

# Scanning Tunneling Microscopy and Quartz Crystal Microbalance Studies of Au Exposed to Sulfide, Thiocyanate, and *n*-Octadecanethiol

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Atomic resolution STM images of Au(111) treated with solutions of Na<sub>2</sub>S, H<sub>2</sub>S, or NaSCN display patterns of atoms in the shape of squares with nearest-neighbor distances of  $0.27 \pm 0.3$  nm. QCM data demonstrate that Au dissolves in aqueous solutions of sulfide and thiocyanate with O<sub>2</sub> present. The square pattern observed is ascribed to images of Au atoms on a reconstructed Au(111) surface caused by dissolution of Au by sulfide or thiocyanate. *n*-Octadecanethiol/Au(111) surfaces damaged by the STM tip display a similar square pattern, indicating removal of Au atoms by the tip in a manner analogous to the dissolution process observed for sulfide or thiocyanate.

## Introduction

We describe here scanning tunneling microscopy<sup>1</sup> (STM) and quartz crystal microbalance<sup>2</sup> (QCM) experiments of Au dissolution in aqueous solutions of sulfide and thiocyanate at room temperature. Au is shown to be solubilized by oxidation in slightly alkaline S<sup>2-</sup> or in near neutral SCN<sup>-</sup> solutions as noted by mass loss from QCM data. STM images obtained in air of Au(111) surfaces treated with oxygenated solutions of H<sub>2</sub>S, Na<sub>2</sub>S, or NaSCN exhibit arrays of atoms arranged in squares, which appear to be reconstructed Au atoms. The amount of Au atom loss from the surface as determined by QCM is shown to be approximately 20% of a monolayer for a 10-mL solution of 10<sup>-4</sup> M S<sup>2-</sup> and agrees well with STM images and previous literature describing the solubility of Au in S<sup>2-</sup> solutions.<sup>3-7</sup> In addition, we present STM images of *n*-octadecanethiol/Au(111) that display the same square pattern as observed with S<sup>2-</sup> or SCN<sup>-</sup>; this suggests that Au is removed from the (111) surface during the STM imaging process.

As early as 1880 the dissolution and transport of Au in Au ores was suggested to occur by oxidation in the presence of alkaline sulfide solutions.<sup>4</sup> The geology literature is abundant with studies that discuss the dissolution of Au in oxygenated, alkaline sulfide solutions,<sup>4-7</sup> but not until 1951 were thermodynamic calculations performed which explained these results.<sup>3</sup> The solubility of Au in sulfide solutions is as high as  $3 \times 10^{-6}$  g L<sup>-1</sup> for sulfide concentrations as low as 10<sup>-6</sup> M.<sup>3</sup> The most probable form of the soluble gold sulfide is AuS<sup>-</sup>, which is more stable than AuO<sub>2</sub><sup>-</sup> by nearly 20 kcal mol<sup>-1</sup>.<sup>3</sup> AuS<sup>-</sup> might be stabilized by solution-phase polysulfides, but the literature is unclear on this point. The solubility of Au in sulfide media was calculated from changes in mass of high surface area gold, e.g., spongy gold, exposed to these solutions at various pH's. Dissolution rates were highest at pH = 7–11.<sup>8</sup> Studies of Au and Au/Ag or Au/Cu alloys in sulfide solutions showed a similar pH trend and also selective dissolution of the less noble metal, indicating that other metals can also be solubilized and transported by sulfides.<sup>9</sup>

Although there is no quantitative data for Au solubility in SCN<sup>-</sup> solutions with oxygen present, there are electrochemical corrosion data<sup>10</sup> which indicate that Au surfaces are attacked to some extent by dilute, aqueous SCN<sup>-</sup> solutions (10<sup>-5</sup>–10<sup>-3</sup> M). There is also some evidence from infrared studies of Au and Ag surfaces immersed in SCN<sup>-</sup> solutions which points to a soluble M(SCN)<sub>x</sub><sup>n-</sup> species.<sup>11</sup>

