

# Substrate-Mediated Interactions and Intermolecular Forces between Molecules Adsorbed on Surfaces

E. CHARLES H. SYKES, PATRICK HAN,  
S. ALEX KANDEL,<sup>†</sup> KEVIN F. KELLY,<sup>‡</sup>  
GREGORY S. MCCARTY,<sup>§</sup> AND PAUL S. WEISS\*

*Departments of Chemistry and Physics,  
The Pennsylvania State University, 152 Davey Laboratory,  
University Park, Pennsylvania 16802*

Received August 19, 2003

## ABSTRACT

Adsorbate interactions and reactions on metal surfaces have been investigated using scanning tunneling microscopy. The manners in which adsorbates perturb the surface electronic structure in their vicinity are discussed. The effects these perturbations have on other molecules are shown to be important in overlayer growth. Interactions of molecules with surface steps are addressed, and each molecule's electron affinity is shown to dictate its adsorption sites at step edges. Standing waves emanating from steps are demonstrated to effect transient molecular adsorption up to 40 Å away from the step edge. Halobenzene derivatives are used to demonstrate how the surface is important in aligning reactive intermediates.

## Introduction

A fundamental understanding of the great diversity of chemistry occurring at surfaces requires the investigation of many aspects of the molecule–surface interaction. To achieve this goal, it is necessary to understand how molecules bind to surfaces and how the binding process alters the properties of both the molecule and the surface. The two-dimensional motion of the adsorbate over the surface potential landscape must then be investigated—in particular, molecular motion and binding with respect to step edges, defects, and modulations of the surface-state electron density. When the molecules are bound to a surface, molecular interactions can be due to both direct chemical forces between the adsorbed molecules and

indirect substrate-mediated interactions: indirect molecule–surface–molecule forces in which the molecular perturbations of the surface mediate the interactions between adsorbates. A thorough study of molecular interactions on surfaces provides the underpinnings for understanding aspects of adsorption, desorption, reaction kinetics, surface reconstructions, and ordering of atomic and molecular overlayers. This fundamental understanding promises new insights into chemical catalysis, device fabrication, and the engineering of new materials.

Depending on the nature of the molecule–surface interaction, surface-bound molecules can possess structural and chemical properties substantially different than those of the isolated molecules; conversely, adsorbate binding can cause changes in the substrate geometry, leading to surface reconstructions.<sup>1</sup> Investigations that use high-resolution electron energy loss spectroscopy (HREELS), X-ray and ultraviolet photoemission spectroscopies (XPS and UPS), near-edge absorption fine structure (NEXAFS), and low-energy electron diffraction (LEED) to determine adsorbate binding, packing, and internal structure are well established. An example of one study with particular relevance to this Account is the EELS investigation of benzene on Pt{111}, in which the observed transitions, their relative intensities, and the frequencies of the benzene vibrational modes were used to determine that the molecules lie flat on the surface, as is the case for benzene on most transition metal surfaces. It was also found that the aromaticity of the benzene molecules is somewhat reduced: the planar and six-fold symmetries of the molecules are broken as the H atoms distort away from the surface, and carbon–carbon bonds alternate in their lengths.<sup>2</sup>

Long-range adsorbate interactions mediated by the surface-state electron density have been postulated for over 50 years. The earliest experimental evidence of such phenomena came from field-ion microscopy (FIM), which demonstrated an oscillatory behavior in the lateral separation of Re atoms on a W surface.<sup>3</sup> Lau and Kohn demonstrated theoretically that this pair potential is indeed oscillatory in nature and that it scales with the inverse square of the adsorbed atom (adatom) separation.<sup>4</sup>

\* To whom correspondence should be addressed. E-mail: stm@psu.edu. Fax: (814) 863-5516.

<sup>†</sup> Present address: Department of Chemistry and Biochemistry, College of Science, University of Notre Dame, Notre Dame, IN 46556.

<sup>‡</sup> Present address: Department of Electrical and Computer Engineering, Rice University, Houston, TX 77005.

<sup>§</sup> Present address: Materials Research Institute, The Pennsylvania State University, University Park, PA 16802.

Charles Sykes obtained an M.Chem. from Oxford University, UK, in 1998, and a Ph.D. in chemistry from Cambridge University, UK, in 2002. He is currently a postdoctoral fellow at The Pennsylvania State University, working on substrate-mediated interactions.

Patrick Han graduated from Ithaca College in 1998, and is currently a Ph.D. student at The Pennsylvania State University. His work now focuses on single-molecule research.

Alex Kandel received a B.S. degree in chemistry in 1993 from Yale University. He obtained a Ph.D. in physical chemistry from Stanford University in 1999. His postdoctoral work at The Pennsylvania State University (1999–2001) focused on fundamental studies of surfaces and catalysis. He is now an Assistant Professor at The University of Notre Dame.

Kevin Kelly obtained a B.Sc. from Colorado School of Mines and a Ph.D. in applied physics from Rice University in 1999. He is currently an Assistant Professor at Rice University.

Gregory McCarty received his M.S. in mechanical engineering in 1995, and his Ph.D. in chemistry in 2001, from The Pennsylvania State University. He currently performs research at the Penn State Nanofabrication Facility.

Paul Weiss is a Professor of Chemistry and Physics at The Pennsylvania State University. He received his S.B. and S.M. degrees in chemistry from MIT in 1980, and his Ph.D. from the University of California, Berkeley, in 1986. He was a Postdoctoral Member of the Technical Staff at Bell Laboratories from 1986 to 1988, and a Visiting Scientist at IBM Almaden from 1988 to 1989. His research involves measurement and control at the atomic scale.

Very recently, scanning tunneling microscopy (STM) studies have again addressed interacting metal adatom systems and reproduced these earlier data.<sup>5,6</sup> Moreover, by comparing the interactions of different adatoms (Cu, Co) on both Cu{111} and Ag{111} surfaces, Knorr et al. were able to demonstrate that the period of the oscillatory pair potentials was dependent solely on the type of metal surface, and not on the nature of the adatom.<sup>6</sup> Thus, atom–atom interactions on close-packed metal surfaces are currently understood in terms of substrate effects via the surface-state electrons. STM has even shown constructive and destructive interference patterns in the surface-state electrons around two adatoms.<sup>5,6</sup> While surface-bound *atom* interactions are fairly well understood, *molecular* interactions via electrons of the surface state have only just recently been investigated, and results to date are discussed in this paper.

