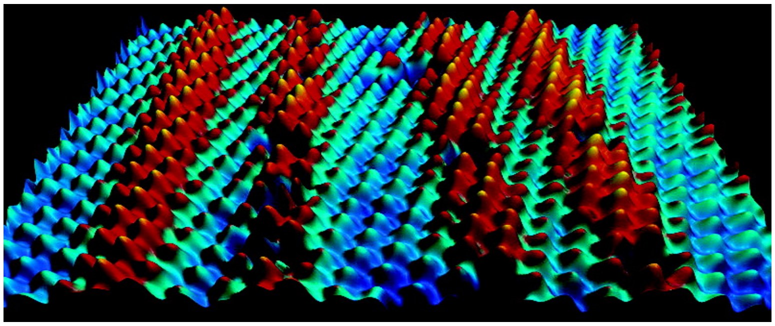
Article

# Substrate-Mediated Intermolecular Interactions: A Quantitative Single Molecule Analysis

E. Charles H. Sykes, Brent A. Mantooth, Patrick Han, Zachary J. Donhauser, and Paul S. Weiss

*J. Am. Chem. Soc.*, **2005**, 127 (19), 7255-7260• DOI: 10.1021/ja0472331 • Publication Date (Web): 20 April 2005



Journal of the American Chemical Society is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

J|A|C|S
ARTICLES
Published on Web 04/20/2005

# Substrate-Mediated Intermolecular Interactions: A Quantitative Single Molecule Analysis

E. Charles H. Sykes,† Brent A. Mantooth, Patrick Han, Zachary J. Donhauser,‡ and
Paul S. Weiss*

*Contribution from the Departments of Chemistry and Physics, 104 Davey Laboratory,
The Pennsylvania State University, University Park, Pennsylvania 16802-6300*

Received May 11, 2004; E-mail: stm@psu.edu

***Abstract:*** Long-range intermolecular interactions mediated by the surface are believed to be responsible for many effects in surface science, including molecular ordering, formation of nanostructures, and aligning reactive intermediates in catalysis. Here, we use scanning tunneling microscopy to probe the weak substrate-mediated interactions in benzene overlayers on Au{111} at 4 K. Using an automated procedure to monitor single molecule motion, we are able to quantify the substrate-mediated interaction strength. We explain quantitatively both the kinetics of the benzene motion and the thermodynamics that determine the packing structures benzene adopts in this system in light of these substrate-mediated interactions.

## Introduction

The roles of catalysts in chemical reactions are to provide sites for accumulation of reactants and/or intermediates and to facilitate reaction by providing lower energy transition states than those available to reactants in the gas or solution phases. Pre-reaction alignment of reactants in favorable interaction geometries can increase the rates of reactions.[1−4] In many industrial catalysts, metal particles provide the active sites for reacting gas molecules, thus investigating adsorption and intermolecular interactions on metal surfaces is key to understanding and controlling surface chemistry. To this end, many model studies have investigated molecular adsorption and ordering on well-defined metal single crystal surfaces.[2,4−9] These studies have revealed that molecules locally perturb the electronic structure of the surrounding surface, and that attractive intermolecular interactions can occur in many cases not directly, but by through-substrate interactions, termed substrate-mediated interactions (SMIs).

A good example of SMIs is the growth of benzene molecules on Cu{111}.[2,5,6] A single row of molecules adsorb at sites above monatomic steps and perturb the electron density of the surrounding surface. This creates additional sites for adsorption for a second and third row of molecules. This observation suggests that SMIs may be responsible for guiding mobile adsorbates to specific sites of a growing structure, and that control over molecular chemistry may provide a means for engineering nanometer-scale, atomically precise structures. An understanding of these types of SMIs may be crucial for the design of the next generation of catalysts, where one could envision enhancing reaction rates by carefully engineering the electronic structure of the metal particles to maximize reactant or intermediate coupling.

The aim of this work is to study molecular motion as a function of the number of nearest neighbors and to relate this quantitatively to the SMI between benzene molecules. Similar effects have been studied previously for atoms on metal surfaces. The earliest experimental data on spatial modulation of adatom position by oscillatory through-substrate interactions were performed by Tsong using field ion microscopy (FIM).[10,11] From adatom separation distribution statistics, the authors concluded that an oscillatory pair potential exists between Re adatoms on a W surface. Very recently, these types of systems have been revisited by scanning tunneling microscopy (STM), and the long-range adatom/adatom interactions have been explained in terms of the Friedel oscillations created by the atoms' perturbation of the surface state.[12,13] A statistical analysis confirmed that the separations between the atoms was oscillatory; this was explained in terms of constructive interference between the Friedel oscillations associated with each atom.[12,13]