STM studies of various adsorbed anions on Au have been shown to enhance the mobility of surface Au atoms. Trevor and Chidsey<sup>12</sup> demonstrated by in situ STM that Cl<sup>-</sup> causes rapid annealing of damaged Au(111) surfaces even at the 10<sup>-5</sup> M

concentration level. Recent STM investigations<sup>13</sup> of Au(111) surfaces immersed in CN<sup>-</sup>/O<sub>2</sub> solutions showed rapid Au dissolution with subsequent healing caused by adsorbed CN<sup>-</sup>. Adsorption of S<sup>2-</sup> or SCN<sup>-</sup> on Au is similar to the effects seen in the CN<sup>-</sup>/Au system. The adsorbed ion causes the potential for oxidation of the surface to be decreased so that O<sub>2</sub> can oxidize the surface.<sup>14</sup> Because the potential shift is much less with S<sup>2-</sup> and SCN<sup>-</sup> (approximately 0.5–0.7 V) in comparison to CN<sup>-</sup> (approximately 2 V), much less dissolution takes place.

## Experimental Section

**Chemicals.** High-purity water (Millipore, Milli-Q, >18 MΩ cm) was used throughout. Sodium sulfide and sodium thiocyanate (EM Sciences and Baker) were used without further purification. Hydrogen sulfide and *n*-octadecanethiol (Aldrich) were used as received. All other chemicals were reagent grade or better.

**Instrumentation.** Images were obtained with a NanoScope II scanning tunneling microscope (Digital Instruments, Santa Barbara, CA) using mechanically cut (GC Electronics diagonal cutters) Pt/Ir (80:20) tips. Large-scale scans were obtained in the topographic mode (constant current) and atomic resolution images were acquired in the constant-height mode.

The quartz crystal microbalance setup consisted of a frequency counter (Simpson 7026), oscillator power supply (home-built), oscillator (Leybold-Inficon, East Syracuse, NY) and 6-MHz Au-coated quartz crystal (Leybold-Inficon). To expose only the front of the crystal to solution, the crystal was mounted in a Teflon holder using Viton O-rings (7/16-in. o.d.). Contact to the crystal was made with 0.1-mm-thick Au foil (Aldrich). The Au crystal surface was cleaned with 1:3 H<sub>2</sub>O<sub>2</sub>:H<sub>2</sub>SO<sub>4</sub> (caution: care must be used with these solutions due to their strong oxidizing power), followed by a high-purity water rinse and drying with N<sub>2</sub>. The crystal was assembled in the O-ring holder and allowed to equilibrate in the ambient until a stable frequency response was obtained (20–30 min). After exposure to 10 mL of Na<sub>2</sub>S or NaSCN solution for 20–30 min, the crystal/holder was rinsed with copious amounts of water, dried in N<sub>2</sub>, equilibrated, and the QCM signal recorded.

**Substrates for STM Studies.** Au(111) films (150–250 nm) were prepared by thermal evaporation<sup>15</sup> of high-purity Au (99.99%) at 0.2 nm s<sup>-1</sup> onto heated mica in a Plasmatron P-30 thin-film system operating at  $2 \times 10^{-6}$  Torr. The mica (Asheville-Schoonmaker, Newport News, VA) was heated to 310 °C and held there for 30 min before deposition was carried out. Once the substrates had cooled to near 100 °C, the chamber was back-filled with nitrogen and the Au/mica films removed. Films used in the S<sup>2-</sup> and SCN<sup>-</sup> experiments were stored in the laboratory

ambient before use. Thiol-modified substrates were prepared by immediately placing the Au/mica film from the evaporator into ethanolic solutions of the alkyl thiol. The Au(111)/mica was exposed to dilute solutions of the Na<sub>2</sub>S or NaSCN for different amounts of time. Hydrogen sulfide was bubbled through water for 10–90 s and the Au(111)/mica was placed in the solution for 20–40 min. All samples were rinsed with copious quantities of high-purity water and dried in N<sub>2</sub> before STM imaging. Ethanolic solutions (1 mM) of *n*-octadecanethiol were prepared and Au(111)/mica placed in them (no N<sub>2</sub> sparging) for 3–72 h. The thiol-modified Au(111) was then rinsed with absolute ethanol, dried with N<sub>2</sub>, and immediately imaged by STM.

