Low-temperature adsorption of H$_2$S on Ag(111)

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H$_2$S forms a rich variety of structures on Ag(111) at low temperature and submonolayer coverage. The molecules decorate step edges, exist as isolated entities on terraces, and aggregate into clusters and islands, under various conditions. One type of island exhibits a ($\sqrt{3} \times \sqrt{3})$R25.3° unit cell. Typically, molecules in the clusters and islands are separated by about 0.4 nm, the same as the S–S separation in crystalline H$_2$S. Density functional theory indicates that hydrogen-bonded clusters contain two types of molecules. One is very similar to an isolated adsorbed H$_2$S molecule, with both S–H bonds nearly parallel to the surface. The other has a S–H bond pointed toward the surface. The potential energy surface for adsorption and diffusion is very smooth. © 2010 American Institute of Physics. [doi:10.1063/1.3481481]

I. INTRODUCTION

Investigations of sulfur and sulfur-containing molecules, adsorbed on metal surfaces, are motivated by applications that range from catalysis to self-assembled monolayers. Concerning the specific interaction of H$_2$S with Ag(111), almost all previous studies have focused on using H$_2$S as a source of adsorbed S. In those studies, dissociative adsorption was achieved using high pressure and/or elevated surface temperature when H$_2$S was in the gas phase, or using electrochemical methods when H$_2$S was in liquid solution. In contrast, the present paper deals with the state of the molecule that is obtained by adsorption at low pressure and at temperatures (T) of 5–30 K.

Previous experiments have shown that H$_2$S adsorbs and desorbs without dissociation on Ag(111) at low pressure, i.e., in ultrahigh vacuum-type experiments. The sticking coefficient is near unity at 80 K, and desorption occurs at T =100 K. Density functional theory (DFT) calculations have shown that H$_2$S has an adsorption energy (E$_a$) of 0.17 eV on Ag(111), and that the adsorbed molecule nearly retains its gas phase geometry. The structural parameters in the gas phase are 0.135 nm for the S–H bond length, and 93° for the internal bond angle, whereas the adsorbed molecule has parameters of 0.136 nm and 92°, respectively. The isolated H$_2$S molecule adsorbs with S on top of a Ag atom, and with both S–H bonds parallel to the surface.

Unlike H$_2$S, molecular H$_2$O on metal surfaces has been studied extensively, and it is useful to review those findings. The isolated H$_2$O molecule on Ag(111) is quite similar to H$_2$S, with the O atom at an on-top adsorption site, O–H bonds parallel to the surface, and E$_a$=0.15 eV. In general, on hexagonal metal surfaces, water forms hydrogen-bonded clusters that consist of buckled hexamers.

II. EXPERIMENTAL AND COMPUTATIONAL DETAILS

All STM imaging were done at 4.7 K with a low temperature STM (Omicron GmbH, Germany) in an UHV chamber with base pressure below 6.7×10$^{-9}$ Pa. In an attached chamber, the Ag(111) sample (MaTeK GmbH) was cleaned by repeated cycles of Ar$^+$ sputtering (1 keV, ~10 μA, 10 min) and annealing (~890 K, 10 min). The clean sample was transferred to the STM stage and cooled to the operating temperature. The surface was exposed to H$_2$S gas through a dosing tube located just outside the STM cryostat. That area was at room temperature so during exposure, the sample was not cooled actively. During exposure the sample warmed to 20–30 K, depending on the time it was out of the cryostat (and hence, on exposure time). STM imaging typically began within 20 min after exposure ended, when the sample temperature had restabilized at 4.7 K. H$_2$S purity was checked with a mass spectrometer in the STM chamber.

STM images were acquired over a range of bias voltages from ~140 to 112 mV, and a range of tunneling currents up to 1.0 nA. Based on previous STM studies of H$_2$O on Ag(111), and also on Pt(111) (Ref. 28) and Pd(111), these conditions are not sufficient to induce dissociation. In
addition, there was no evidence of diffusion or rearrangement during imaging if the bias potential was about 100 mV or less.

