

Voltage-Dependent STM Images of Covalently Bound Molecules on Si(100)

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Several alkenes chemisorbed on silicon(100)-(2 × 1) have been studied by scanning tunneling microscopy. Images of these molecules are strongly bias dependent, typically changing from mounds to depressions as the sample bias voltage is changed from −2.5 to −1.0 V. Image contrast involves both a reduced barrier for tunneling through the molecule and alteration of the silicon surface states by bonding.

I. Introduction

Scanning tunneling microscope images of molecules often strikingly match the chemist's intuition, but exactly how molecules are imaged is not obvious. Adsorbed molecules alter surface electronic structure, produce complex couplings between tip and substrate, and can be directly involved in resonant tunneling. Theoretically, the fundamentals of tunneling are well established and many computational approaches have been developed.^{1–3} Detailed calculations of STM imaging have often been done for atoms on surfaces, but molecular adsorbates greatly increase the complexity and cost of computation.^{4–6} There is a need for systematic experimental results on well-characterized systems to which theory can be compared. It is also worthwhile to develop intuitive viewpoints to complement computational methods and suggest new avenues for research.

Of the many STM experiments on adsorbed molecules, a number have specifically addressed the mechanisms of image contrast. Recently an extensive experimental and computational study of alkanes physisorbed on graphite examined the influence of different functional groups to illuminate the interplay of “topographic” and “electronic” effects.⁷ Other recent STM experiments bear on general problems of electron transport through molecules, such as conduction through “molecular wires” or conditions for resonant tunneling.^{8–10}

This paper presents experimental observations of dramatic voltage-dependent variations in images of organic molecules chemisorbed on silicon. The experimental system is well-characterized and versatile. For the clean silicon(100)-(2 × 1) surface, the connection between electronic structure and STM images is thoroughly understood.¹¹ Organic molecules can be covalently bound to silicon by the reaction of alkenes with the Si(100)-(2 × 1) surface in a vacuum. Though this chemistry is new and still being actively explored, the bonding and resulting geometries have been established for a number of molecules.¹² This reaction is very clean, applicable to a variety of molecules, and the resulting silicon–carbon bonds are very stable. Most molecules examined gave reproducible images for low coverages at room temperature during rapid bias voltage

changes. This allowed precise location of the molecules with respect to the silicon lattice and parallel imaging of multiple biases during a single scan. A simple qualitative model explains our results and suggests a variety of further experiments.

II. Experimental Section

Substrates were cut from commercial silicon(100) wafers (Wacker-Chemtronic, <0.10 Ω-cm n-type, P- or Sb-doped), rinsed in methanol (Baker certified electronic grade), and mounted on a tungsten holder with tantalum clips and silicon spacers. Surface contaminants were oxidized by a 15 min UV–ozone treatment. The sample was introduced into the UHV system through a load-lock. After outgassing in UHV for 8 h at 575 °C, the silicon was flashed briefly to 1150 °C to remove surface oxide while maintaining the chamber pressure below 5×10^{-10} Torr. To further reduce reactive gases, a titanium sublimation pump with a LN₂ cold trap was run prior to flashing and the trap kept filled throughout imaging.

Dosing was typically done 1 h after flashing the sample. Alkenes (cyclopentene, 98%; *cis*-cyclooctene, 95% (remainder cyclooctane); 1,5-cyclooctadiene, 99+%; and 1,3,5,7-cyclooctatetraene, 98%, all Aldrich) were degassed by several freeze–pump–thaw cycles. The alkenes were admitted through a leak valve and dosing tube a few centimeters from the surface. Chamber pressures of 1×10^{-9} to 1×10^{-8} Torr for 10–20 s resulted in coverages on the order of 5% of saturation. Imaging began shortly after dosing and continued for several hours.

The STM used a Burleigh “inchworm” coarse approach mechanism, a tube scanner, and custom electronics. Tips were electrochemically etched tungsten, annealed in a vacuum. Tunneling currents ranged from 100 pA to 2 nA. All images were taken in constant current mode. Images at multiple biases could be obtained simultaneously by switching the bias on alternate scan lines. Sets of images were also taken sequentially at differing bias, adjusting the current for constant gap resistance.