## Results and Discussion

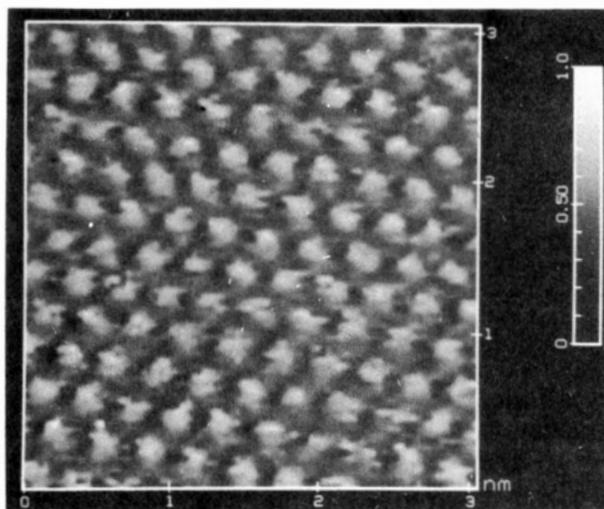
**QCM Studies of Au Dissolution.** Mass changes of Au upon exposure to sulfide or thiocyanate solutions were monitored by QCM experiments. The change in frequency ( $\Delta f$ , Hz) for an oscillating crystal can be related to the change in mass ( $\Delta m$ ) by the Sauerbrey equation:<sup>2</sup>

$$\Delta f = -2\Delta m(f_0)^2 nA(\mu\rho)^{1/2} \quad (1)$$

where  $\rho$  is the density of quartz (2.648 g cm<sup>-3</sup>),  $A$  is the area in cm<sup>2</sup> (0.97 cm<sup>2</sup>),  $n$  is the harmonic ( $n = 1$ ),  $\mu$  is the shear modulus of quartz ( $2.947 \times 10^{11}$  g cm<sup>-1</sup> s<sup>-2</sup>) and  $f_0$  is the fundamental frequency of the crystal (5.9 MHz). For our system this yields a 13-ng change for each 1 Hz change in frequency. If one assumes a Au surface roughness factor of 1.6–2.0 (from STM) and the number of Au atoms in a monolayer to be  $1.5 \times 10^{15}$  atom cm<sup>-2</sup>, the mass change for one monolayer of Au atoms would correspond to 780–980 ng or a frequency change of 60–75 Hz. The expected frequency decrease for adsorption of one monolayer of S<sup>2-</sup> is approximately 3 Hz (assuming a 1:2 ratio of S<sup>2-</sup> to Au). After exposure of the crystal to 10 mL of 10<sup>-4</sup> M Na<sub>2</sub>S (pH 8.8; predominant species, HS<sup>-</sup>) or 10<sup>-2</sup> M NaSCN (pH 8.7) for 20–30 min, frequency increases of  $12 \pm 3$  Hz and  $10 \pm 2$  Hz, respectively, were noted. Blank rinses or soakings in high-purity water did not show substantial frequency increases; readings were within  $\pm 3$  Hz of the original value. This indicates that the increase in frequency observed with the sulfide or thiocyanate solutions was not due simply to exposure to a liquid and drying. In addition, repeated exposure of the crystal to fresh aliquots of the sulfide or the thiocyanate solutions caused repeated frequency increases. Thus, we conclude that the decrease in mass is due to loss of Au from the surface. We cannot disregard the expected increase in mass due to ion adsorption, which certainly does occur, but the projected maximum value (3 Hz) is within experimental error and would not be detected. From the magnitude of the frequency increase we calculate that the mass loss in 10-mL solution volumes is approximately 20–30% of a monolayer, or 140–160 ng of Au.