To investigate SMIs more quantitatively, we have used STM to study benzene on Au{111}, a system with weak molecule−metal interactions. The weak molecule−metal interaction en-

---

[†] Current address: Department of Chemistry, Tufts University, 62 Talbot Avenue, Medford, MA 02155

[‡] Current address: Department of Chemistry, Vassar College, Poughkeepsie, NY 12604

(1) Sautet, P.; Paul, J. F. *Catal. Lett.* **1991**, *9*, 245.
(2) Kamna, M. M.; Stranick, S. J.; Weiss, P. S. *Science* **1996**, *274*, 118.
(3) Sykes, E. C. H.; Han, P.; Kandel, S. A.; Kelly, K. F.; McCarty, G. S.; Weiss, P. S. *Acc. Chem. Res.* **2003**, *36*, 945.
(4) Weiss, P. S.; Eigler, D. M. *Phys. Rev. Lett.* **1993**, *71*, 3139.
(5) Stranick, S. J.; Kamna, M. M.; Weiss, P. S. *Surf. Sci.* **1995**, *338*, 41.
(6) Stranick, S. J.; Kamna, M. M.; Weiss, P. S. *Science* **1994**, *266*, 99.
(7) Bohringer, M.; Schneider, W.-D.; Berndt, R.; Glockler, K.; Sokolowski, M.; Umbach, E. *Phys. Rev. B* **1998**, *57*, 4081.
(8) Bohringer, M.; Schneider, W.-D.; Berndt, R. *Surf. Sci.* **1998**, *408*, 72.
(9) Kamna, M. M.; Graham, T. M.; Love, J. C.; Weiss, P. S. *Surf. Sci.* **1998**, *419*, 12.
(10) Tsong, T. T. *Phys. Rev. Lett.* **1973**, *31*, 1207.
(11) Tsong, T. T. *Phys. Rev. B* **1972**, *6*, 417.
(12) Repp, J.; Moresco, F.; Meyer, G.; Rieder, K.-H.; Hyldgaard, P.; Persson, M. *Phys. Rev. Lett.* **2000**, *85*, 2981.
(13) Knorr, N.; Brune, H.; Epple, M.; Hirstein, A.; Schneider, M. A.; Kern, K. *Phys. Rev. B* **2002**, *65*, 115420.

**10.1021/ja0472331 CCC: $30.25 © 2005 American Chemical Society**

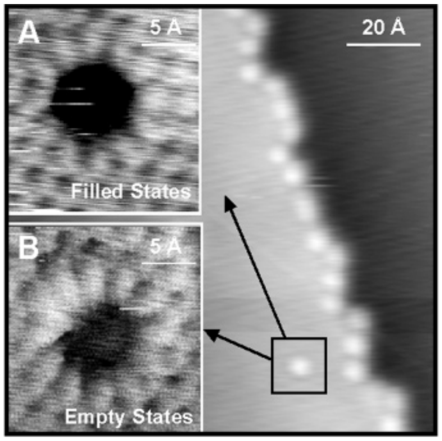


***Figure 1.*** STM constant current image (65 Å × 115 Å) of 0.1 ML of benzene molecules adsorbed on Au{111} at 4 K ($V_{\mathrm{sample}} = -0.8$ V, $I_t = 10$ pA). The insets (A and B) show two high-resolution images (17 Å × 17 Å) of the benzene molecule on the terrace taken with a benzene-modified tip: (A) $V_{\mathrm{sample}} = -1.0$ V, $I_t = 10$ pA; (B) $V_{\mathrm{sample}} = +1.5$ V, $I_t = 10$ pA).

ables the interrogation of SMIs between the benzene molecules by careful analysis of the benzene motion.

## Experimental Section

All experiments were performed in a low-temperature, ultrahigh vacuum (UHV) STM, described elsewhere.[14] All images were recorded at 4 K in constant−current mode with a mechanically cut Pt/Ir (85/15%) tip. An ordered Au{111} surface was prepared from a Au/mica sample (Molecular Imaging) by repeated cycles of sputtering and annealing. Liquid benzene (99.9% purity) was obtained from Sigma Aldrich and was further purified by cycles of freeze/pump/thaw prior to introduction to the UHV chamber via a leak valve. Benzene was deposited on the sample at 4 K by line-of-sight dosing.[14]