This Account details several recent studies of aromatic species on metal surfaces: benzene on Pt{111},<sup>7</sup> Cu{111},<sup>8–11</sup> and Ag{110};<sup>12–14</sup> 7,7',8,8'-tetracyanoquinodimethane (TCNQ) molecules<sup>15</sup> and phenyl and phenylene reaction intermediates<sup>11,16,17</sup> on Cu{111}; and CS<sub>2</sub> on Au{111}.<sup>18,19</sup> The static and dynamic properties of these systems are investigated through the use of STM operated at low temperature and ultra-high vacuum. In our studies, STM allows direct observation of individual surface-bound species; therefore, the relative binding affinity at surface defects compared to surface terraces can be measured. Furthermore, by conducting measurements at different surface temperatures, the mobility of the adsorbed species can be investigated.

## Benzene Adsorbed on Pt{111}

Benzene serves as an excellent probe molecule in the investigation of substrate–adsorbate interactions, due to its structural simplicity, high symmetry, and relatively simple electronic interactions, as well as the high contrast with which it appears in STM images. The interaction with the surface is typically weak; for example, temperature-programmed desorption (TPD) measurements show that the majority of the adsorbed benzene desorbs from the Cu{111} surface at 250 K.<sup>20</sup> However, benzene binds more strongly at defect sites and step edges, as evidenced by the data to be presented in this Account, as well as by the long, high-temperature tail observed in TPD studies.<sup>20</sup>

At low temperatures, the rate of diffusion on terraces can be lowered enough for isolated benzene molecules to be observed. This was first accomplished in an STM study of benzene on Pt{111} at 4 K.<sup>7</sup> The STM images of the adsorbed benzene displayed three distinct molecular shapes which were attributed to benzene bound at three types of surface sites. The different binding sites were proposed to lead to changes in the interactions between the adsorbed molecules and the surface electronic states; this explanation has been supported by theoretical calculations in which the roles of interference between the molecular and the surface electronic states were established.<sup>21</sup>

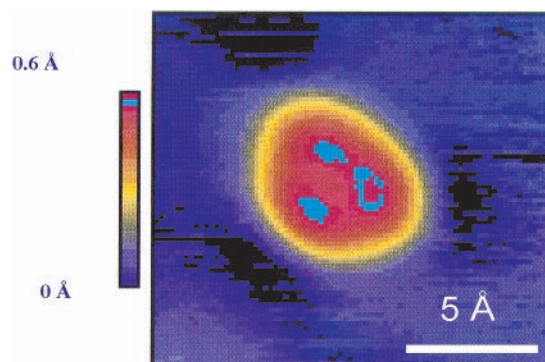


FIGURE 1. STM image of benzene adsorbed on a Pt{111} three-fold hollow site at 4 K ( $V_{\text{sample}} = 50$  mV,  $I_t = 100$  pA).

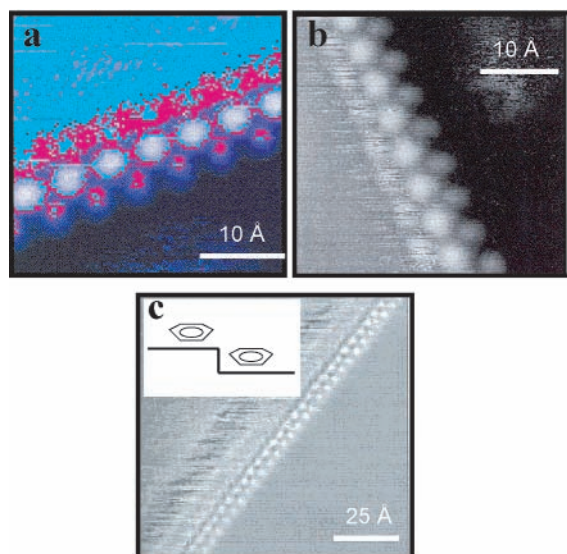
This measurement demonstrated that the interaction between adsorbed benzene molecules and the electronic states of the surface can be observed by STM. This is important in elucidating the nature of substrate-mediated interactions, in which molecular perturbation of the surface is the first stage of intermolecular interaction. The images of benzene adsorbed at three-fold hollow sites is of particular interest, and one is shown in Figure 1. Here benzene appears as a protrusion on the surface, with three-fold symmetry and a central depression. Additionally, there are three small but pronounced depressions in the STM image that appear symmetrically about the periphery of the molecule. These depressions indicate that the perturbation of the surface electronic structure, or local density of states (LDOS), is significantly larger than the molecule, extending up to 6–10 Å away from the center of the molecule.

An example of how these long-range, through-substrate interactions affect ordering is observed when benzene and CO are coadsorbed on Pt{111}.<sup>22</sup> LEED has shown that benzene at monolayer coverages on Pt{111} has no long-range order. However, through-substrate interactions of benzene with coadsorbed CO induce long-range ordering; this effect has been observed by LEED with benzene and CO on Pt{111}.<sup>22</sup> In the next section, we show how these long-range, through-substrate perturbations influence the ordering of benzene molecules on the Cu{111} surface.

## Benzene Adsorbed on Cu{111} Steps and Terraces

As mentioned in the previous section, benzene interacts weakly with Cu{111}, forming disordered monolayers, and desorbs from terrace sites at <250 K. The high mobility of benzene on terraces and its transient occupancy of sites makes this system ideal for the study of substrate-mediated interactions. At a sample temperature of 77 K, benzene molecules are observed by STM only when bound at step edges or in clusters (at higher coverages), as elsewhere molecular diffusion occurs on too fast a time scale for isolated benzene molecules to be imaged on the surface terraces.

