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# Molecule/Metal Surface Interactions Evidenced Quantum Mechanically via Tip-Induced CS<sub>2</sub> Interaction with Friedel Oscillations on Au{111}

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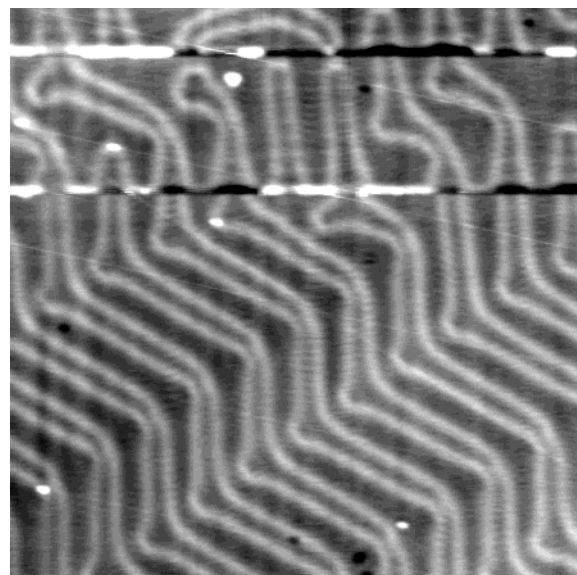
Submonolayer coverages of CS<sub>2</sub> adsorbed on Au{111} at 4 K were studied using scanning tunneling microscopy. The molecule forms well-ordered islands on the terraces and molecular chains at the bottoms of the steps. The adsorption of the CS<sub>2</sub> molecule at specific surface sites is explained in terms of the substrate electron density. Strong tip/molecule interactions are shown to be prevalent in this system at negative tip biases and yield images showing reversed corrugation. At low positive tip bias, the tip again perturbs the molecules, but in this regime, the tip/molecule interaction is comparable to the molecule/surface interaction and higher residence times at certain surface sites are observed. This effect is explained fully in terms of the CS<sub>2</sub> molecule having increased interactions with the areas of high electron density on the peaks of standing waves arising from electrons close to the Fermi energy. The importance of this result is discussed in terms of the fundamental surface physics of adsorbate/metal bonding.

## Introduction

One of the most basic and useful concepts in chemistry is the classification of molecules as either electrophilic or nucleophilic. This allows for the explanation of molecular interactions and reactions in terms of attractive interactions between opposing species, with all types of bond formation lowering the total electron energy in the system. This general concept is prevalent in all areas of chemistry and has typically been verified by macroscopic techniques examining large ensembles of interacting molecules.

Recently the use of scanning tunneling microscopy (STM) has enabled the study of single molecules and their interactions with each other and with their local surface environment. Many studies of small molecules on metal surfaces have found the formation of ordered structures,<sup>1–4</sup> dynamic 2D solid/gas systems,<sup>5,6</sup> and the interactions of single atoms and molecules with surface state electrons.<sup>7–13</sup> The earliest work on spatial modulation of adatom position by oscillatory through substrate interactions was performed by Tsong using field ion microscopy (FIM).<sup>11,12</sup> Work done with benzene on Cu{111} by Stranick et al.<sup>6,8</sup> demonstrated that outward growth of benzene from a step edge was mediated by the LDOS modulation arising from the step edge and from the tightly bound benzene molecules themselves. Very recently, long-range adatom/adatom interactions have been explained in terms of the Friedel oscillations created by the atoms' perturbation of the surface state.<sup>7,9,10</sup> A statistical analysis revealed that the distributions of separations of the atoms are oscillatory; this is explained in terms of constructive interference between the Friedel oscillations associated with each atom.