Barrier height images were obtained by applying a small modulation voltage to the *z*-piezo to vary the sample-tip distance and using a lock-in amplifier to extract the resulting variation in tunneling current. Because the piezoelectric had not been calibrated against modulation frequency, barrier heights were approximate.

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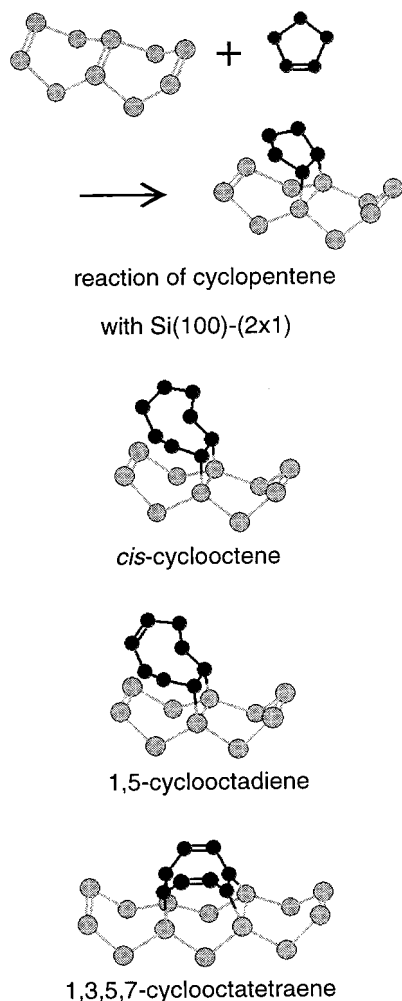


Figure 1. Bonding of cycloalkenes to Si(100)-(2 × 1). A silicon dimer, depicted as Si=Si, reacts with a C=C bond to form a pair of C-Si bonds. The proposed structures are most consistent with experiments; multiple products are possible for polyenes.

III. Results

The clean silicon (100)-(2 × 1) surface shows rows of dimers alternating direction across steps. Alkenes react with the silicon dimers to form pairs of C-Si bonds. The reaction is very clean: after reaction of C=C with the Si dimer, the C-C σ -bond and hydrogens remain intact and there are no additional products on the surface.¹² The mechanism and products of this reaction have been the subject of a number of recent experimental and theoretical studies.¹²⁻¹⁷ While a concerted 2 + 2 cycloaddition is symmetry-forbidden, a three-atom intermediate or insertion into the Si-Si σ -bond provides possible pathways. Figure 1 shows the silicon surface geometry and proposed bonding for several alkenes. We schematize the dimer as a Si=Si double bond, though it might be better described as a diradical. Images of the Si(100) surface with low coverages of each alkene are shown in Figure 2. Molecules with one C=C bond react with a single Si=Si dimer, with the resulting alkane centered over the reacted dimer. Cyclopentene is typically imaged as a single dot, while cyclooctene appears as a pair of dots or a more variable streak due to its height and interaction with the tip. Images of cyclooctadiene and cyclooctatetraene are flatter and broader, with cyclooctatetraene clearly spanning a pair of adjacent dimers. The two unreacted C=C bonds in cyclooctatetraene are not apparent.