Figure 2a,b shows the adsorption of benzene molecules at Cu steps. In Figure 2a, two rows of benzene are imaged, one below the step and one above. The presence of

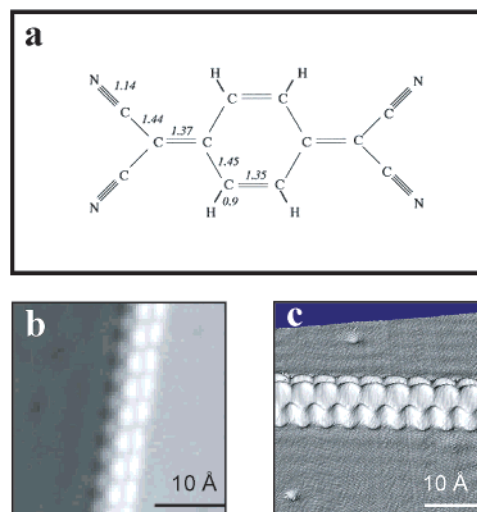


**FIGURE 2.** (a) STM image of benzene adsorbed at a Cu{111} step at 77 K ( $V_{\text{sample}} = 100$  mV,  $I_t = 100$  pA). (b) An image of a similar step where the tip has pushed additional molecules to the second and third rows above the step ( $V_{\text{sample}} = 100$  mV,  $I_t = 100$  pA). Reprinted with permission from ref 8. Copyright 2003 American Association for the Advancement of Science. (c) A larger image showing additional adsorption sites for benzene molecules  $\sim 20$  Å from step ( $V_{\text{sample}} = 100$  mV,  $I_t = 100$  pA).

adsorbed molecules creates perturbations of the surface LDOS above the step, as shown in red in Figure 2a. This is the same effect that was discussed for benzene on Pt{111} in the previous section, but now the effects of nearby molecules constructively and destructively interfere. The image in Figure 2b is taken after increasing the local population of benzene adsorbed at the step edge on the upper terrace by scanning the STM tip at higher bias voltage over the adjoining terrace, thus sweeping benzene from the terrace up against the step edge.<sup>8,9</sup> Again, two complete rows of benzene molecules are present at the step edge. In addition, third and fourth “phantom” rows can be observed; in these rows, the noisy, speckled appearance of the imaged molecules indicates that benzene is diffusing into and out of or between the binding sites created by adsorption of the first row of molecules on time scales faster than that of STM imaging.

Figure 2c shows a region  $\sim 20$  Å away, running parallel to the step where this same “phantom” occupancy is observed. The higher residence time of benzene in this region is understood in terms of regions of enhanced LDOS near the step edge caused by scattering of the surface-state electrons from the step.<sup>8–10,19</sup> This effect is discussed in greater detail in the section on CS<sub>2</sub> adsorption on Au{111}. At higher coverages, small islands of benzene molecules accumulate in bands parallel to the step edge. The islands typically contain 3–9 molecules. This clustering allows us to conclude that both the interactions of the molecules with the surface step and the intermolecular through-substrate interactions are important in determining molecular binding and structure.

Steps, like other surface defects, often act as preferential sites for adsorption, as they represent a disruption in



**FIGURE 3.** (a) Chemical structure of tetracyanoquinonodimethane (TCNQ). (b) STM image of TCNQ adsorbed on a Cu{111} step edge at 77 K ( $V_{\text{sample}} = 1$  V,  $I_t = 100$  pA). (c) Three-dimensional perspective view of a similar area ( $V_{\text{sample}} = 1$  V,  $I_t = 100$  pA).

surface periodicity. At steps, the 2D electronic structure is also perturbed. This can lead to both positive and negative changes in the local adsorption energy. The smoothed electron density at step edges is often referred to as the Smoluchowski effect,<sup>23</sup> where the filled surface electronic state density is decreased above step edges while it is increased near the lower edges of the steps. The empty states are affected in the opposite way: enhanced above the step and depleted below. Benzene is nucleophilic and thus donates electrons to the surface; therefore, it has a higher affinity for binding at the upper step edges due to the Smoluchowski effect.<sup>9,10</sup> The first row of benzene molecules adsorbed on top of the step creates additional favorable sites for second- and third-row growth (Figure 2b). We postulate the mechanism for this effect to be modulation of the surface LDOS by benzene in the first row. Adsorption of first-row benzene molecules creates adjacent sites with a high density of empty states on which second-row molecules nucleate and, in turn, create sites for adsorption of a third row. This effect of benzene perturbing its surrounding surface LDOS was seen in Figure 1.

In summary, the increase in the electronic interactions of the molecules at the step edges on metal surfaces is due to a combination of the following, in order of decreasing strength: the charge transfer at the step edge (Smoluchowski effect), the perturbations due to molecules already at the step (Figure 2b), and the enhanced LDOS near the step edge caused by surface-state electron scattering (Figure 2c).<sup>8–10,19</sup>

### TCNQ Adsorbed at Cu{111} Steps and Monolayer Ordering

To investigate substrate-mediated interactions further, TCNQ was studied on a Cu{111} surface. The structure of TCNQ is shown in Figure 3a. TCNQ is a strong electrophile and is known to form charge-transfer com-



plexed solids with copper.<sup>24</sup> TCNQ is thus expected to perturb the electronic structure of the surface strongly, and consequently to order via substrate-mediated intermolecular interactions. The investigation of TCNQ molecules on Cu{111} described below was performed in a manner similar to the benzene studies.

Since TCNQ is an electron acceptor, we expect it to behave differently from benzene, which is an electron donor. For example, while benzene is observed to bind preferentially at the electron-poor region above step edges, TCNQ would be expected to bind at electron-rich step bottoms. This behavior is corroborated by our STM images.<sup>15</sup> An STM image of TCNQ on Cu{111} at 77 K is shown in Figure 3b, along with a 3D rendering of the same area in Figure 3c. TCNQ, like benzene, forms ordered rows along the step edge but has a stronger affinity for the bottoms of steps; the different binding behavior of benzene and TCNQ results from their differing electron affinities.

Figure 3b shows that TCNQ molecules align with their long axes perpendicular to the step direction. Presumably, this packing allows for the maximum number of electron-deficient cyano groups to interact with the electron-rich bottom step edge. Multiple rows of TCNQ are apparent at higher surface coverages, in a fashion analogous to that seen for images of benzene. Furthermore, adsorbate-induced surface depressions are observed between the molecules of the final row; the perspective view in Figure 3c highlights these features.

The adsorption of TCNQ at the bottom of the step edge also perturbs the electronic structure of the top of the step in a manner similar to the way in which benzene perturbs its surrounding LDOS on Pt{111} (discussed in the first section). This effect can be seen in Figure 3b, where the top edge takes on a scalloped appearance. We propose that this perturbation allows for the adsorption of TCNQ along the top of the step, and in accord with this idea, no adsorption is observed at tops of step edges until the bottoms of the steps are completely filled. Once the sites at the step bottom are filled, multiple rows or islands of TCNQ then form at the top of the step.