The substrate of interest in this study is the Au{111}-(23 × √3) surface. When examining adsorption on this surface, one must consider the complex potential landscape imposed by the herringbone reconstruction and the modulations in electron density created by interaction of the surface state electrons with defects such as steps and missing atoms. Careful measurements



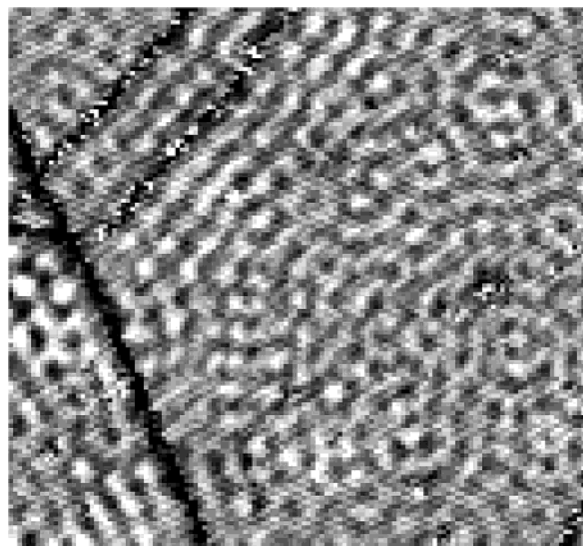
**Figure 1.** STM constant current image (600 Å × 600 Å) of a clean Au{111} surface at 4 K ( $V_{\text{sample}} = +0.1$  V;  $I_t = 100$  pA). Steps, the herringbone reconstruction, and standing waves around single atom defects are seen.

of molecular interactions with such surface features can yield valuable information about the adsorbate/surface bond and give new insight into molecular adsorption accompanied by charge transfer at the stochastic level. In this paper, we examine the interaction of a molecule, namely, CS<sub>2</sub>, with the Au{111} surface and show that, while tip/adsorbate interactions are normally undesirable in STM, scanning in the dynamic regime can actually yield useful information about preferred adsorption sites. We demonstrate directly that molecules prefer surface sites where electron density and energy suit formation of the adsorbate/surface bond.<sup>13</sup>

## Experimental Methods

All experiments were performed in a low-temperature, ultrahigh vacuum STM, described elsewhere.<sup>14</sup> All images were

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**Figure 2.** STM  $dI/dV$  image ( $440 \text{ \AA} \times 440 \text{ \AA}$ ) of clean Au{111} surface at 4 K ( $V_{\text{sample}} = -0.15 \text{ V}$ ;  $I_t = 200 \text{ pA}$ ). Friedel oscillations are observed around single atom defects and parallel to step edges.

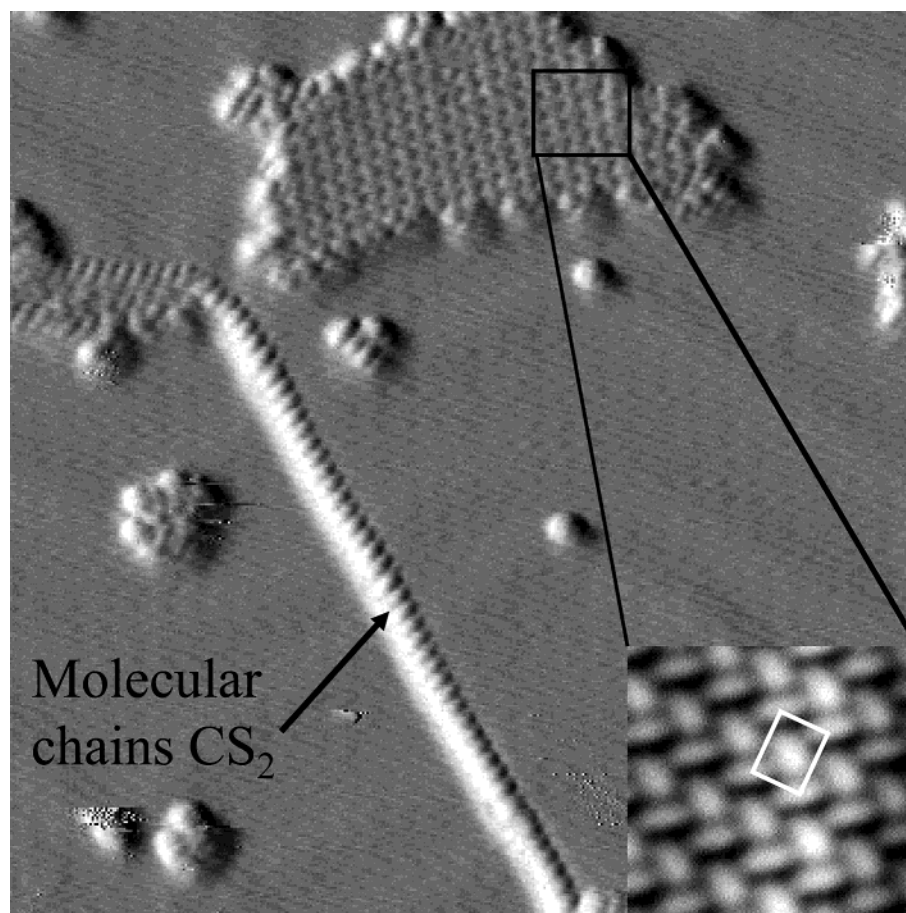
recorded at 4 K in the constant-current mode with a cut Pt/Ir (85/15%) tip. An ordered Au{111} surface was obtained from a Au/mica sample (Molecular Imaging) by repeated cycles of 1 keV sputtering and annealing at 900 K. Sputtering was performed at a sample temperature of 900 K and  $4.0 \times 10^{-5}$  Torr Ar pressure. Surface crystallinity and cleanliness were verified using both LEED and STM. Liquid CS<sub>2</sub> (99% 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. The deposition of CS<sub>2</sub> was performed after the Au{111} substrate had reached a temperature of 4 K by line of sight dosing described elsewhere.<sup>14</sup> Differential conductance ( $dI/dV$ ) imaging was performed by lock-in detection of a 500 Hz, 0.01 V modulation added to the sample bias.<sup>15</sup>