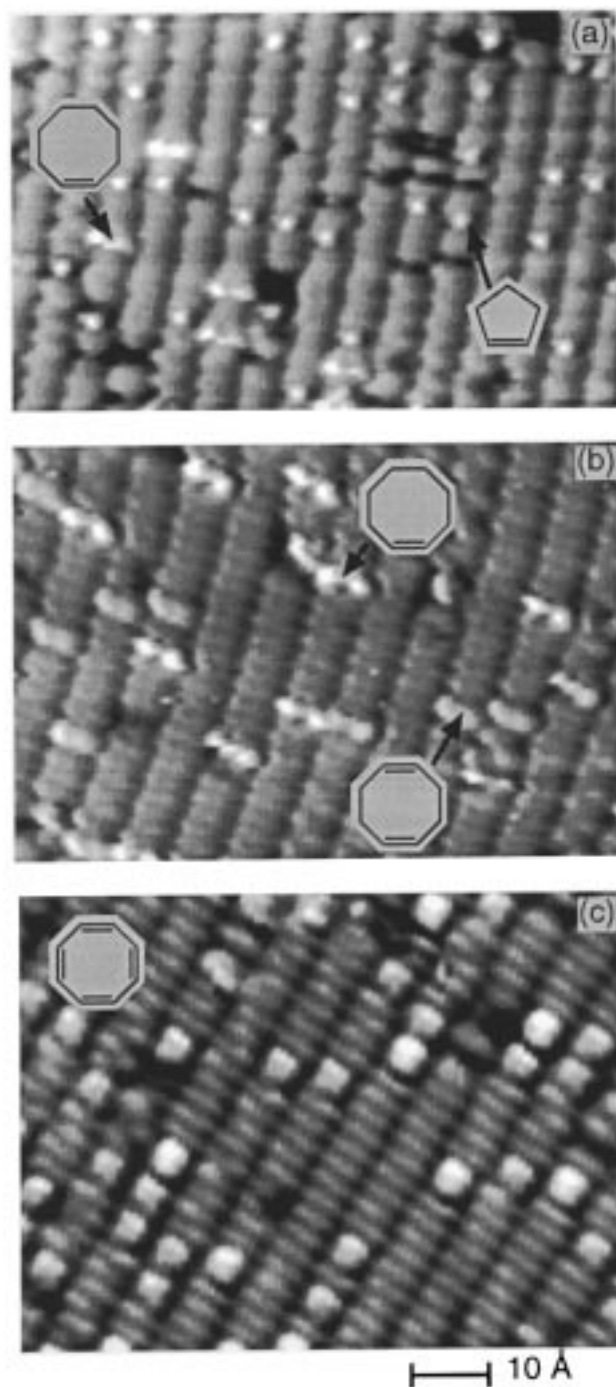


Figure 2. Topographic (constant current) images at -2.5 V sample bias and 2 nA current. (a) Cyclopentene and a few cyclooctenes. (b) *cis*-Cyclooctene and 1,5-cyclooctadiene. (c) 1,3,5,7-Cyclooctatetraene. Insets identify typical images for each molecule. The inset structures are the molecules as dosed, before reaction on the surface. One or more C=C bond is converted to C-C in the product.

Images of these molecules vary strongly with bias. At a sample bias of -2.5 V, the molecules are seen as protrusions in constant-current images. In constant-current mode, lighter areas correspond to greater height of the tip above the sample. At a bias of -1.0 V the molecules generally appear as depressions, with a brighter irregular core at high currents. This behavior is similar for the four molecules examined, despite differences in geometry, bonding, or remaining alkene groups. Pairs of simultaneous images at high and low bias for various molecules are shown in Figure 3.