Adsorbed TCNQ exhibits many properties analogous to those observed for benzene, including a strong interaction with surface steps and perturbation of the electronic structure of the surface. TCNQ molecules exhibit stronger intermolecular interactions than benzene; this is evidenced in the fact that benzene monolayers on Cu{111} are disordered but TCNQ forms ordered structures on this surface (Figure 4). The growth of these structures is directed by strong intermolecular interactions between adjacent cyano groups that create domains extending over 200 Å, in which a number of different packing structures are apparent.

We observe that TCNQ substantially perturbs the electronic structure of the Cu{111} surface near step edges, more so than benzene molecules, and that the formation of molecular rows along the step can be attributed to strong substrate-mediated interactions. It is likely that substrate-mediated intermolecular interactions on the

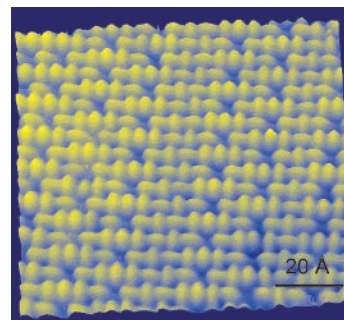


FIGURE 4. STM image of TCNQ monolayers on Cu{111} at 77 K ( $V_{\text{sample}} = 1$  V,  $I_t = 100$  pA).

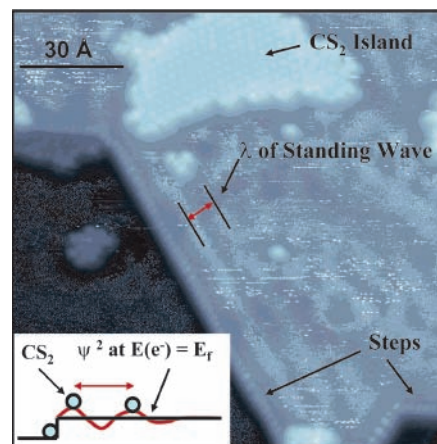


FIGURE 5. STM image of CS<sub>2</sub> adsorbed on Au{111} at 4 K ( $V_{\text{sample}} = -100$  mV,  $I_t = 200$  pA). (Inset) Schematic of the CS<sub>2</sub> molecule's lateral interaction with the standing waves arising from steps on Au{111}.

terraces determine overlayer structures, though this cannot be observed directly in our STM images. The high degree of order near step edges and the subsequent nucleation of the monolayer indicate that multilayer TCNQ film growth could be highly dependent on surface structure and initial growth conditions.

### CS<sub>2</sub> Adsorption on Au{111}

To investigate the interactions of molecules with standing waves, submonolayer coverages of CS<sub>2</sub> were studied on Au{111}.<sup>18,19</sup> Most small molecules are mobile on Au{111} when dosed at low temperature.<sup>18</sup> Au{111} has a free-electron-like surface state that scatters at step edges, producing standing wave patterns.<sup>25</sup> By  $dI/dV$  imaging at different tip voltages, one is able to resolve standing waves of different electron energies and measure their corresponding wavelengths. In this way, one can relate oscillatory features on the surface to actual surface-state electron energies. Therefore, when scanning molecules in the dynamic regime, it is possible to correlate fluctuations in their average residence time at certain positions with the standing waves created by electron scattering from surface defects and ascertain the energy levels of electrons involved in the adsorbate–surface bonding scheme.

Figure 5 shows an STM image of 0.2 ML of CS<sub>2</sub> on Au{111}. The CS<sub>2</sub> forms ordered islands on the gold

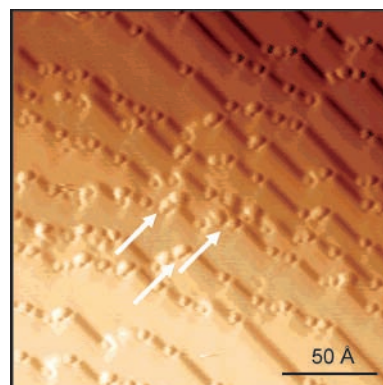
terraces in a molecular herringbone structure<sup>18</sup> and adsorbs at electron-rich areas below steps.<sup>18,19</sup> This adsorption below steps is understood in terms of the electron-deficient carbon center of the CS<sub>2</sub> molecule seeking sites of high electron density. The “fuzziness” in the image occurs when, at certain tunneling conditions, the tip sweeps around the molecules weakly bound to the terraces. This fuzziness is not uniform; distinct “phantom” lines are observed running parallel to the steps, and rings appear around single-atom defects. In this case we observe two phantom lines parallel to the steps as in the benzene/Cu{111} experiments. This indicates that the molecule’s interaction with the standing waves of the metal is stronger in the present system. The appearance of two phantom lines allows us to determine a period for the transient adsorption ( $17.8 \pm 0.3 \text{ \AA}$ ) and correlate it to a specific electron energy, namely electrons at the Fermi level ( $E = E_F$ ). We assign these phantom lines to be heightened CS<sub>2</sub> interactions at positions on the surface of maximum LDOS at the Fermi level (schematic shown in the inset of Figure 5).

The assignment of maximum CS<sub>2</sub> interaction at positions of  $\psi^2_{\max}$  rather than  $\psi^2_{\min}$  is made considering that the electron-deficient center of the CS<sub>2</sub> molecule directs growth at electron-rich areas below steps and presumably also dictates its adsorption at crests of the Fermi-level electron standing waves. This result is important in terms of fully understanding the weakest of the three interactions in molecular adsorption at steps discussed in the benzene/Cu{111} section. We now know that the molecule’s electron affinity dictates its interactions with the modulations of LDOS created by surface-state electron scattering at steps and that this interaction occurs with standing waves arising from electrons at the Fermi level.