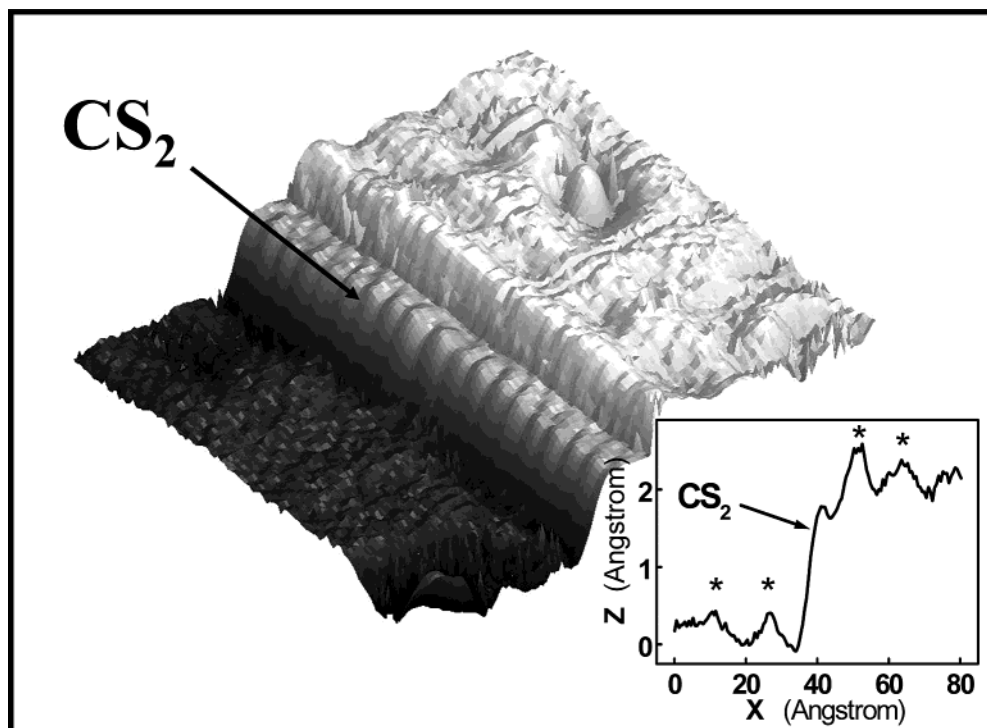
## Results and Discussion

### Topographic and Spectroscopic Imaging of Bare Au{111}.

A typical scan of the clean Au{111} surface at 4 K before deposition of CS<sub>2</sub> is shown in Figure 1. Terrace widths were typically 300 Å and single atom defects were observed in a concentration of approximately 1 per 1000 surface atoms. Standing waves of the surface state electrons were routinely observed in constant current images at 4 K associated with electron scattering from single atom defects and steps. Scanning in differential conductance ( $dI/dV$ ) mode<sup>16</sup> provides direct information on the surface LDOS and also clearly images these standing waves. Figure 2 shows a  $dI/dV$  image of clean Au at 4 K taken at a sample bias of  $-0.15 \text{ V}$ . Standing waves can be seen emanating from steps and single atom defects. The wavelengths of the standing waves are dependent on the surface state electron's energy, and thus, by taking  $dI/dV$  images at different bias voltages, we examine only surface states of a particular electron energy.<sup>16,17</sup> The measured wavelength of the standing waves associated with the steps in this particular image is  $19.7 \pm 0.3 \text{ \AA}$ . The corresponding Fermi wave vector for this wavelength is  $0.1595 \pm 0.0025 \text{ \AA}^{-1}$ , which is in good agreement



**Figure 3.** STM derivative image ( $236 \text{ \AA} \times 236 \text{ \AA}$ ) of 0.2 ML CS<sub>2</sub> on Au{111} at 4 K ( $V_{\text{sample}} = -0.5 \text{ V}$ ;  $I_t = 200 \text{ pA}$ ). Islands of CS<sub>2</sub> in the herringbone structure and molecular chains (see arrow) at the bottom of steps are observed. The inset shows a high-resolution scan of a CS<sub>2</sub> island, and the unit cell is marked with a white rectangle.



**Figure 4.