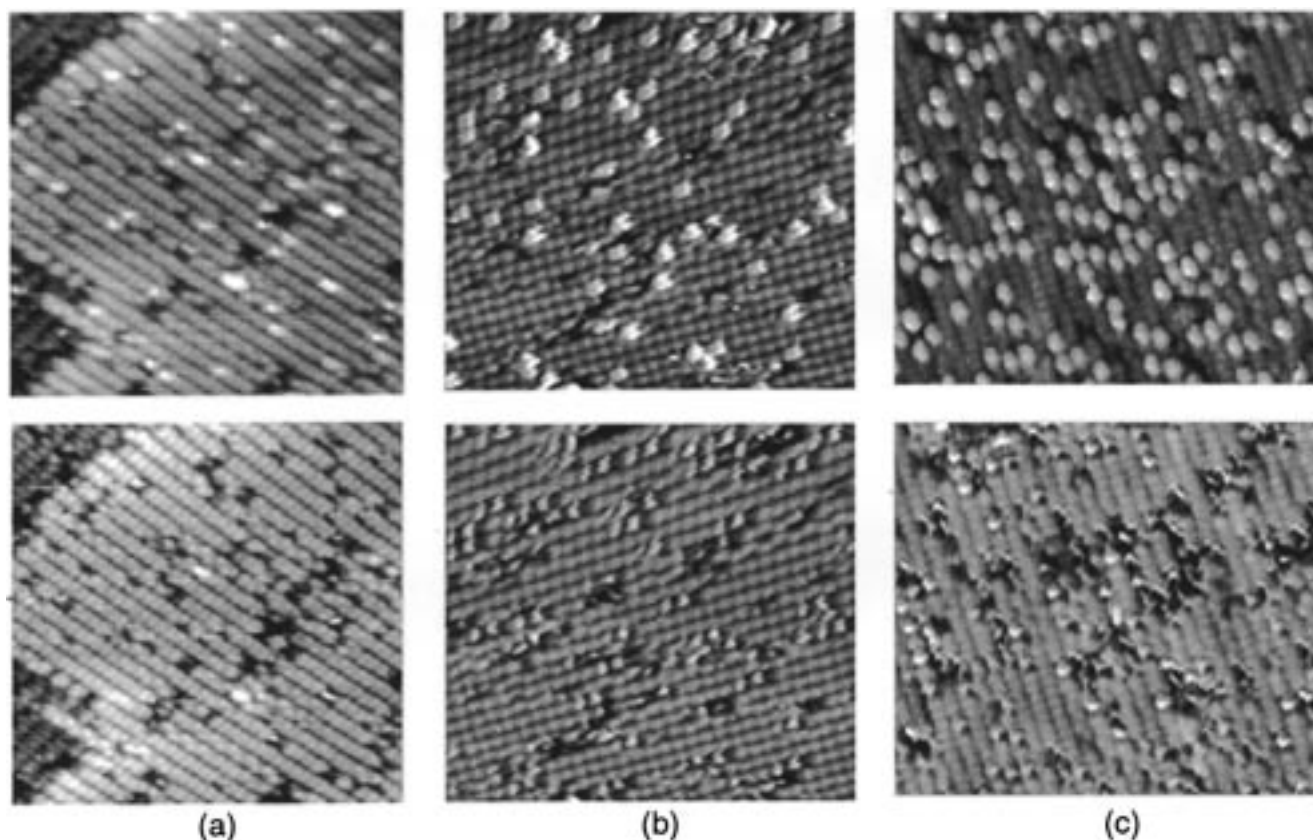


Figure 3. Bias-dependent images. The top and bottom images in each pair were taken simultaneously with different bias on alternate scan lines. (a) Mixture of cyclopentene and cyclooctatetraene. Top -2.5 V, bottom -1.25 V. (b) Mixture of cyclooctene and cyclooctadiene. Top -2.25 V, bottom -1.25 V. (c) Cyclooctatetraene. Top -3.0 V, bottom -1.0 V.

At -2.5 V bias, C=C double bonds are not distinguishable from C—C single bonds in the images. Comparing cyclopentene, in which only single bonds remain after adsorption, and cyclooctatetraene, with a surviving pair of C=C bonds, shows that topography dominates over any effect of the double bonds. However, we note a hint of greater complexity in that cyclooctatetraene appears to form two surface species, with different bias dependencies. A conjugated triene, product of reaction with a single Si=Si dimer, may be the other species.

An apparent barrier height can be defined in terms of the decay of tunneling with distance, $\partial \ln(I)/\partial z$, where I is the tunneling current and z is the tip-sample distance.¹⁸ Simultaneous topographic and barrier height images are shown in Figure 4. The values are approximate because of uncertainty in the tip-sample separation, but show a significant reduction in the barrier over the adsorbed molecules.