As noted earlier, it is well established that Au dissolves in sulfide solution,<sup>3–7</sup> with the soluble product assumed to be AuS<sup>-</sup>. From the literature<sup>3</sup> and the concentration of S<sup>2-</sup> used here ( $1 \times 10^{-4}$  M), we calculate the solubility of Au to be  $1.4 \times 10^{-7}$  M or  $1.4 \times 10^{-9}$  mol in 10 mL. If a roughness factor of 1.6–2.0 is used for the Au surface, the amount of Au that should be lost in 10 mL is predicted to be 130–170 ng, or 25–30% of a monolayer, assuming Au(111) as the principle texture,<sup>16</sup> in good agreement with the QCM data. There is no literature describing, in detail, the dissolution of Au in thiocyanate, but Au appears to dissolve in SCN<sup>-</sup> at a level comparable to that in S<sup>2-</sup>. On the basis of previous studies,<sup>14</sup> SCN<sup>-</sup> adsorption should not cause as large a shift in the potential for oxidation of the Au surface, in comparison to S<sup>2-</sup>. There is no information in the literature regarding the rate of dissolution of Au by S<sup>2-</sup> or SCN<sup>-</sup>.

**STM of Au(111) Exposed to Aqueous Sulfide or Thiocyanate.** Figure 1 is a constant-height STM image of a clean Au(111) surface displaying individual atomic species with a spacing characteristic<sup>17,18</sup> of Au(111) atoms ( $0.29 \pm 0.02$  nm). We have

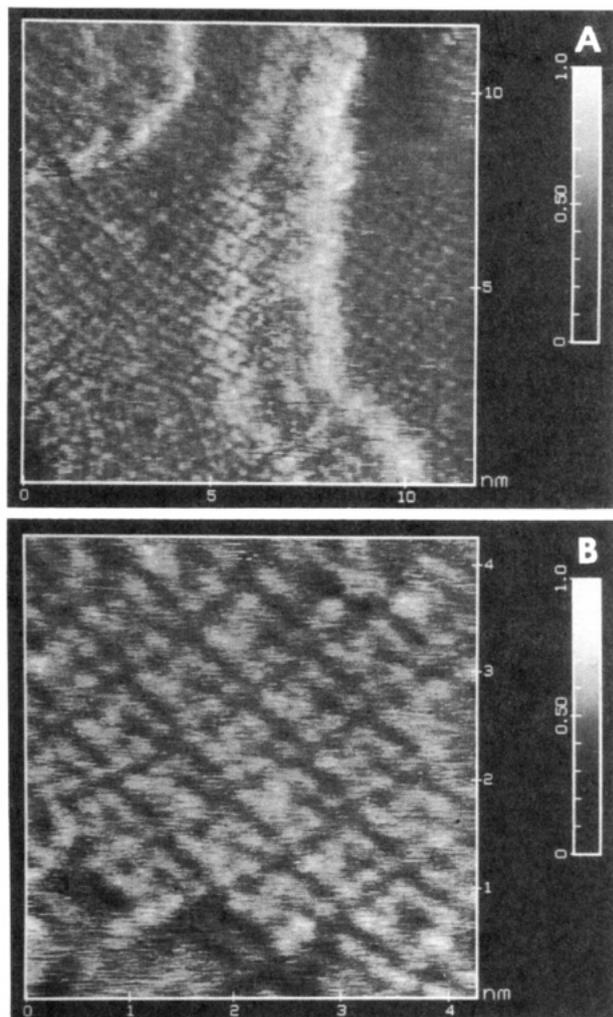


**Figure 1.** Unfiltered  $3 \times 3$  nm constant-height image of bare Au(111).  $i_t = 3$  nA;  $V_t = 20$  mV.

obtained many images like this one in air.<sup>19</sup> After exposure to an oxygen-saturated (1 part O<sub>2</sub>/32 parts H<sub>2</sub>O by volume at 25 °C) 10<sup>-5</sup> M solution of Na<sub>2</sub>S for 30 min, atomic resolution images of the surface showed a new pattern (Figure 2A). The surface was composed of a series of squares, each of which contains 8 Au atoms, seen at higher resolution in Figure 2B. Nearest-neighbor distances were  $0.27 \pm 0.03$  nm in these highly ordered areas. Images like these were also obtained for samples treated with H<sub>2</sub>S. As shown in Figure 2A, these square structures span over several plateaus, indicating some long range order. However, in some areas, the arrangement of atoms was less ordered, and some groups had 10 atoms in the shape of a pentagon, while others showed a zig-zag structure. Similar structures were seen in images of Au exposed to 10<sup>-2</sup> M NaSCN for 20–40 min (Figure 3A,B). Although areas with a square pattern are easily discerned in Figure 3A, disorder does exist as shown in Figure 3B. There were many different structures observed in these regions of disorder, including squares, pentagons, zig-zag chains, and defect sites (missing groups of atoms). In these disordered areas, the surface structure changed with time during scanning in air (thermal drift was not a factor). In fact, over a 10-min time span (approximately 20 passes of the tip across the area imaged), the squares in Figure 3B converted to pentagons or zig-zag chains and then back again. This did not seem to be affected by tip proximity or tip scan rate. Such mobility indicates a surface structure which is not strongly bound to the underlayer, as would be expected for strongly adherent adsorbates like S<sup>2-</sup> or SCN<sup>-</sup> on Au, but could also be explained by an adlayer containing many defect sites. Tip interaction with such a defective adlayer can cause “pushing” of the adsorbate.