** STM image ( $115 \text{ \AA} \times 75 \text{ \AA}$ ) of  $\text{CS}_2$  molecules adsorbed at positions below a step riser ( $V_{\text{sample}} = -0.5 \text{ V}$ ;  $I_t = 200 \text{ pA}$ ). The inset shows a line scan taken over the step and the molecules can be seen with an apparent height of  $1.55 \text{ \AA}$ . Standing waves are observed parallel to the step with those on the top terrace imaged with greater contrast and are highlighted in the inset with asterisks.

with the energy dispersion of surface states of  $\text{Au}\{111\}$  measured by Hasegawa et al.<sup>16</sup> Our ability to relate oscillatory features on the  $\text{Au}\{111\}$  substrate to particular surface state electron energies in this way will be used below.

**Submonolayer Growth of  $\text{CS}_2$  on  $\text{Au}\{111\}$ .** Figure 3 shows a  $236 \text{ \AA} \times 236 \text{ \AA}$  image of  $\text{CS}_2$  molecules adsorbed on  $\text{Au}\{111\}$  at a coverage of 0.2 ML. The herringbone reconstruction is still observed after deposition of  $\text{CS}_2$  revealing that  $\text{CS}_2$  is only weakly interacting with the Au substrate.<sup>4</sup> On top of the  $\text{Au}\{111\}$  terrace,  $\text{CS}_2$  forms highly ordered islands, assigned as a herringbone structure,<sup>4</sup> which maximizes intermolecular quadrupolar interactions. For clarity the reader must remember to distinguish between the herringbone reconstruction of the Au substrate and the *herringbone* structure of the  $\text{CS}_2$  islands. A higher resolution image of the  $\text{CS}_2$  island is shown in the inset. The apparent height of the island in the STM images is measured to be  $1.5 \text{ \AA}$ . This corresponds to the  $\text{CS}_2$  adsorbed with its molecular axis parallel to the surface. Individual  $\text{CS}_2$  molecules are aligned at the bottom of the monatomic step edge of the substrate (see arrow in Figure 3). Figure 4 shows a higher resolution image of this phenomena. The inset line scan shows a “bulge” at the step edge with an apparent protrusion of  $1.55 \text{ \AA}$  (as compared to  $2.35 \text{ \AA}$  for the Au step height): this demonstrates that the molecules are indeed adsorbed on the lower terrace at the step.