More negative biases and positive sample biases did not image as reproducibly. At positive bias, the unoccupied π^* orbitals of the Si dimers are seen. The molecules generally appear as protrusions centered between the rows of antibonding orbitals. Beyond -3.5 V bias the image becomes more diffuse, the surface more labile, and the tip more variable.

The basic voltage-dependent features we observed were highly reproducible, but the detailed appearance of some molecules was sensitive to tip changes. The tip geometry was particularly evident for cyclooctene, which is flexible and extends some 5 \AA from the surface. It is known that the electronic structure of a tip can influence the quantitative bias dependence and can strongly alter I/V curves.¹⁹ Changes in the work function of the tip due to adsorption or restructuring can cause shifts in apparent bias up to several tenths of a volt. We obtained series of images at constant tunneling junction

resistance that showed changes with bias similar to those at a single current, so the voltage dependence of the images is not an artifact of changing tip-sample separation. However, the brighter core seen in the depressions at low bias and high current is likely due to close contact and strong interaction between molecule and tip.⁵

IV. Discussion

Consideration of the electronic states of the surface and molecule allows a qualitative interpretation of these observations. The dominant features in images of the unreacted Si-(100)-(2 \times 1) surface at all voltages are the silicon dimers. As determined by UPS and tunneling spectroscopy, the density-of-states of the dimer π orbitals peaks about 0.8 eV below the Fermi level.²⁰ The dimer π^* orbitals are seen at about +0.35 V. The surface density-of-states for the silicon valence band peaks around -2 eV.

The energy levels of the adsorbed molecules have not been measured, but an estimate is instructive. An unsubstituted alkane or unconjugated alkene has an ionization potential of 9–11 eV and a small negative electron affinity. Since there is not a great difference in electronegativity between silicon and carbon, the levels are not expected to be influenced significantly by charge transfer. Making a somewhat artificial distinction between states involved in bonding and the “bulk” adsorbate, the HOMO of the adsorbed molecule will be 3–5 eV below the Fermi level. The LUMO, corresponding to the negative ion and stabilized relative to the original electron affinity, will fall at least 1 eV below the vacuum level. New states resulting from carbon-silicon bonding are as yet undetermined. Molecular orbital calculations suggest that adsorption induces