## Results and Discussion

Figure 1 shows an STM image of 0.1 monolayers (ML) of benzene adsorbed on Au{111} at 4 K. The line running diagonally through the image is a monatomic step on the Au substrate; the protrusions are benzene molecules adsorbed above the step. Smoluchowski described the charge redistribution at metallic steps that results in a net flow of electrons from the edge of the upper terrace to the lower terrace, and this effect has been shown to influence the growth of molecular overlayers.[15,16] The fact that benzene adsorbs preferentially above step edges indicates that it seeks areas of high empty state density and that it behaves as a nucleophile on the Au surface. This point will become pertinent when we discuss how benzene perturbs its surrounding electronic structure and creates favorable adsorption sites for neighboring benzene molecules.[2,6]

At low coverages (<0.8 ML), benzene molecules on Au terraces are not stationary during imaging; however, in Figure 1, a single benzene molecule (black square) is observed pinned at a single atom defect. The density of these defects is typically 1 per ∼10 000 Au atoms. The STM images in insets A and B of Figure 1 show high-resolution scans over this benzene molecule taken with a benzene molecule attached to the tip. With this tip, the corrugation of the substrate Au atoms is enhanced and the benzene molecules appear as depressions.[17] By picking up a molecule or an atom on a tip, one can enhance contrast; our images atomically resolve the Au surface in the vicinity of the pinned benzene molecule.[7,17] Panels A and B of Figure 1 are taken at negative and positive sample bias, respectively, and, hence, depict the filled and empty state densities of the surface, respectively. A key point to note is that the 12 Au atoms nearest the benzene molecule appear misshapen, indicating that benzene perturbs the surface's filled and empty state electronic structures in its vicinity. This effect is not observed around single atom defects free of adsorbed benzene molecules.[18] This perturbation of the electron density in the vicinity of a molecule is the basis of the SMI effect in the benzene/Au system described below.

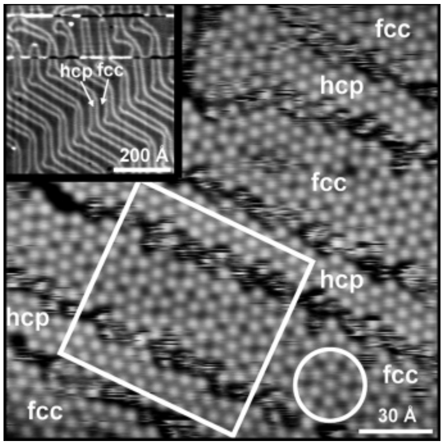


***Figure 2.*** STM constant current image (180 Å × 180 Å) of 0.9 ML of benzene molecules adsorbed on Au{111} at 4 K ($V_{\mathrm{sample}} = +0.2$ V, $I_t = 10$ pA). Note the different overlayer structure of benzene adsorbed on the different regions of the Au surface (hcp, fcc). The white square denotes the area where the movie was taken; the white circle shows the unit cell pinwheel structure. The inset shows an image, (600 Å × 600 Å) of a clean Au{111} surface at 4 K ($V_{\mathrm{sample}} = +0.1$ V, $I_t = 100$ pA). Monatomic steps and the herringbone reconstruction are seen.

The inset of Figure 2 shows a typical STM image of the clean Au{111} surface at 4 K before benzene deposition. The lines running diagonally across the surface are the soliton walls of the herringbone reconstruction, which separate areas where the underlying Au is hexagonal close-packed (hcp) or face-centered cubic (fcc), as labeled in Figure 2.[19] The soliton walls are 0.3 Å protrusions with a structure intermediate between hcp and fcc. For the rest of this paper, we will refer to each region of the Au{111}($23 \times \sqrt{3}$) surface as hcp, fcc, and soliton.

Figure 2 shows an STM image of Au{111} with a benzene coverage of 0.9 ML. We note that the benzene packing structure is dependent on the underlying gold structure; benzene is hexagonally close-packed in hcp areas, less tightly packed in a "pinwheel" structure in the fcc areas (see white circle in Figure 2), and tends to avoid adsorption on the soliton walls. From our measurements, we assign the close-packed benzene in the hcp areas as a ($\sqrt{52} \times \sqrt{52}$)$R$13.9° commensurate overlayer structure.[20] The pinwheel structure of benzene adopted in the fcc regions has long-range order ($\sqrt{133} \times \sqrt{133}$)$R$17.5°. A

---

[14] Stranick, S. J.; Kamna, M. M.; Weiss, P. S. *Rev. Sci. Instrum.* **1994**, *65*, 3211.

[15] Smoluchowski, R. *Phys. Rev.* **1941**, *60*, 661.