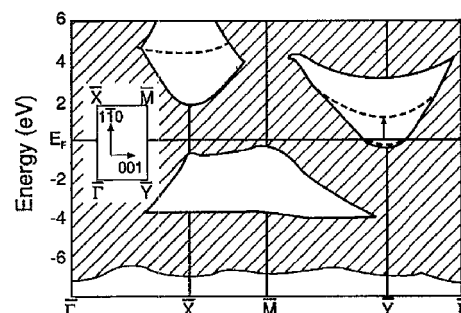
### Benzene Adsorbed on Ag{110}

In addition to the studies of molecules on Cu{111} and Au{111}, we have also investigated adsorption of benzene on Ag{110}.<sup>12–14</sup> Unlike Cu{111} and Au{111} surfaces, the Ag{110} surface does not possess an accessible surface state. In simple terms, the close-packed {111} surfaces allow for greater orbital overlap of the surface atoms. This greater electron freedom leads to a two-dimensional free-electron gas confined to the surface, the so-called surface state that does not exist for the {110} and {100} surfaces. Consequently, there is one less factor that can affect the interaction of the benzene with the metal surface. Our results indicate that benzene molecules prefer even more specific binding sites on Ag{110} than found for the Cu{111} surface.

In these experiments, benzene was deposited on Ag{110} at 66 and 4 K. After an initial benzene dose at 66 K, only molecules decorating the [110] step edges were observed in STM images. In Figure 6, it is shown that molecules (white arrows in Figure 6) adsorb only at the ends of the silver closed-packed atomic rows, which form the [110] steps. At these sites, benzene molecules adsorb either isolated or in small rows parallel to the step; these



**FIGURE 6.** STM image acquired at 4 K after the deposition of benzene molecules on Ag(110) at 66 K ( $V_{\text{sample}} = 0.05 \text{ V}$ ,  $I_t = 4 \text{ nA}$ ). The benzene molecules (see white arrows) adsorb only on the [110] step edges.

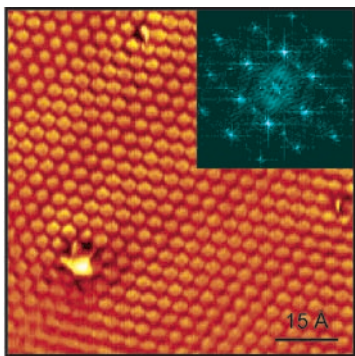


**FIGURE 7.** Ag{110} surface projected band structure. A band gap exists at the Y point of the surface Brillouin zone. It is this gap that is believed to reduce the Smoluchowski effect and therefore inhibit adsorption on the [001] step edge. Reproduced with permission from ref 26. Copyright 1992 American Physical Society.

molecules do not act as nucleation sites for any further growth at this temperature, even after additional similar doses of benzene vapor. It is apparent from these images that the terraces and the [001] steps remain completely free of molecules. These results indicate that the sites at the end of the close-packed rows are the only active sites for the adsorption of benzene at 66 K.

As previously discussed, electronic effects such as the Smoluchowski effect can generate preferential adsorption at step edges. However, a necessary condition for this to occur on surfaces is the availability of free charge and the availability of states for the free charge to occupy. In the case of Ag{110}, anisotropy in the projected bulk density of states exists (Figure 7).<sup>26</sup> A gap in the density of states at the Fermi level is found at the Y point of the surface Brillouin cell. This gap causes a reduction in charge transfer for [001] steps, thereby reducing the ability of the step sites to accept charge from the benzene. In other words, the [001] step edges are less active adsorption sites for benzene because of their different electronic structure as compared to the [110] step edges.

In contrast with the results at 66 K, dosing larger quantities of benzene at 4 K results in saturation of the surface and formation of an ordered benzene monolayer.<sup>12–14</sup> However, a different adsorption state is now populated, one in which benzene molecules interact weakly with the



**FIGURE 8.** STM image of a complete monolayer of benzene adsorbed on  $\text{Ag}\{110\}$  ( $V_{\text{sample}} = -100$  mV,  $I_t = 100$  pA). (Inset) Fourier transform of image.

substrate. As shown in Figure 8, the weak surface–adsorbate interaction of these species allows an incommensurate overlayer to form with a highly ordered hexagonal lattice on an underlying rectangular lattice.

We additionally observe that the benzene monolayer is oriented along the substrate  $[001]$  direction. This orientation is found exclusively; we have never found domains oriented otherwise. We propose that the overlayer orientation is dictated by the step direction. While the Smoluchowski effect is dominant at the  $[\bar{1}10]$  step edge, this charge transfer is localized very close to the steps. This results in a single row of benzene molecules adsorbed at the step edge, as shown in the image in Figure 6. Additionally, the short-range nature of this effect has been calculated by Yang et al. for similar steps on the  $\text{Cu}\{110\}$  surface.<sup>27</sup> Therefore, the formation of the second and subsequent rows is dominated by molecule–molecule interactions and/or adsorbate-induced surface electronic perturbations. As mentioned earlier, the latter was found to control the adsorption of benzene on  $\text{Cu}\{111\}$  steps.<sup>8,10</sup> Either or both of these effects, in combination with Smoluchowski pinning, would account for the one-dimensional commensurate orientation of the benzene monolayer.

## Intermolecular Forces between Reaction Intermediates

**(A) Iodobenzene on  $\text{Cu}\{111\}$ .** We now turn the discussion to molecules that dissociate upon adsorption and act as intermediates in surface-catalyzed chemical reactions. A good example is the catalytic formation of biphenyl ( $\text{C}_6\text{H}_5\text{—C}_6\text{H}_5$ ) from iodobenzene and other halobenzenes on metal surfaces that was first reported in 1901 by Ullman.<sup>28</sup> Recently, the reaction has been studied on well-defined single-crystal surfaces in a vacuum.<sup>29</sup> On the  $\text{Cu}\{111\}$  surface, the reaction proceeds via a number of steps. First, iodobenzene adsorbs to the copper surface, dissociating above 180 K to form surface-bound iodine atoms and phenyl intermediates. Then, between 180 and 300 K, phenyl moieties diffuse about the surface. Above 300 K, they react to form biphenyl. Biphenyl then desorbs upon formation between 300 and 400 K, followed finally by iodine removal as  $\text{CuI}$  at  $\sim 950$  K.