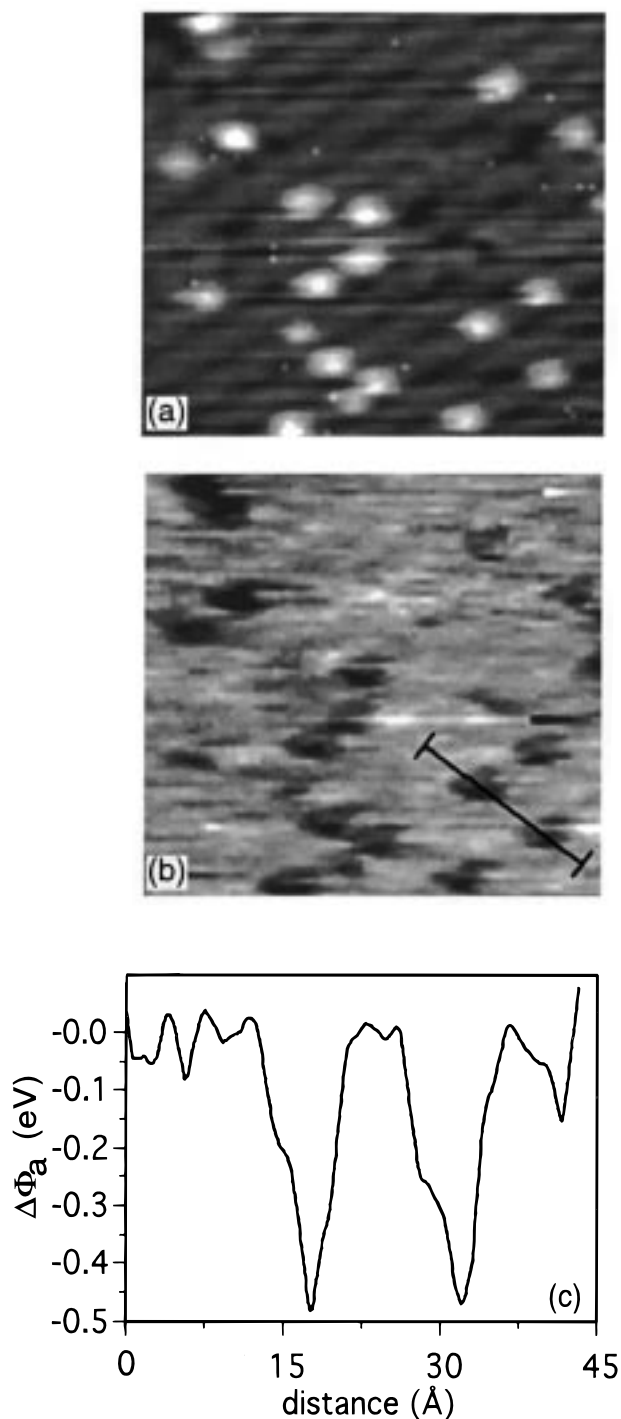


Figure 4. The apparent barrier is reduced over the adsorbates. (a) Topographic image of cyclopentene molecules. (b) Barrier height image taken simultaneously. (c) Change in apparent barrier height relative to bare silicon along the section in (b). The values are approximate.

silicon surface states above the bulk valence band edge, but photoemission is inconclusive. The various energy levels are sketched in Figure 5.

For tunneling at -1.0 V, neither bulk silicon states nor molecular states are accessible. The clean surface is imaged by means of the surface state of the dimer π -bond at -0.85 eV below the Fermi level. This state is removed by reaction with alkenes, so the tunneling low bias is reduced and the molecules image as depressions similar to missing dimer defects.

At -2.5 V bias electrons can tunnel from the valence band as well as the surface dimers. On the unreacted surface,

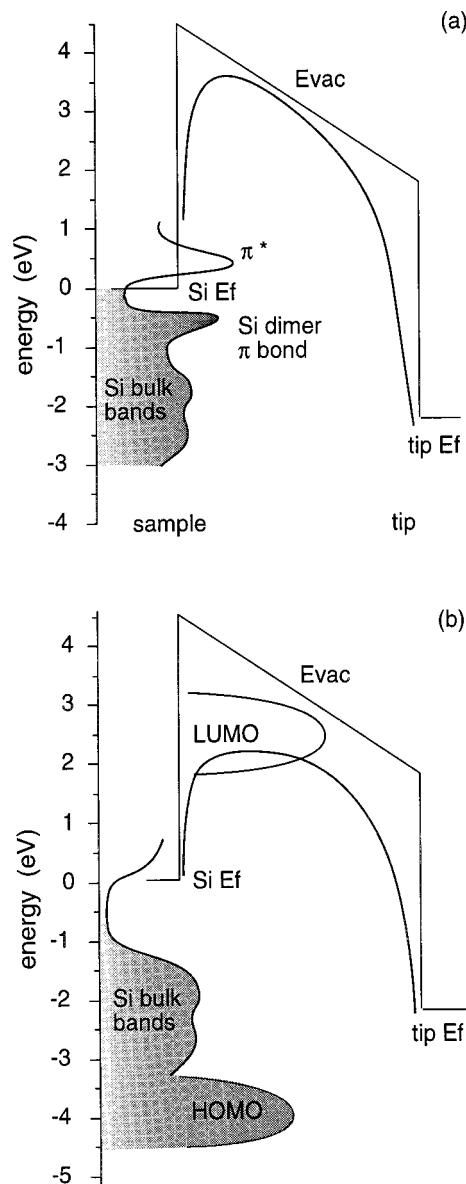


Figure 5. Energy levels for bare silicon (a) and the reacted surface (b). This figure is highly schematic; the abscissa mixes density-of-states and distance. At -1 V bias, only the dimer π state is accessible to tunneling, but it is removed by adsorption. At -2.5 V, tunneling occurs from silicon valence levels, perhaps shifted by adsorption. The molecule's HOMO is well below the energy range involved in elastic tunneling, resonant tunneling through real molecular states probably does not occur for most of the molecules and biases we have examined. This is supported by the lack of visible distinction between C–C and C=C bonds remaining in the adsorbate. At positive biases, resonant tunneling into the LUMO is possible and may partly account for the difficulties in maintaining stable tunneling.