In the more ordered areas of sulfide-treated sample ( $[S^{2-}] < 10^{-4}$  M) displaying the square pattern (Figure 2A), the number of atoms in a given area was 9–10 atoms nm<sup>-2</sup>, whereas in untreated Au(111) it was 12–14 atoms nm<sup>-2</sup>. If the atomic species in Figure 2 was an adsorbate, the surface coverage would correspond to 0.7–0.8, a rather high value. The highest surface coverage known in the literature for sulfide adsorbed on Au is 0.6, which was obtained in solution at fairly high electrode potentials.<sup>20</sup> Thus it seems unlikely that such a high adsorbate coverage would come about from adsorption from solution.

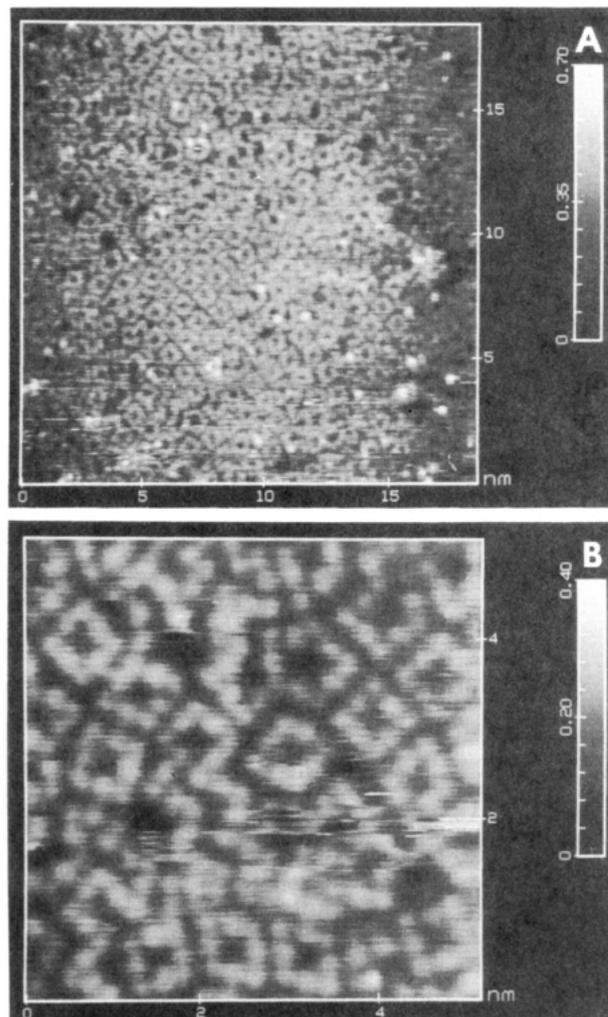
At higher concentrations of Na<sub>2</sub>S (10<sup>-2</sup> M for 40 min) or H<sub>2</sub>S (10 s bubbling, 20 min exposure time) approximately 10-nm-diameter monolayer-deep holes in the Au(111) surface were seen by STM. It was not possible to obtain atomic resolution images of these surfaces, possibly because of the large number of defects in the surface. Exposure of Au(111)/mica to 10 mL of water which had H<sub>2</sub>S bubbled through it for 3 min caused complete removal of the Au film from the mica within 20 min. We have