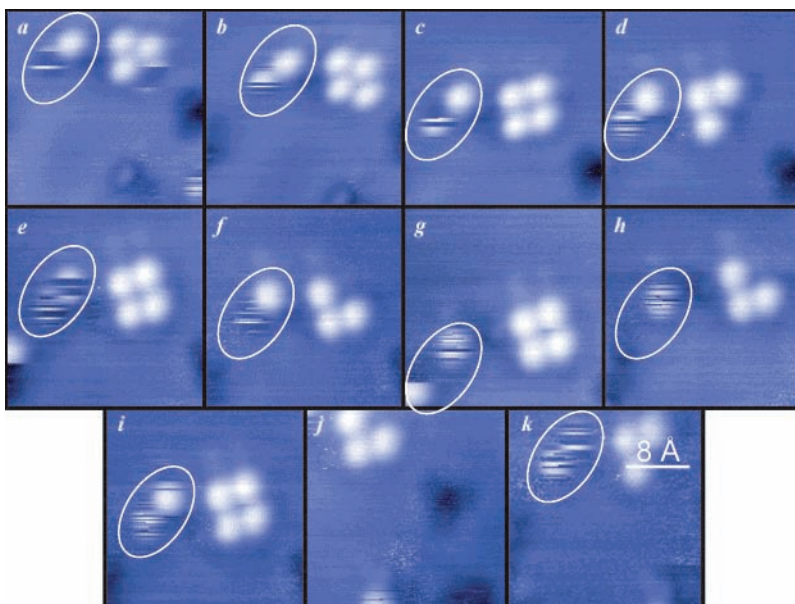
Rieder and co-workers employed a low-temperature STM tip to dissociate, position, and couple iodobenzene molecules adsorbed adjacent to a  $\text{Cu}\{111\}$  atomic step.<sup>30</sup> Each step of the reaction that ultimately formed biphenyl from iodobenzene was controlled with the probe tip.

We have investigated the intermolecular forces between phenyl reaction intermediates on  $\text{Cu}\{111\}$ <sup>11</sup> in order to understand the roles played by substrate-mediated interactions in a reactive system. In our experiments, we exposed the  $\text{Cu}\{111\}$  crystal to iodobenzene at 293 K and then cooled it to 77 K for STM measurements.<sup>11</sup> Using this method, the reaction can be quenched into an intermediate state, after iodobenzene dissociation and phenyl formation, but before the reaction is completed and biphenyl is formed. By examining the motions of the phenyl moieties on the surface, we can observe the intermolecular forces that bring the phenyl species together and ultimately promote reaction.

Phenyl is known from NEXAFS measurements to bind to  $\text{Cu}\{111\}$  in a  $43^\circ$  tilted geometry.<sup>31</sup> At a surface temperature of 77 K, phenyl binds both at step edges and at terrace sites. There is moderate diffusion on open terraces, though some phenyl species can be observed at normal STM scanning rates, especially when stabilized by defects or by nearby adsorbed iodine atoms (that appear as depressions in STM images). Phenyl pairs are also observed to form and to dissipate on a time scale on the order of the STM measurement, as shown in Figure 9. These images show phenyl pairs breaking apart and reforming over a period of 6 h. This volatility indicates that intermolecular forces are relatively weak, and the intermediates have not been coupled via covalent bonds. As biphenyl is stable on  $\text{Cu}\{111\}$  at this temperature, these clusters cannot be interpreted as being due to biphenyl formation, either prior to or subsequent to cooling the sample to 77 K.

In order for a surface bimolecular reaction to occur, the reagents or intermediates must have enough energy to surmount an activation barrier that is usually available from thermal sources. Additionally, the reagents or intermediates must be in close proximity to react, and for molecular (as opposed to atomic) species, the relative orientation can also be critical. The frequency with which all of these conditions are met determines the reaction rate. The formation of stable phenyl clusters should increase the rate substantially, as once the activation energy is available to form biphenyl, the phenyl intermediates are already sufficiently close to react. Furthermore, STM data indicate that phenyl pairs form with definite molecular orientations. This can be seen in Figure 9, in which a phenyl moiety dissociates from a dimer and then reattaches at the identical site (white ovals in images). The phenyl intermediate is  $C_2$ -symmetric; thus, this behavior implies that the geometry of the dimer requires the phenyl dangling bonds to be facing either toward or away from each other. (In contrast, if the phenyls in the dimer were to bind with the dangling bonds facing in the same direction, either front-to-end or side-to-side, two equivalent binding sites would result, in contradiction to the





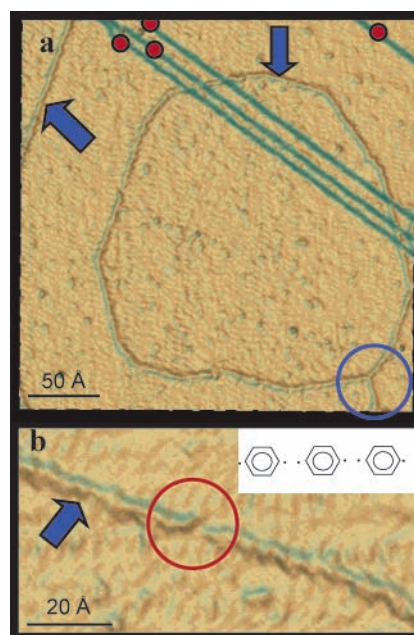
**FIGURE 9.** STM images showing clusters of phenyl intermediates on Cu{111} at 77 K ( $V_{\text{sample}} = 200$  mV,  $I_t = 80$  pA). The images are taken sequentially from (a) to (k) over a period of 6 h.

images observed.) It seems probable, then, that of these two possibilities, the geometry of the cluster would be the same as that required for chemical reaction, forming with the dangling bonds facing one another.

The role of the surface in this reaction is two-fold. The surface creates the phenyl reaction intermediate via dissociation of the iodobenzene reagent. Additionally, our experiments show that the phenyl species on the surface experience intermolecular forces, resulting in the formation of loosely bound complexes that place the phenyls in close proximity and likely in the correct orientation for eventual biphenyl formation. To investigate this effect further, we studied the dissociation of *p*-diiodobenzene on the same Cu{111} surface.