[16] Unguris, J.; Bruch, L. W.; Moog, E. R.; Webb, M. B. *Surf. Sci.* **1981**, *109*, 522.

[17] Meyer, G.; Neu, B.; Rieder, K. H. *Chem. Phys. Lett.* **1995**, *240*, 379.

[18] Han, P.; Sykes, E. C. H.; Pearl, T. P.; Weiss, P. S. *J. Phys. Chem. A* **2003**, *107*, 8124.

[19] Barth, J. V.; Brune, H.; Ertl, G.; Behm, R. J. *Phys. Rev. B* **1990**, *42*, 9307.

[20] Han, P.; Mantooth, B. A.; Sykes, E. C. H.; Donhauser, Z. J.; Weiss, P. S. *J. Am. Chem. Soc.* **2004**, *126*, 10787.

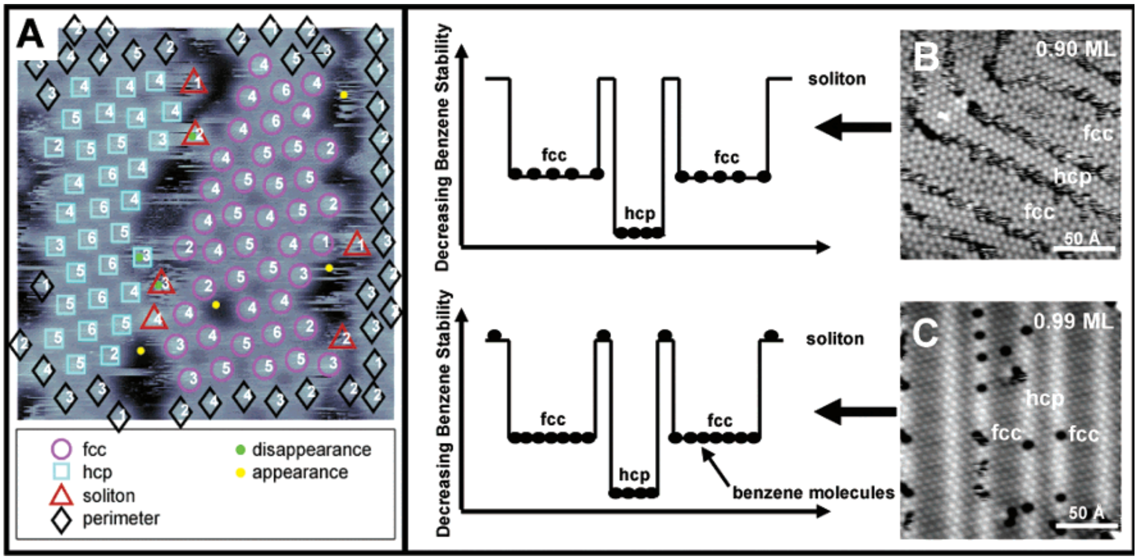


***Figure 3.*** (A) STM constant current image (81 Å × 81 Å) of 0.9 ML of benzene on Au{111} at 4 K ($V_{\text{sample}} = +0.3$ V, $I_t = 5$ pA). Each of the benzene molecules has been identified, using image processing, as indicated by circles. The white numbers indicate the number of nearest neighbors that each molecule has. (B and C) Images revealing benzene packing evolving as a function of surface coverage. At 0.9 ML of coverage, benzene molecules close-pack at the most stable sites (hcp); next most favorable sites (fcc) are also occupied, but with a lower packing density. The most unfavorable regions (soliton) remain unoccupied. At 0.99 ML of coverage, benzene close-packs on all areas, and the majority of the vacancy sites occur on the least favorable binding areas, the soliton walls. Corresponding schematic depicting the energy level diagram of the system is also shown. Imaging conditions are as follows: (B) $V_{\text{sample}} = +0.2$ V, $I_t = 10$ pA (180 Å × 180 Å); (C) $V_{\text{sample}} = -1$ V, $I_t = 10$ pA (180 Å × 180 Å).

detailed description of these overlayer structures is the subject of a companion publication.[20]

The soliton walls appear as depressions on the benzene-covered surface due to the absence of benzene molecules in these locations.[14] The regions near the soliton walls also appear streaky (Figure 2); this effect is common in STM images and arises from molecular motion in and out of the tunnel junction on a time scale faster than scanning.[6,21] On the time scale of imaging (seconds−minutes), the benzene molecules are not localized on a specific site like the overlayer structures (two-dimensional (2D) solids on the hcp and fcc regions); the molecules are better described as a 2D gas.[6,21,22] The apparent height of the streaks is 0.6 ± 0.1 Å, which is consistent with the height of transiently adsorbed benzene molecules on Au{111}.[20] We utilize this as a system in which dynamics of molecular motion can be studied and compared directly on structurally different parts of the Au surface.