**Figure 2.** Unfiltered constant-height images of Au(111) exposed to  $10^{-5}$  M  $\text{Na}_2\text{S}$  for 30 min. A:  $12 \times 12$  nm region. B:  $4.2 \times 4.2$  nm region (different from A).  $i_t = 3$  nA;  $V_t = 50$  mV.

noted similar delamination behavior for Au/mica in  $\text{CN}^-/\text{O}_2$  media.<sup>13</sup> The holes in the Au(111) surface are due to dissolution and are larger and more prominent at high sulfide concentration. At lower concentrations of sulfide ( $10^{-5}$  M), smaller holes (approximately 1–2 nm) were observed, e.g., in Figure 2A, where a square of atoms is missing. We did not observe large holes in Au(111) treated with high concentrations of  $\text{SCN}^-$ , but we did see small defects, approximately 1–2 nm (Figure 3A).

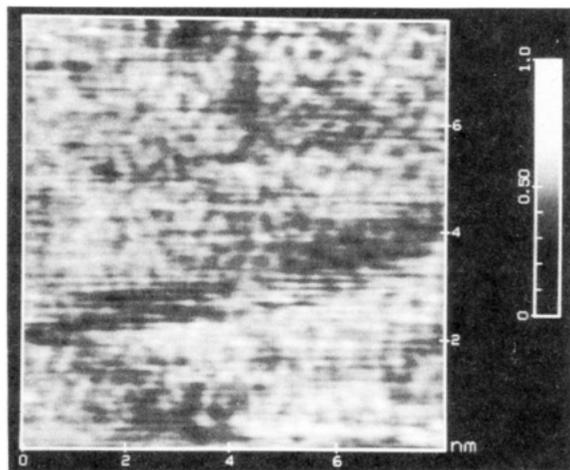
**STM of Au(111) Exposed to *n*-Octadecanethiol.** The structure of *n*-alkanethiols adsorbed on Au(111) has been shown to be  $(\sqrt{3} \times \sqrt{3})R30^\circ$  by helium<sup>21</sup> and electron diffraction<sup>22</sup> studies. Recently, a  $(\sqrt{3} \times \sqrt{3})R30^\circ$  structure on Au(111) for ethanethiol and *n*-octadecanethiol was reported using STM.<sup>18</sup> We have tried many times (in excess of 20 experiments) to reproduce these images for *n*-octadecanethiol on Au(111), but have so far been unsuccessful. Under the same conditions as reference 18, we find images like those shown in Figure 4. The arrangement of atoms is the same as that observed for Au(111) exposed to oxygenated solutions of  $\text{S}^{2-}$  and  $\text{SCN}^-$ , i.e., the square pattern. Values of atomic spacing in Figure 4 were  $0.27 \pm 0.03$  nm, identical to those reported above for Au(111) exposed to  $\text{S}^{2-}$  and  $\text{SCN}^-$  solutions. Observation of the square pattern did not depend on the exposure time (3–72 h) of the Au(111) to the thiol solution. We also observed the square pattern on *n*-octadecanethiol covered Au(111) after removal of the thiol with the tip.<sup>23</sup> In this case, removal was caused by a large physical interaction between the organic layer and the tip and was observed under various tunneling parameters. During scanning, interconversion between squares and chains was observed similar to the  $\text{S}^{2-}$  and  $\text{SCN}^-$  cases.



**Figure 3.** Unfiltered constant-height images of Au(111) treated with  $10^{-2}$  M  $\text{NaSCN}$  for 30 min. A:  $18 \times 18$  nm area. B:  $5 \times 5$  nm enlarged area of upper left of A.