tunneling from the dimer π -bond still dominates, since these states are localized at the surface and are closer to the top of the barrier. Where molecules have adsorbed, the dimer surface states are absent. Tunneling originates from the silicon valence band and perhaps from new adsorption-induced silicon states. Since the HOMO is below the energy range involved in elastic tunneling, resonant tunneling through real molecular states probably does not occur for most of the molecules and biases we have examined. This is supported by the lack of visible distinction between C–C and C=C bonds remaining in the adsorbate. At positive biases, resonant tunneling into the LUMO is possible and may partly account for the difficulties in maintaining stable tunneling.

Regardless of the states from which the electrons originate, tunneling through the molecule is enhanced. This is clear from

the barrier height measurements. Electron transfer theory predicts that low-lying unoccupied states of the adsorbate play a dominant role in enhanced tunneling through the molecule.²¹ Other workers have similarly interpreted STM images showing bright spots in the alkane portions of linear dienes reacted with Si(111) as enhanced "through bond" tunneling.²² A simple picture is that tunneling occurs through a virtual negative ion rather than vacuum. An analogy is tunneling through thin insulating films, in which the conduction band replaces the vacuum level as the top of the tunneling barrier.²³ Note that the threshold for electron injection from the substrate into the molecule is not equivalent to the local work function, which still requires promotion of an electron to the vacuum level.

The alkanes and unconjugated alkenes examined here are essentially insulators, enhancing tunneling through virtual states. This suggests that, if the HOMO is not directly accessible and adsorption does not induce new states near the Fermi level, the image is shaped by the unoccupied states, primarily the LUMO, at either positive or negative bias. This would account for the frequently observed symmetry between positive and negative polarity images at low bias voltages.

This work can be extended in many ways. To confirm changes in the silicon surface states and locate the molecular levels, valence band photoemission, tunneling spectroscopy, and further molecular orbital calculations would all be useful. Organic molecules on silicon can be widely varied to explore tunneling. Altering the alignment of molecular energy levels and substrate bands suggests a number of possibilities. Resonant tunneling, involving real molecular ions, will be possible if the adsorbate's orbitals fall within a few electronvolts of the Fermi level. If the molecular states are degenerate with bulk bands, tunneling should be strongly enhanced. Where molecular states fall within the band gap of a semiconductor substrate, the outcome depends on the lifetime of the ion. If charge transfer to the substrate is inhibited, telegraph noise, Coulomb blockade, or electron-stimulated reactions might be observed.

V. Conclusion

We have seen that images of several cycloalkenes chemisorbed on silicon, resulting in both alkanes and unconjugated alkene adsorbates, show similar bias dependence. At small negative sample bias, only the surface states due to the silicon dimers are accessible to tunneling. These states are removed by bonding and so the molecules image as depressions, frequently with a brighter core due to close tip-molecule interactions. At more negative bias, the molecules image as protrusions. Here the electrons are likely to originate primarily from the substrate, but tunneling through the molecule is enhanced. Measurements show a reduced apparent barrier at the molecules.

These results can be qualitatively interpreted. For the unsubstituted and unconjugated molecules studied, the occupied

molecular levels are largely outside the range of normal bias voltages. Resonant tunneling through real states of the molecule is therefore unlikely. Tunneling occurs between substrate and tip, indirectly influenced by the adsorbate. The molecules are imaged by altering the substrate electronic structure by bonding and by enhancing electron transfer through the virtual molecular ion. Intuitively, the image can be pictured as the modified substrate viewed through the LUMO of the molecule.

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