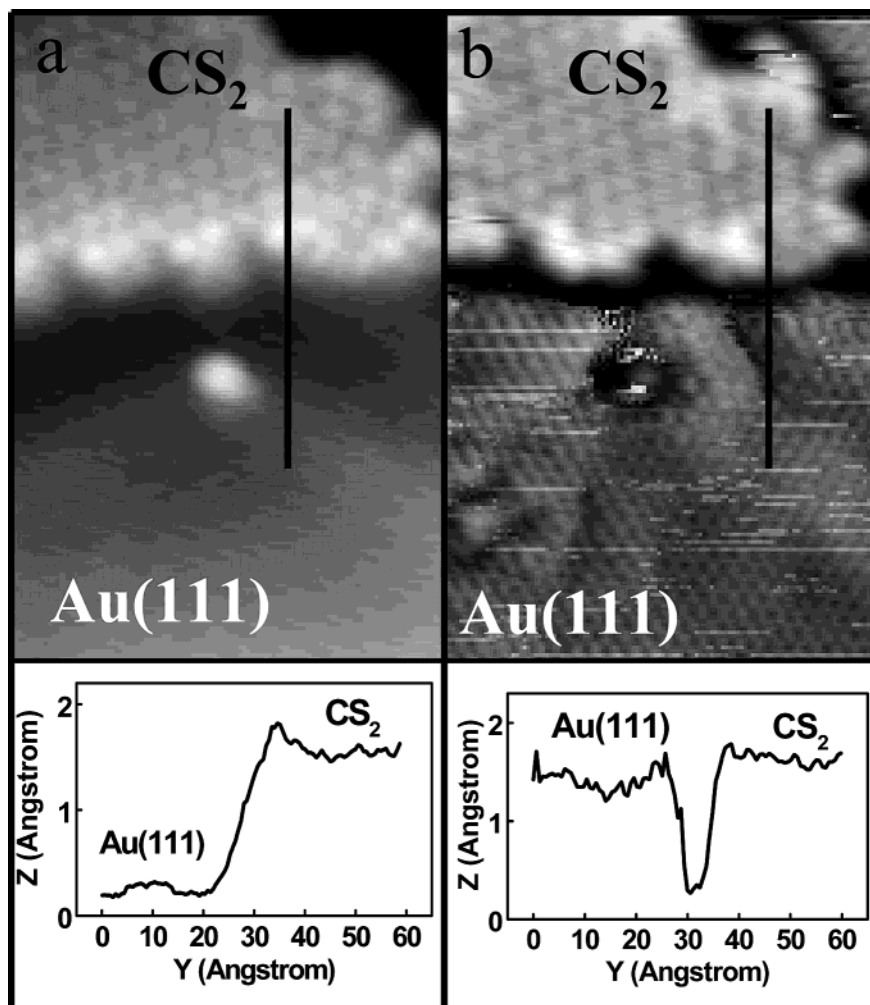
Smoluchowski showed that at metallic steps there is a charge redistribution that results in a net flow of electrons from the edge of the upper terrace to the lower terrace.<sup>18</sup> We have described how this is typically the strongest electronic perturbation of the surface; the edge of the upper terrace contains a higher population of unfilled LDOS and the edge of the lower terrace contains enhanced filled LDOS; hence, nucleophilic and electrophilic molecules interact differently with these two sites.<sup>6,8,19,20</sup> That  $\text{CS}_2$  nucleates at the lower edge of the terraces on this surface demonstrates that  $\text{CS}_2$  does behave as expected for a molecule with an electrophilic carbon center.<sup>21</sup> We have

previously shown such effects for benzene and 7,7',8,8'-tetracyanoquinonodimethane on metal surfaces; the molecules first adsorb at step sites with specific local density of states to enhance the charge-transfer surface/molecule bond.<sup>8,13,20,22</sup> Yoon et al. studied benzene, a nucleophilic molecule, on  $\text{Rh}\{111\}$  and also observed preferential nucleation of the molecule above steps.<sup>19</sup> This issue of molecules nucleating preferentially at sites of specific electron density will become pertinent for understanding our data presented below.

The packing density of the linear  $\text{CS}_2$  chains at the step edges (Figures 3 and 4) is 24 molecules per  $100 \text{ \AA}$  as opposed to 19 molecules per  $100 \text{ \AA}$  for the closest packed direction of the  $\text{CS}_2$  *herringbone* structure.<sup>4</sup> This close packing at the step edges hints that the molecules are aligned with their molecular axes parallel to each other and that the whole chain is either standing upright or lying flat on the surface. In contrast, the end-on alignment would produce a molecular chain much less densely packed. Figure 4 also shows two standing waves associated with the step both above and below the riser. The peaks in the oscillations are highlighted in the inset with asterisks. The oscillations above the step are imaged with greater contrast than those on the lower terrace because the electron reflection coefficient is higher on the upper terrace.<sup>16</sup>