Recently, Porter reported<sup>24</sup> observation of the square pattern on Au(111) samples treated with ethanolic solutions of *n*-octadecanethiol, but also images with the  $(\sqrt{3} \times \sqrt{3})R30^\circ$  structure. We have recently seen images consistent with the  $(\sqrt{3} \times \sqrt{3})R30^\circ$  structure for 4-aminothiophenol adsorbed on Au(111) and confirmed the expected adsorbate surface coverage of about 0.33 by electrochemical techniques.<sup>25</sup> However, we have also seen this structure with long-chain thiols which are too large to pack in this arrangement.<sup>25</sup>

**Origin of the "Square Pattern" Observed by STM.** There are several possible explanations for the square and other arrangements of atoms found in STM images of Au(111) exposed to  $\text{S}^{2-}$ ,  $\text{SCN}^-$ , and *n*-octadecanethiol. Gas-phase dosing ( $\text{H}_2\text{S}$ ) of Au(111) surfaces with subsequent LEED analysis gave a very complex LEED pattern for the adlayer<sup>26</sup> that was interpreted as a reconstructed adlayer resulting in a 2-dimensional sulfide, possibly caused by heating of the Au(111) crystal (100–300 °C). No LEED studies of solution dosing of Au with  $\text{S}^{2-}$  have been carried out, but solution dosing of Pt(111) with  $\text{S}^{2-}$  and  $\text{SCN}^-$  leads to diffuse LEED patterns for both  $\text{S}^{2-}$  and  $\text{SCN}^-$  on Pt(111).<sup>27</sup> However, heating the Pt following dosing in vacuum produced a distinct  $(2 \times 2)$  pattern for the  $\text{SCN}^-$  and a  $(\sqrt{3} \times \sqrt{3})R30^\circ$  pattern for  $\text{S}^{2-}$ .<sup>27</sup> Thus, disorder is evident in the  $\text{S}^{2-}$  and  $\text{SCN}^-$  systems on Pt, which may also be true for Au. The nature and cause of the disorder is unknown but may be due to multilayers or corrosion of the surface. Weaver has presented in situ electrochemical STM images of Au(111) at  $-0.1$  V in  $\text{S}^{2-}$  solution which are similar to the square patterns shown here.<sup>28</sup> They attributed the square pattern to  $\text{S}_8$  rings on top of a  $(\sqrt{3}$



**Figure 4.** Unfiltered constant-height image of *n*-octadecanethiol treated Au(111);  $i_t = 5$  nA;  $V_t = -20$  mV.

$\times \sqrt{3}$ ) $R30^\circ$  sulfur monolayer. Rings with higher numbers of atoms (10–12) were also reported at higher electrode potentials. Porter has reported STM images of Au(111) treated with  $\text{CCl}_4$  solutions of  $\text{S}^0$  that exhibit a square pattern as well.<sup>24</sup> Because, in the present work,  $\text{S}^{2-}$ ,  $\text{SCN}^-$ , and *n*-octadecanethiol all gave the same pattern, the question of what species the STM images must be addressed.

We do not think the square pattern observed by STM, can be attributed to imaging of the adsorbed species. It is unlikely that such chemically different molecules would adopt the same packing on Au(111). Monolayers of *n*-alkanethiols have been shown by He and electron diffraction<sup>21,22</sup> to adopt a  $(\sqrt{3} \times \sqrt{3})R30^\circ$  adlattice on Au(111) and electrochemical desorption confirmed the surface coverage expected for such an adlayer structure.<sup>16</sup> Although we have not been able to obtain STM  $(\sqrt{3} \times \sqrt{3})R30^\circ$  structures for *n*-octadecanethiol on Au(111) using STM, the observation of such images might depend strongly on imaging conditions. It could be argued that the STM tip breaks any bond except the Au–S bond, and the resulting image corresponds to S on Au(111). We have demonstrated that organothiols on Au surfaces can be removed with the STM tip using various tunneling parameters,<sup>23</sup> resulting in the square pattern displayed here. We speculated that along with the organothiol, Au atoms were abstracted from the surface (similar to dissolution in a  $\text{S}^{2-}$  medium), giving rise to a Au surface which reconstructs. There is no evidence, however, that the C–S bond is cleaved.<sup>23</sup> It is also unlikely that the C–S bond in  $\text{SCN}^-$  would be broken, liberating  $\text{CN}^-$  and leaving S on the Au surface. Both of these bond cleavage schemes would require that the remaining surface sulfur reconstructs to form a high-coverage adlayer ( $\theta = 0.7$ – $0.8$ ), which would not be possible with an initial sulfur concentration present in a  $(\sqrt{3} \times \sqrt{3})R30^\circ$  structure for the *n*-octadecanethiol ( $\theta = 0.33$ ) or a  $(2 \times 2)$  adlattice for the  $\text{SCN}^-$  (the structure determined<sup>27</sup> by LEED on Pt(111),  $\theta = 0.5$ ). Another argument against tip-induced bond cleavage is based on the scan area size. When an atomic resolution image of  $\text{SCN}^-$ -treated Au(111) was obtained over a small scan area, the scan area could be doubled or quadrupled in size or the tip translated to a new spot nearby without loss in image resolution. If the images we observe are due to leftover sulfur from a tip-induced bond cleavage reaction, the rate of bond cleavage would have to exceed the rate of image acquisition, which seems unlikely. Moreover, decomposition of  $\text{SCN}^-$  in aqueous solution to give S and  $\text{CN}^-$  does not seem favorable.

