length in the $[\bar{1}10]$ direction to 4 to 6 molecules, exposing the extremities of these cascades to the 2D gas phase benzene molecules of the soliton wall regions. Moreover, the directions of the majority (95 %) of the cascades are also almost aligned with the scanning direction of the STM tip. This suggests that the direction of a cascade is not only determined by the morphology of the overlayer structure, but also is influenced by the STM tip. The red line in Figure 9 is the probability that n molecules would randomly move, based on eq 1 normalized to the observed number of occurrences for one molecule movements (52 counts). In comparing the two curves, we note that the projected curve rapidly decays to a probability of 1×10^{-12} for $n = 12$. This suggests that if the observed cascades movements resulted from individual *independent random* molecular motions, the observation of a twelve-molecule cascade would have been extremely unlikely under our experimental conditions. Therefore, we conclude that although the tip contributes to inducing motion, as well as affecting the direction of cascade events, the fact that cascades of 11 and 12 benzene molecules were observed suggests that the cascade motion is concerted, not independent in nature.

We have shown that when perturbed, benzene molecules adsorbed on a Au{111} surface can undergo small displacements, not randomly but in long chains of small concerted moves up to 12 molecules in length. This phenomenon relies on intermolecular forces mediated by the substrate, so-called substrate-mediated interactions (SMIs).^{11,19,21} Previously, we have shown in ref 21 that SMIs have a direct effect on the stability of individual benzene molecules as a function of number of nearest neighbors. These interactions are found to be attractive and of ~ 0.4 kJ/mol per neighboring benzene molecule, i.e., a benzene molecule with four nearest neighbors would be stabilized on its adsorption site by 1.6 kJ/mol with respect to one with no nearest neighbors.^{21,27}

These data help us understand the mechanism of the cascades and explain their predominance in the molecular motion of this system. Cascades can be thought of as being sequential changes of molecules' numbers of nearest neighbors. For example, a cascade is often initiated in the fcc region by a molecule at the edge of the region undergoing a small move. This in turn reduces the number of nearest neighbors of the surrounding molecules, thus destabilizing them. This makes them more likely to undergo small moves in order to stabilize themselves and in turn destabilize the next set of molecules along the chain. We believe this SMI effect to be the basis of the cascade motion we observe in the benzene overlayer.

Conclusions

We have used STM to investigate the growth of benzene monolayer on Au{111}, and characterize the various structures over different regions of the substrate. At low coverage, benzene adsorbs at the top of the monatomic step edges and is weakly physisorbed on terraces. At higher coverages, different long-range commensurate structures were observed, namely a $(\sqrt{52} \times \sqrt{52})R13.9^\circ$ structure over the hcp and a $(\sqrt{133} \times \sqrt{133})R17.5^\circ$ pinwheel structure over the fcc regions, as well as a 2D

(28) It should be noted that $N_{\text{cascade, fcc}}$ is an overestimation, as out of the total of 385 cascade events observed, the number of benzene molecules involved could not be determined for 98 events. For the calculation of ρ , these 98 events were assumed to involve five-molecule cascades, the most probable cascade event. The values used for our calculation are as follows: $N_{\text{cascade, fcc}} = 1644$ counts, $N_{\text{total, fcc}} = 27\,046$ counts.

gas phase over the soliton wall areas. Moreover, the time-lapse STM images have revealed tip-induced cascade motion at near-monolayer coverage. We have demonstrated that the observed cascade motion is not the result of random motion of individual benzene molecules, but rather is a concerted motion. This observation may be relevant to the mechanism of mass transport of molecules over surfaces, where instead of a STM tip triggering the cascade motion, the removal of the product molecules might result in cascade motion.

Acknowledgment. The authors gratefully acknowledge financial support of the Army Research Office, the National Science Foundation and the Office of Naval Research. We are also appreciative of Prof. dr. Joost W. M. Frenken and Prof. Vin Crespi for helpful discussions. B.A.M. is grateful for a fellowship from the ACS Division of Analytical Chemistry sponsored by GlaxoSmithKline.

Supporting Information Available: Molecular cascades imaged as a series of scanning tunneling micrographs. The movie is a compilation of 600 STM time-lapse images ($81 \text{ \AA} \times 81 \text{ \AA}$, $V_{\text{sample}} = 1 \text{ V}$, $I_t = 20 \text{ pA}$, images taken at 4 K) over 0.9 ML benzene molecules on Au{111}. Each molecule that takes part in a cascade event or single molecule motion is marked by a pair of dots, one blue and one red. The blue dot indicates the location of the benzene molecule as found in the STM image before it moves, while the red dot indicates the location of the same molecule after it moves (in the subsequent image). A total of 1798 dot pairs are shown. Some molecular events were eliminated for the generation of Figure 9 and the calculation of ρ , due both to tip drift during the movie and to possible errors in identifying the center of each benzene molecule. A total of 1154 molecular cascade events that were imaged completely were detected by manual counting. This material is available free of charge via the internet at <http://pubs.acs.org>.

JA049113Z