**Tip Bias Dependent Imaging of the  $\text{CS}_2/\text{Au}\{111\}$  System: Contrast Reversal.** Parts a and b of Figure 5 show the 0.2 ML  $\text{CS}_2$  covered  $\text{Au}\{111\}$  scanned at different sample biases. Figure 5a was scanned at negative sample bias ( $-0.5 \text{ V}$ ), and islands of  $\text{CS}_2$  appear to protrude  $1.5 \text{ \AA}$  above the Au surface, which is not atomically resolved at this high bias voltage. However, if this surface is scanned at positive sample bias ( $+0.3 \text{ V}$ , Figure 5b), one observes a very different image. Islands of  $\text{CS}_2$  are still present, but at the same apparent height as the bare Au surface. Such a bias-dependent corrugation reversal effect has been observed before for two other systems<sup>23,24</sup> and has been explained as a molecule being dragged under the tip but being lost to the island every time the tip





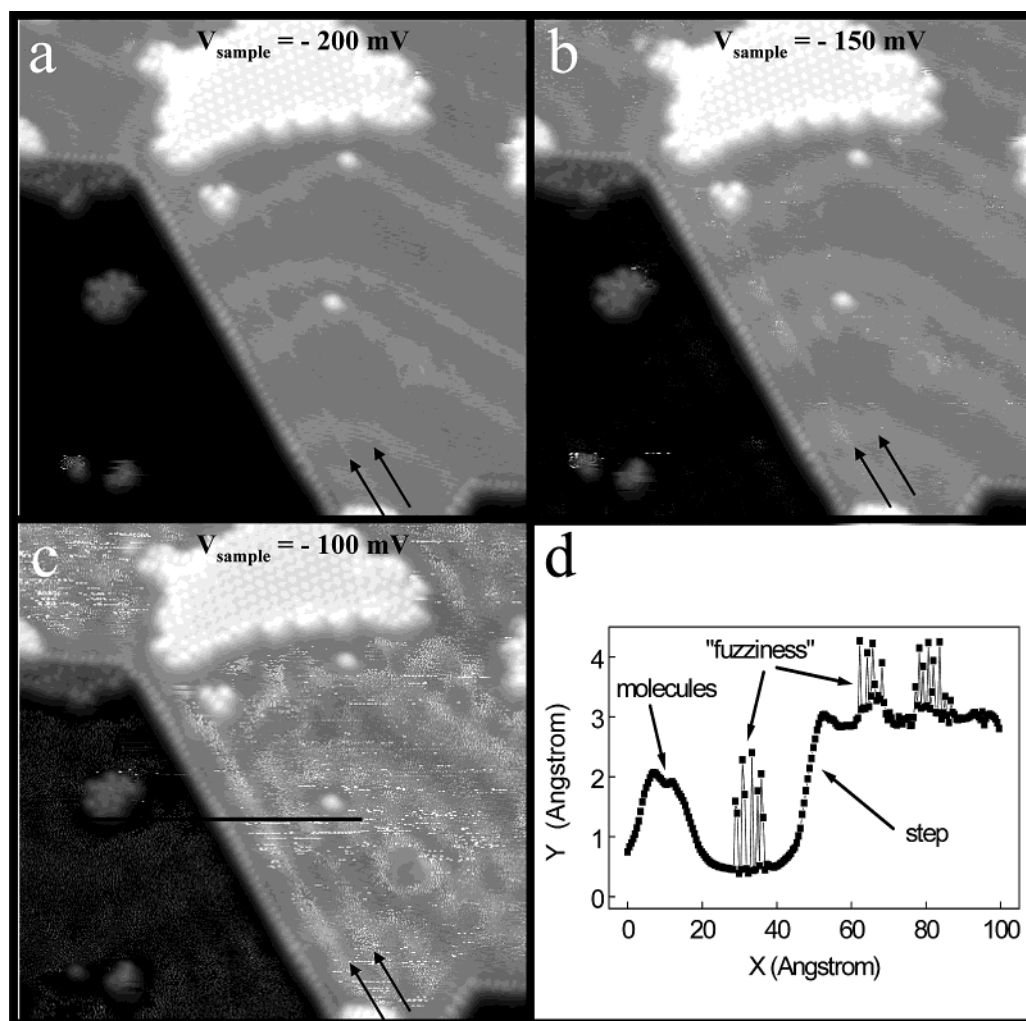
**Figure 5.** (a and b) STM images, ( $70 \text{ \AA} \times 100 \text{ \AA}$ ) of 0.2 ML  $\text{CS}_2$  on Au{111} at 4 K. Image in part a is taken with  $V_{\text{sample}} = -0.5 \text{ V}$  and  $I_t = 200 \text{ pA}$ . At negative sample bias, islands are imaged  $1.5 \text{ \AA}$  higher than the bare Au terraces. The STM image in Part b shows that at positive sample biases ( $V_{\text{sample}} = +0.3 \text{ V}$ ;  $I_t = 200 \text{ pA}$ ) corrugation reversal is observed with the island at the same apparent height as the bare Au substrate which is atomically resolved.