To investigate the dynamics of benzene on Au{111}, we recorded a series of time-lapse images over the area marked by a white square in Figure 2. The resulting series of images is included in the Supporting Information (Movie S1). Digital image processing was employed to identify the location, number of nearest neighbors, Au region of adsorption (hcp, fcc, soliton), and if motion is detected for each benzene molecule (Movie S2). Each of these parameters is indicated in Figure 3A, where identified benzene molecules are marked by a colored shape describing the Au region; the number indicates the molecule's number of nearest neighbors, and dots show where molecules move between successive frames. It is important to note that the identified benzene molecules in the outside perimeter of the image do not show regional information. These molecules were omitted from the analysis because their nearest neighbor molecules are outside of the imaging area and, therefore, do not yield valid information.

In total, 600 frames of the movie were analyzed; 76 000 molecular positions were measured, and 3200 instances of molecular motion were recorded. Three distinct types of benzene motion were observed: (1) 2D "desorption" from fixed adsorption sites followed by uncorrelated "readsorption" of benzene molecules at nearby sites, (2) isolated single molecule motions of a few Ångstroms, and (3) many-molecule concerted small motions, so-called molecular cascades.[23] This paper is mainly concerned with the 2D desorption/readsorption type of motion; the others are discussed in greater detail in a companion publication.[20]

For each region and frame, the number of 2D desorption/readsorption events was recorded as a function of nearest neighbors, $M_{\text{region,frame}}(n)$. Similarly, the number of molecules in a given region was counted for each frame as a function of the number of nearest neighbors, $C_{\text{region,frame}}(n)$. The probability that a molecule will move per frame, $P(n)$, is averaged by dividing by the number of frames $N(n)$ where there is at least one molecule with $n$ nearest neighbors in that frame (i.e., $C_{\text{region,frame}}(n) > 0$):

$$P_{\text{region}}(n) = \frac{\displaystyle\sum_{\text{frame}|C_{\text{region,frame}}(n)\neq 0} \frac{M_{\text{region,frame}}(n)}{C_{\text{region,frame}}(n)}}{N(n)}. \qquad (1)$$

From the measurement of the relative rates of benzene motion on the different regions of the surface, we can fit the data to the Arrhenius equation in order to determine the barrier to motion of benzene in each region ($\Delta E_{\text{BAu}}$). The standard Arrhenius expression for over-the-barrier hopping is

---

[21] Berner, S.; Brunner, M.; Ramoino, L.; Suzuki, H.; Guntherodt, H. J.; Jung, T. A. *Chem. Phys. Lett.* **2001**, *348*, 175.

[22] Sykes, E. C. H.; Han, P.; Weiss, P. S. *J. Phys. Chem. B* **2003**, *107*, 5016.

[23] Heinrich, A. J.; Lutz, C. P.; Gupta, J. A.; Eigler, D. M. *Science* **2002**, *298*, 1381.

$$\text{Rate} = A \exp\left(\frac{-\Delta E_{\text{BAu}}}{RT + \Delta E_{\text{TIP}}}\right). \qquad (2)$$

In our experiment, the attempt frequency, $A$, for benzene to leave its adsorption site can be estimated from inelastic electron tunneling spectroscopy (IETS), in which we found benzene molecules in a monolayer on the Au{111} surface gave peaks at 10 and 105 meV. We previously studied benzene weakly adsorbed on Ag{110} and measured IETS peaks at 7 and 43 meV and assigned these peaks as external adsorbate−substrate modes.[24,25] High-resolution inelastic He atom scattering data for hydrocarbons on metals surfaces reveal that peaks corresponding to the molecule's frustrated translation normal to the surface occur between 5 and 10 meV.[26,27] Therefore, we believe our peak at 10 meV corresponds to a frustrated translation mode (or at least is close in energy to such modes) and, therefore, constitutes a good approximation for the attempt frequency, $A$ ($2.42 \times 10^{12}$ Hz).