Considering the QCM and STM data and the literature concerning Au dissolution or corrosion in  $\text{SCN}^-$  or  $\text{S}^{2-}$  solutions, we propose that the images for Au(111) treated with solutions of  $\text{S}^{2-}$  and  $\text{SCN}^-$  are of a reconstructed, mobile Au surface. At the low concentrations of sulfide used (10 mL of a  $10^{-4}$ – $10^{-5}$  M

solution) in STM and QCM experiments, the amount of Au calculated to dissolve from solubility considerations (20%–30% of a Au(111) monolayer) agrees very well with that observed by STM and QCM. The number of atoms (assumed to be Au) per unit surface area in the STM images of Au(111) treated with solutions containing low concentrations of sulfide was  $10 \text{ nm}^{-2}$ , or about 20% fewer than expected for a virgin Au(111) surface. QCM data under similar conditions indicated a Au loss of 20%–30% of a monolayer as well. Thus, a loss of Au should be reflected in the STM images.

On the basis of the QCM and STM results for the dissolution of Au in  $\text{S}^{2-}$  or  $\text{SCN}^-$  solutions, we feel that the images observed for the damaged *n*-octadecanethiol films can also be explained by treating the removal of the organic layer by the STM tip as a dissolution reaction. As Au atoms are removed from the surface along with the organothiol by the tip (dissolution), the modified surface adopts the square pattern structure reported here. We have heated  $\text{SCN}^-$ -treated Au(111) samples, which displayed the square pattern, to  $60^\circ \text{C}$  and observed the square pattern once again. A similar heating process was previously used to increase the quality of LEED data for  $\text{SCN}^-$ -treated Pt(111).<sup>27</sup> Thus, the removal of Au atoms by the methods described here appears to cause a reconstructed surface to form. We do not have direct evidence of Au dissolution in oxygenated solutions of *n*-octadecanethiol or other thiols, but it seems possible that the thiol plays a “sulfide-like” role and causes Au dissolution at a very small rate, even in the absence of STM scanning. Although we feel that the STM images are primarily those of the electron density of Au atoms, one might attribute these to S on the Au surface or S on a reconstructed Au surface.<sup>29</sup> However, our results, including QCM data and STM images of surfaces treated with molecules not likely to cleave and leave S behind, do not support this assertion. We do know, from various methods of analysis, that the adsorbates ( $\text{S}^{2-}$ ,  $\text{SCN}^-$ , or *n*-octadecanethiol) remain on the surface. XPS indicates some  $\text{Na}^+$  and  $\text{S}^{2-}$  on the Au surface. This bound  $\text{S}^{2-}$  may cause the Au atoms to be stabilized in the square pattern observed. The images we observe for these different molecules may also be due to an electronic effect, as we have recently reported<sup>25</sup> for various thiols on Au(111), but the loss of Au atoms should have a large effect on the STM images.

## Conclusions

We have presented STM and QCM data which indicate that Au dissolves in sulfide or thiocyanate solutions containing oxygen, consistent with the geology literature concerned with Au/sulfide systems. STM images of Au(111) surfaces treated with dilute solutions of sulfide, thiocyanate, or *n*-octadecanethiol displayed surface structures containing eight atoms in the shape of a square. Occasionally pentagons or chains of atoms were observed. The square patterns observed by STM are proposed to be Au atoms that have reconstructed to form these images.

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