traverses it. This effect is observed in our system at all sample voltages between  $+1.0$  and  $+0.15 \text{ V}$ . This bias dependence can be understood in terms of increased interaction of the electro-positive carbon center of the  $\text{CS}_2$  molecule with the negative tip.<sup>24</sup> The analogous effect of reversible *atom* attachment and detachment from the tip as a function of bias has been reported previously by Eigler et al.<sup>25</sup> and Neu et al.<sup>26</sup> In our system negative sample biases between  $-1.0$  and  $-0.3 \text{ V}$  yield images of bare Au{111} with  $1.5 \text{ \AA}$  high islands of  $\text{CS}_2$  in a regime where the tip/ $\text{CS}_2$  interactions are weak, whereas at positive sample voltages the tip scans the bare Au{111} with a  $\text{CS}_2$  molecule located at its apex and yields a reversal of image corrugation. This effect also manifests itself in atomically resolving the bare Au at fairly high positive sample bias voltage;<sup>27</sup> see the Au{111} terrace in Figure 5b. A corollary of this observation is that we now have a more localized probe and that imaging the bare Au atomically means that the orientation of the  $\text{CS}_2$  molecule is fixed on the tip.<sup>27</sup> A different tip/adsorbate interaction is observed at sample biases between  $-0.3$  and  $-0.1 \text{ V}$  and is discussed in the next section.

**Spatial Resolution of the Au/ $\text{CS}_2$  Interaction via Tip-Induced  $\text{CS}_2$  Motion.** Figure 6 shows a series of images taken on the same area at different bias voltages. At a sample bias of  $-0.2 \text{ V}$ , the tip is just starting to interact with the  $\text{CS}_2$  molecules and faint “fuzzy” lines are observed parallel to the step edge, indicating that the molecules are not fixed rigidly on the surface,

even at 4 K. This is attributed to the low electronic corrugation of the Au{111} surface making the barrier to diffusion of physisorbed species very low.<sup>4</sup> As the bias voltage is increased further from  $-0.2 \text{ V}$ , the tip/surface distance is decreased until at a sample bias of  $-0.1 \text{ V}$  the entire Au{111} terrace is now “fuzzy,” the tip moving molecules as it scans.<sup>5,24,27</sup> The line scan in Figure 6d demonstrates this effect. The step and  $\text{CS}_2$  islands shown in Figure 6c are scanned normally but at certain segments noise appears in the line scan. This “fuzziness” is of the same apparent height as a  $\text{CS}_2$  molecule and is attributed to higher residence times of the  $\text{CS}_2$  molecule at specific surface sites. The Au{111} in this case is not atomically resolved; thus, the  $\text{CS}_2$  molecule is not fixed rigidly under the tip as discussed for positive sample biases in the corrugation reversal section above. Rather, the  $\text{CS}_2$  molecule is being pushed around by the tip and interacting both with the tip and the surface. This effect is completely reversible in that restoring the sample voltage  $< -0.2 \text{ V}$  yields a clean Au{111} terrace as the bare tip is then scanning the surface at a separation great enough so as not to interact strongly enough with the molecules to move them.