It is unlikely that the degree of molecular motion we observe would occur at 4 K without the STM tip present. Therefore, we have included an additional term, $\Delta E_{\text{Tip}}$, to the conventional $RT$ term to account for tip-induced motion of benzene. Our model will yield a value for this interaction and provide insight into the degree of perturbation that molecules experience in an STM experiment. Attempts were made to study this system with different tunneling currents and voltages in order to further demonstrate the perturbative effect of the tip. However, this proved impossible; when the tunneling current was increased (>30 pA) or the bias voltage was decreased (<0.2 V), the tip no longer imaged the adsorbed benzene molecules, but rather the underlying Au atoms of the surface. We previously observed this effect for benzene on Ag{110} and explained it in terms of stronger coupling of the tip with adsorbate or surface atom wave functions, depending on the tip−sample separation.[28]

By first measuring total motion as a function of area, and using eq 2, we are able to calculate relative values for $\Delta E_{\text{BAu}}$. The motion probability (number of movements/total number of frames) in each area is $0.217 \pm 0.0076$, $0.0667 \pm 0.0016$, and $0.0169 \pm 0.0010$ (soliton, fcc, and hcp, respectively). Throughout this calculation, we quote error bars only arising from our automated sampling procedure, neglecting to count motion occurring between movie frames. From these figures, our analysis yields relative values for $\Delta E_{\text{BAu}}$ in the three regions with a ratio of 0.96:1.00:1.04 for soliton:fcc:hcp. An estimate of absolute energies of $\Delta E_{\text{BAu}}$, the diffusion barrier, can be made from a knowledge of the temperature-programmed desorption (TPD) value for the benzene adsorption strength on Au and from the corrugation ratio for nonmetallic adsorbate diffusion on Au.[29] Syomin et al. found that submonolayer coverages of benzene desorbed from Au{111} at 239 K, which correlates to a Au/benzene bond strength of 61.5 kJ/mol.[30] The adsorbate−surface bond strength can be related to its diffusion barriers via the corrugation ratio of the specific surface. Therefore, we calculate the energy barrier for benzene to leave its adsorption site and move into the 2D gas by multiplying the (3D) desorption enthalpy (61.5 kJ/mol) by the corrugation ratio (0.230) for nonmetallic adsorbate diffusion on Au.[29] This yields a value for $\Delta E_{\text{BAu}}$ of 14.2 kJ/mol and is a reasonable estimate as corrugation ratios are found to be rather insensitive to adsorbate type over many metal surfaces.[29] We can now present real diffusion barriers for benzene molecules adsorbed on the Au{111} surface: $\Delta E_{\text{BAu}} = 14.8$, 14.2, and $13.6 \pm 0.1$ kJ/mol for hcp, fcc, and soliton regions, respectively. This analysis also yields a value for $\Delta E_{\text{Tip}}$ of $0.42 \pm 0.01$ kJ/mol, which demonstrates that the tip influence in this STM diffusion study is significant, equivalent to ∼50 K in thermal energy. The error bars of the $\Delta E_{\text{Tip}}$ value are associated with both the counting errors arising from the digital image processing and the linear fit of our data with 90% confidence intervals. The influence of the tip becomes pertinent when considering another type of motion in this system, namely, molecular cascades; this topic is covered at length in a companion publication.[20]

As mentioned above, the finite scanning speed of STM does not allow us to image mobile molecules with short residence times, and thus our analysis underestimates the motion over the soliton walls. To this end, we speculate that benzene binding at soliton walls is even weaker than that calculated (i.e., <13.6 kJ/mol). However, this uncertainty does not affect the following discussion as the benzene/soliton interaction is certainly the weakest interaction of the three regions.

Assuming the energy of the benzene in the 2D gas is the same regardless of the region from which it moved, we can relate the magnitude of the diffusion barrier to stability of the molecule adsorbed in that region. For example, if the diffusion barrier is large, then the benzene molecule was strongly adsorbed on the Au in the particular region from which it desorbed. Panels B and C of Figure 3 show schematics with the relative stability of benzene molecules in each region. This trend is also observed in the STM images showing benzene packing structures as a function of coverage. From Figure 3B, we can see that at 0.9 ML coverage, the molecules completely fill the most favorable regions (hcp) and pack with lower density in the fcc areas (pinwheel structure).[20] The soliton pairs are almost completely unoccupied as they are the least favorable adsorption sites. As the coverage is increased to 0.99 ML (Figure 3C), the molecules are forced to close-pack in the next lowest-energy site, the fcc regions, and also partially fill the most energetically unfavorable soliton sites. It is interesting that the subtle differences in the benzene/Au interaction strength in the three regions of the Au{111}($\sqrt{3} \times 23$) substrate affect both diffusion rates and packing density of the molecule so dramatically. This result is particularly interesting in light of recent STM data relating electron potential to position on the Au{111} surface.[31] Kern and co-workers demonstrated that the electron potential varies as a function of region on the Au surface, being greatest in the fcc areas and least at the soliton walls. We suggest that these differences in electronic structure may explain the regional variation in benzene binding stability; however, at this point, we cannot offer any quantitative backing for this suggestion.