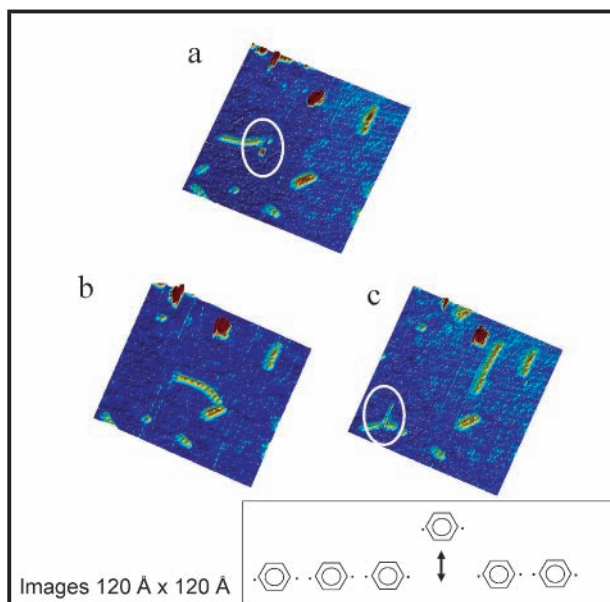
**(B) Diiodobenzene on Cu{111}.** In addition to the dissociation of iodobenzene, we have studied the dissociative chemisorption of *p*-diiodobenzene on Cu{111}.<sup>16</sup> At low surface coverages of the molecule, STM was able to resolve both phenylene radicals and pairs of iodine atoms bound near defect sites. No stationary individual phenylene species were imaged on defect-free Cu{111} terraces, since presumably they remain mobile in these areas at 77 K, as we reported for phenyl radicals on Cu{111}.<sup>11,32</sup>

At higher coverages, we observe self-assembly of the phenylene species into chains, as shown in Figure 10. These chains (marked with arrows) traverse monatomic steps (marked with dots) on the Cu surface. These chains are not mobile during imaging, whereas phenylene species that are not in chains remain mobile. Individual phenylene molecules can be extracted from the molecular chains by applying voltage pulses (2.5 V) to the STM tip (Figure 10b), indicating that the chains are not covalently bound. Further evidence for the weakly bound structure of the chains comes at higher coverages of *p*-diiodobenzene, when small chains can be moved across



**FIGURE 10.** (a) STM image of phenylene chains (arrows) on Cu{111} at 77 K ( $V_{\text{sample}} = 1$  V,  $I_t = 200$  pA). Dots mark monatomic steps, and the circle shows the position of a 1,3,5-phenylene impurity ( $C_6H_3$  with three possible linking sites) in the chain. (b) Image of phenylene chain with a missing link ( $V_{\text{sample}} = 1$  V,  $I_t = 200$  pA). Tip was pulsed at 2.5 V to remove a link in the phenylene chain (red circle).

a phenylene-covered Cu{111} surface. In Figure 11, we manipulate short ( $\sim 8$  units) phenylene chains across the surface. The ovals show parts of the chain where the tip has swept the individual phenylene links into and out of the chain during imaging. Since the chains can be moved on this phenylene-passivated Cu{111} system, we infer that, on a phenylene precovered surface, the chain–substrate interaction is weakened as compared to



**FIGURE 11.** STM images showing motion of protopolymer chains on a phenylene-precovered Cu{111} surface ( $V_{\text{sample}} = -200$  mV,  $I_t = 100$  pA). Circles show that the STM tip sweeps phenylene links into and out of the chain during imaging.

the interaction on the bare metal surface. For the above reasons, we refer to such chains as “protopolymers”, as they are not yet chemically bound, but rather held together weakly by molecule–molecule and surface-mediated interactions.

In conclusion, the work described in this section demonstrates that intermolecular forces between molecules are crucial for aligning and stabilizing reaction intermediates. Additionally, we have shown that complex structures such as these protopolymers can be formed via fairly weak intermolecular interactions, and we have control over motion and placement of reactive intermediates.

## Conclusions

We have investigated the nature of adsorbate interactions on surfaces. We have presented examples in which adsorbates interact with each other through electronic perturbations that modify the surface electronic structure. These perturbations are experienced by mobile adsorbates, thus affecting their dynamics and the structures that they form. These substrate-mediated interactions can be imaged directly using STM, and, in addition, their effects on adsorbate dynamics, chemical reactions, and two-dimensional ordering on surfaces can be observed. These studies provide promise for understanding molecular adsorption and surface catalysis, and for constructing designed nanomaterials and supramolecular assemblies.

*We thank the Army Research Office, the National Science Foundation, the Office of Naval Research, and the Petroleum Research Fund, administered by the American Chemical Society, for support of the work described here. We further acknowledge the insightful contributions of Phaeton Avouris, Tracy Graham, Jennifer Jackiw, Marilyn Kamna, J. Ignacio Pascual, Hans-Peter Rust, and Stephan Stranick to this work.*