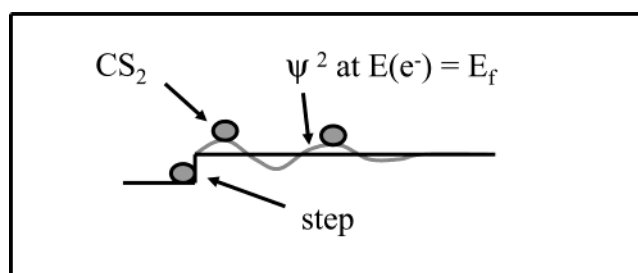
From Figure 6c it is seen that the “fuzziness” on the terrace is not uniform, distinct lines are observed running parallel to steps and rings appear around single atom defects. This increased fuzziness at certain lateral positions is related to higher residence times of the  $\text{CS}_2$  molecules at these positions.<sup>4,8</sup> Note that from a comparison of parts a and c of Figure 6 that the fuzziness is



**Figure 6.** STM images in parts a–c ( $125 \text{ \AA} \times 125 \text{ \AA}$ ) at different sample bias of  $\text{CS}_2$  on  $\text{Au}\{111\}$  at 4 K,  $I_t = 200 \text{ pA}$ . At low tip voltages the tip/surface separation is small and the tip begins moving the molecules around the surface as it scans, this creates the characteristic “fuzziness”. The fuzziness, therefore average residence time of the molecule, is higher at certain lateral positions on the surface associated with standing waves. Part d shows a line scan taken from the image shown in Figure 6c where the “fuzziness” shows up as noise at certain distances from the step in the line scan.

not affected by the herringbone reconstruction. We now discuss the higher residence times of the  $\text{CS}_2$  molecule at certain positions on the surface in relation to positions of standing waves of certain energies associated with steps and single atom defects on the Au substrate. The fuzziness in the three images in Figure 6 is modulated with a lateral period of  $17.85 \pm 0.3 \text{ \AA}$ , independent of the bias voltage over this range. The corresponding surface state Fermi wave vector for this period is  $0.1760 \pm 0.0025 \text{ \AA}^{-1}$ , which correlates to the electron energy at the Fermi level in  $\text{Au}\{111\}$ .<sup>16</sup> We therefore explain these oscillations in average residence times of the molecules in terms of heightened  $\text{CS}_2$ /surface interactions at positions on the surface of maximum filled LDOS at the Fermi level (i.e., at lateral positions of  $\psi^2_{\text{max}}$  of the standing wave as shown schematically in Figure 7). The assignment of maximum  $\text{CS}_2$  interactions at positions of  $\psi^2_{\text{max}}$  rather than  $\psi^2_{\text{min}}$  is made considering the conclusion from section 2, namely, that the molecule preferentially nucleates at positions of maximum electron density at the bottom of steps.

It has always been an intuitive argument that species undergoing charge transfer with a surface in order to form a bond will do so with electrons at the Fermi level. This is because these surface electrons are the least “stable” and therefore have the greatest ability to lower the system’s overall energy by



**Figure 7.** A schematic of our proposed model for the  $\text{CS}_2$  molecule’s lateral interaction with the standing waves arising from steps on  $\text{Au}\{111\}$ .

redistributing to levels of lower energy associated with the adsorbed molecule. Here we observe directly molecules binding more strongly to the surface at lateral positions that are maxima of  $\psi(E_F)^2$ .

## Conclusions

That  $\text{Au}\{111\}$  ( $23 \times \sqrt{3}$ ) surface reconstruction is not lifted upon adsorption of  $\text{CS}_2$ , coupled with the facile manipulation of the molecules at 4 K demonstrates that  $\text{CS}_2$  is weakly physisorbed on  $\text{Au}\{111\}$  at 4 K. Island formation occurs in the molecular herringbone structure, as is expected for quadrupolar

packing of molecules that are weakly interacting with the substrate. The preferred adsorption of CS<sub>2</sub> at the bottom of the steps demonstrates the molecule's affinity for binding at electron rich areas on Au{111}. Tip/molecule interactions at positive sample biases show reversed corrugation, and this effect is associated with the electrophilic carbon of the CS<sub>2</sub> molecule interacting strongly with the tip. At low negative sample biases, the tip moves the molecules over the sample and preferred adsorption sites are observed. We demonstrate that this preferred adsorption occurs at  $\psi^2_{\text{max}}$  of the Friedel oscillations at step edges and that these standing waves have a surface state electron energy equal to the Fermi level.

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