To investigate the effect of neighboring molecules on molecular motion, we analyzed our data to relate the probability

---

(24) Pascual, J. I.; Jackiw, J. J.; Song, Z.; Weiss, P. S.; Conrad, H.; Rust, H. P. *Phys. Rev. Lett.* **2001**, *86*, 1050.

(25) Pascual, J. I.; Jackiw, J. J.; Song, Z.; Weiss, P. S.; Conrad, H.; Rust, H. P. *Surf. Sci.* **2002**, *502*, 1.

(26) Witte, G.; Woll, C. *J. Chem. Phys.* **1995**, *103*, 5860.

(27) Witte, G.; Fuhrmann, D.; Woll, C. *Chem. Phys. Lett.* **1997**, *265*, 347.

(28) Pascual, J. I.; Jackiw, J. J.; Kelly, K. F.; Conrad, H.; Rust, H. P.; Weiss, P. S. *Phys. Rev. B* **2000**, *62*, 12632.

(29) Seebauer, E. G.; Allen, C. E. *Prog. Surf. Sci.* **1995**, *49*, 265.

(30) Syomin, D.; Kim, J.; Koel, B. E.; Ellison, G. B. *J. Phys. Chem. B* **2001**, *105*, 8387.

(31) Burgi, L.; Brune, H.; Kern, K. *Phys. Rev. Lett.* **2002**, *89*.

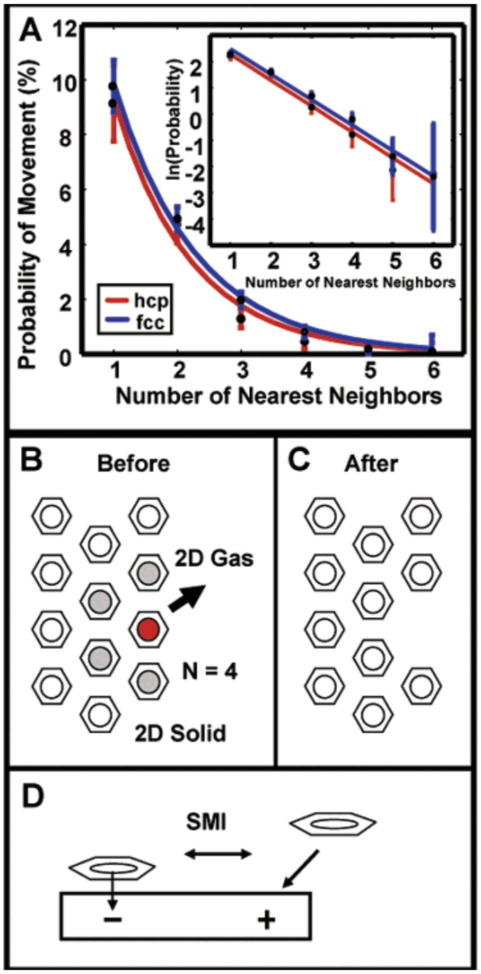


***Figure 4.*** (A) Probability that a benzene molecule moves depends strongly on its number of nearest neighbors, plotted separately for hcp (blue) and fcc (red) regions. The data represent only the desorption of benzene molecules to the 2D gas. The inset shows the exponential fit of the data. (B and C) Schematic of the benzene overlayer in hcp and fcc areas. The arrow shows a benzene molecule (red) leaving the 2D solid, and the molecules with gray centers depict its four nearest neighbors. (D) Schematic of the SMI effect for benzene on Au. The nucleophilic benzene on the left adsorbs on the surface and donates negative charge, thereby, forming a positive image charge, which creates a favorable site for binding of another benzene molecule.

of motion of each molecule to its number of nearest neighbors as a function of region. In this way, we are able to interrogate the stabilizing/destabilizing effect adjacent molecules have on each other's residence times at each adsorption site, that is, the SMI strength. This effect is studied independently in both the hcp and fcc regions. Due to the difficulty in tracking all of the motion in the soliton areas mentioned earlier, we cannot give an accurate value for the SMI in this region. Figure 4A shows the probability of a molecule moving as a function of its number of nearest neighbors for hcp and fcc regions. Benzene molecules adsorbed in both regions show a strong correlation between probability of motion and number of nearest neighbors. This can be described with a modified version of the earlier Arrhenius expression (eq 2) that accounts for the lateral benzene−benzene interactions as well as the benzene−Au bond strength:

$$\text{Rate} = A \exp\left(\frac{-(n\Delta E_{\text{SMI}} + \Delta E_{\text{BAu}})}{RT + \Delta E_{\text{TIP}}}\right) \qquad (3)$$