## References

- (1) Somorjai, G. A. The Flexible Surface: New Techniques for Molecular Level Studies of Time Dependent Changes in Metal Surface Structure and Adsorbate Structure during Catalytic Reactions. *J. Mol. Catal. A* **1996**, *107*, 39–53.
- (2) Lehwald, S.; Ibach, H.; Demuth, J. E. Vibrational Spectroscopy of Benzene Adsorbed on Pt(111) and Ni(111). *Surf. Sci.* **1978**, *78*, 577–590.
- (3) Tsong, T. T. Direct Observation of Interactions between Individual Atoms on Tungsten Surfaces. *Phys. Rev. B* **1972**, *6*, 417–426.
- (4) Lau, K. H.; Kohn, W. Indirect Long-Range Oscillatory Interaction between Adsorbed Atoms. *Surf. Sci.* **1978**, *75*, 69–85.
- (5) Repp, J.; Moresco, F.; Meyer, G.; Rieder, K.-H.; Hyldgaard, P.; Persson, M. Substrate Mediated Long-Range Oscillatory Interaction between Adatoms: Cu/Cu(111). *Phys. Rev. Lett.* **2000**, *85*, 2981–2984.
- (6) Knorr, N.; Brune, H.; Epple, M.; Hirstein, A.; Schneider, M. A.; Kern, K. Long-Range Adsorbate Interactions Mediated by a Two-Dimensional Electron Gas. *Phys. Rev. B* **2002**, *65*, 115420–115421.
- (7) Weiss, P. S.; Eigler, D. M. Site Dependence of the Apparent Shape of a Molecule in Scanning Tunneling Microscope Images—Benzene on Pt(111). *Phys. Rev. Lett.* **1993**, *71*, 3139–3142.
- (8) Stranick, S. J.; Kamna, M. M.; Weiss, P. S. Atomic-Scale Dynamics of a Two-Dimensional Gas–Solid Interface. *Science* **1994**, *266*, 99–102.
- (9) Stranick, S. J.; Kamna, M. M.; Weiss, P. S. Interactions and Dynamics of Benzene on Cu(111) at Low Temperature. *Surf. Sci.* **1995**, *338*, 41–59.
- (10) Kamna, M. M.; Stranick, S. J.; Weiss, P. S. Imaging Substrate-Mediated Interactions. *Isr. J. Chem.* **1996**, *36*, 59–62.
- (11) Weiss, P. S.; Kamna, M. M.; Graham, T. M.; Stranick, S. J. Imaging Benzene Molecules and Phenyl Radicals on Cu{111}. *Langmuir* **1998**, *14*, 1284–1289.
- (12) Pascual, J. I.; Jackiw, J. J.; Kelly, K. F.; Conrad, H.; Rust, H. P.; Weiss, P. S. Local Electronic Structural Effects and Measurements on the Adsorption of Benzene on Ag(110). *Phys. Rev. B* **2000**, *62*, 12632–12635.
- (13) Pascual, J. I.; Jackiw, J. J.; Song, Z.; Weiss, P. S.; Conrad, H.; Rust, H. P. Adsorbate–Substrate Vibrational Modes of Benzene on Ag(110) Resolved with Scanning Tunneling Spectroscopy. *Phys. Rev. Lett.* **2001**, *86*, 1050–1053.
- (14) Pascual, J. I.; Jackiw, J. J.; Song, Z.; Weiss, P. S.; Conrad, H.; Rust, H. P. Adsorption and Growth of Benzene on Ag(110). *Surf. Sci.* **2002**, *502*, 1–6.
- (15) Kamna, M. M.; Graham, T. M.; Love, J. C.; Weiss, P. S. Strong Electronic Perturbation of the Cu{111} Surface by 7,7',8,8'-Tetracyanoquinodimethane. *Surf. Sci.* **1998**, *419*, 12–23.
- (16) McCarty, G. S.; Weiss, P. S. Footprints of a Surface Chemical Reaction: Dissociative Chemisorption of *p*-Diiodobenzene on Cu{111}. *J. Phys. Chem. B* **2002**, *106*, 8005–8008.
- (17) McCarty, G. S.; Weiss, P. S. Intermolecular Forces Form and Maintain Linear Chains of Protopolymer Phenylene Intermediates on Cu{111}. submitted for publication.
- (18) Han, P.; Sykes, E. C. H.; Pearl, T. P.; Weiss, P. S. A Comparative Scanning Tunneling Microscopy Study of Physisorbed Linear Quadrupolar Molecules: C<sub>2</sub>N<sub>2</sub> and CS<sub>2</sub> on Au{111}. *J. Phys. Chem. A* **2003**, *107*, 8124–8129.
- (19) Sykes, E. C. H.; Han, P.; Weiss, P. S. Molecule–Metal Surface Interactions Evidenced Quantum Mechanically via Tip-Induced CS<sub>2</sub> Interaction with Friedel Oscillations on Au{111}. *J. Phys. Chem. B* **2003**, *107*, 5016–5021.
- (20) Xi, M.; Yang, M. X.; Jo, S. K.; Bent, B. E.; Stevens, P. Benzene Adsorption on Cu(111)—Formation of a Stable Bilayer. *J. Chem. Phys.* **1994**, *101*, 9122–9131.
- (21) Sautet, P.; Bocquet, M. L. A Theoretical Analysis of the Site Dependence of the Shape of a Molecule in STM Images. *Surf. Sci.* **1994**, *304*, L445–L450.
- (22) Ogletree, D. F.; Vanhove, M. A.; Somorjai, G. A. Benzene and Carbon-Monoxide Adsorbed on Pt(111): A LEED Intensity Analysis. *Surf. Sci.* **1987**, *183*, 1–20.
- (23) Smoluchowski, R. Anisotropy of the Electronic Work Function of Metals. *Phys. Rev.* **1941**, *60*, 661–674.
- (24) Long, R. E.; Sparks, R. A.; Trueblood, K. N. The Crystal and Molecular Structure of 7,7',8,8'-Tetracyanoquinodimethane. *Acta Crystallogr.* **1965**, *18*, 932–939.
- (25) Crommie, M. F.; Lutz, C. P.; Eigler, D. M. Imaging Standing Waves in a 2-Dimensional Electron Gas. *Nature* **1993**, *363*, 524–527.
- (26) Urbach, L. E.; Percival, K. L.; Hicks, J. M.; Plummer, E. W.; Dai, H. L. Resonant Surface 2nd Harmonic Generation—Surface-States on Ag(110). *Phys. Rev. B* **1992**, *45*, 3769–3772.
- (27) Yang, C. K.; Cheng, Y. C.; Wu, S. Y. Electronic Structure Calculation for a Stepped Cu(110) Surface using a Real Space Approach. *Phys. Lett. A* **1994**, *188*, 68–72.



- (28) Ullmann, F.; Bielecki, J. Ueber Synthesen in der Biphenylreihe. *Ber. Dtsch. Chem. Ges.* **1901**, *34*, 2174–2185.
- (29) Xi, M.; Bent, B. E. Iodobenzene on Cu{111}: Formation and Coupling of Adsorbed Phenyl Groups. *Surf. Sci.* **1992**, *278*, 19–32.
- (30) Hla, S. W.; Bartels, L.; Meyer, G.; Rieder, K.-H. Inducing All Steps of a Chemical Reaction with the Scanning Tunneling Microscope Tip: Towards Single Molecule Engineering. *Phys. Rev. Lett.* **2000**, *85*, 2777–2780.
- (31) Yang, M. X.; Xi, M.; Yuan, H.; Bent, B. E.; Stevens, P.; White, J. M. NEXAFS Studies of Halobenzenes and Phenyl Groups on Cu{111}. *Surf. Sci.* **1995**, *341*, 9–18.
- (32) Kamna, M. M.; Graham, T. M.; Weiss, P. S. Enhancing Catalytic Reactions by Aligning Reactive Intermediates: Phenyl on Cu{111}. submitted for publication, 2003.

AR970286L