In this model, for benzene to move, it must overcome the barrier to diffusion on the gold substrate ($\Delta E_{\text{BAu}}$) and each of its attractive interactions with its $n$ nearest neighbors ($n\Delta E_{\text{SMI}}$). For example, in Figure 4B, the benzene marked in red is leaving the 2D solid and must overcome the barrier to lateral motion and its attraction to four nearest neighbors, marked in gray, thus $n = 4$. By fitting the data to this model, we are able to quantify the strength of the SMI. The inset of Figure 4A shows the exponential fit of the data using this model. The identical gradients of the plots indicate that the benzene−benzene SMI in both the hcp and fcc regions is the same strength within the precision of our measurement: $\Delta E_{\text{SMI}} = 0.44 \pm 0.05$ kJ/mol (in hcp and fcc regions).

We now turn this discussion to the nature of the SMI we have just quantified. The average benzene−benzene spacing in our system is 6.95 Å, whereas benzene overlayers on other metals are known to pack with spacings as small as 3.60 Å.[28] Therefore, it is likely that any direct molecule−molecule interaction is negligible at this 6.95 Å separation, as van der Waals interaction strength decays as $1/d^6$ (a 50-fold decrease between 3.60 and 6.95 Å separations). However, it has been shown that when benzene adsorbs on a metal surface, it perturbs the substrate's LDOS up to 10 Å away.[4] Hence, the dominant interactions are likely to be substrate-mediated. Similar long-range effects were seen in Figure 1A,B, in which the high-resolution STM images demonstrate how the filled and empty LDOS of the Au surface are perturbed in the vicinity of each molecule. Figure 4D shows a schematic of such a system. We postulate that the mechanism of this interaction involves adsorbed benzene molecules donating charge to the surface, which in turn creates image charges at a distance of 5−10 Å from the molecule. This perturbation of the electronic state of the surrounding surface creates both favorable and unfavorable sites for adsorption of other benzene molecules.[2,3,6] We have shown that the SMI strength is weak (<0.5 kJ/mol per neighboring molecule) compared to typical physisorption energies (~10 kJ/mol). Surprisingly, this SMI energy is almost 2 orders of magnitude smaller than most molecule−substrate bond strengths and, yet, plays a crucial role in molecular alignment and overlayer formation on metal surfaces.[2,5,6,32]

## Conclusions

By setting up a system with weak adsorbate−substrate interactions and automating the analysis of single molecule diffusion, we are able to quantify substrate-mediated interaction strength. We show how interplay between intermolecular interactions and molecular binding to the substrate controls the evolution of structure observed in our scanning tunneling microscope images and demonstrate that the thermodynamics of the system dictate molecular ordering as the coverage is increased. Tailoring these weak SMIs by adding functionality to molecular building blocks may also provide a method for advancing self-assembly of more complex molecular architectures on surfaces.[2]

**Acknowledgment.** The authors gratefully acknowledge financial support of the Army Research Office, the National Science Foundation, and the Office of Naval Research. We thank

---

(32) Kreuzer, H. J. *Surf. Sci.* **1995**, *344*, L1264.

Jennifer Hampton, Tom Pearl, and Sanjini Nanayakkara for many helpful discussions about the data. We thank the Pennsylvania State University statistical consulting center for their technical assistance. B.A.M. is grateful for a fellowship from the ACS Division of Analytical Chemistry sponsored by GlaxoSmithKline.

**Supporting Information Available:** S1: A movie compiled from a series of 600 time-lapse STM images (81 Å × 81 Å, $V_{\text{sample}} = 1$ V, $I_t = 20$ pA, $T_{\text{sample}} = 4$ K) of a Au{111} surface covered with 0.9 ML of benzene. The movie shows the 2D adsorption/desorption, small motion, and cascade events described in the text. S2: The same data as shown in Movie S1, in which each of the benzene molecules has been identified using digital image processing, as indicated by the black circles. The white numbers indicate the number of nearest neighbors for each molecule. The colored shapes show which region each benzene molecule is adsorbed on. The pink squares indicate hcp regions; blue parallelograms indicate fcc regions, and red triangles indicate soliton walls. The green stars show the occurrence of correlated motion among the benzene molecules. This material is available free of charge via the Internet at http://pubs.acs.org.

JA0472331