Data from three types of experiments are described in this paper. In the first, the sample was placed in front of the gas doser for about 1 s at 20 K, after which STM images were acquired continuously over a 3 h period, and intermittently over the following 72 h. Second, the sample was placed in front of the H₂S doser for 10 s at about 30 K, and STM images were acquired over the following 2 h. Third, the same 10 s exposed sample was allowed to age for 17 h at 4.7 K, after which images were acquired again over an 8 h period. After the 1 s exposure, 2%–3% of the surface was covered, both immediately after exposure and after aging. The surface that resulted from the two exposures will be referred to as “low $\theta_{\text{rel}}$” and “higher $\theta_{\text{rel}}$” respectively. Here the relative coverage, $\theta_{\text{rel}}$, is simply based on the area of the STM images covered by adsorbate-related features. In the STM images, lateral (x and y) distances were calibrated using the atomic separation of Ag(111), 0.289 nm.

After deposition to higher $\theta_{\text{rel}}$, aging, and scanning, the sample was allowed to warm to 200 K. When checked again with STM, the surface was clean, consistent with expectations from previous work, showing that adsorption and desorption at low temperature are reversible (nondissociative). Total energy calculations were performed using the VASP code with the Perdew–Burke–Ernzerhof (PBE) approximations of the exchange-correlation functional. The electron-ion interactions were described by an improved version of the projector augmented wave (PAW) method for transition metals. The surface was modeled by periodic slabs of varying thickness separated by 1.2 nm of vacuum, using the theoretical lattice constant 0.4149 nm. The energy cutoff was 280 eV. Molecules were adsorbed on one side of the slab, and an external potential was applied to correct the artificial dipole interactions induced by the adsorbate in the direction perpendicular to the surface, when necessary. Results quoted below were obtained from averages of slab thickness varying from four to seven layers, with varying supercell sizes up to $4 \times 4$ (16 atoms in each layer). In the calculations, absolute coverages ($\theta^{\text{abs}}$) are relevant, and these are defined as the ratio of the density of H₂S molecules to Ag atoms in the surface plane. STM images were simulated using the Tersoff–Hamann method. The simulated images were obtained from the partial charge density of the sample within $\pm 0.1$ eV of the Fermi level, and the isodensity surface at a density 1% of the average bulk density. This would correspond experimentally to an ideal point tip with spherical tip wave function about 0.4 nm above the surface, with low tunneling bias.

The main intermolecular interactions between H₂S molecules in a cluster should be hydrogen bond interactions, which can be reasonably described by DFT. For example, the PBE value for H₂O dimer interactions is about 0.02 eV higher than the benchmark number from high level quantum chemistry calculations. It should be noted that the DFT-PBE error could be as high as 0.05 eV for highly nonlinear H bonds. However, DFT at the generalized gradient approximation (GGA) level is not suitable for dispersion interactions, which may play a more important role for larger complex structures. In this paper, we report results only for small clusters where hydrogen bond interactions dominate.

III. RESULTS

A. Step edges

Figure 1(a) shows an atomic-scale image of a region of a Ag(111) terrace. Arrows show the close-packed directions. This serves to define the crystallographic directions in all other STM images.

Figure 1(b) shows the smooth, straight appearance that is typical of a clean Ag(111) step at 4.7 K. The appearance
changes considerably when H$_2$S adsorbs, as shown in Fig. 1(e) for low $\theta_{H_2S}^{rel}$. Clearly, molecules saturate the step edges. At higher magnification, as in Fig. 1(d), a double row of protrusions is visible along the step edge. The protrusions are separated by 0.42 $\pm$ 0.09 nm, as shown in the inset in Fig. 1(d). Other data to be presented in this paper will repeatedly show protrusions with similar nearest-neighbor separation of 0.4 nm, in various environments. This robust feature is reasonably assigned as a H$_2$S molecule hydrogen-bonded to one or more other molecules. See Table I.

At higher $\theta_{H_2S}^{rel}$, protrusions still cover the step edges, as in Fig. 1(e). They have the same separation as at low $\theta_{H_2S}^{rel}$, although they comprise a wider band. After aging at higher $\theta_{H_2S}^{rel}$, one sees islands extending outward from step edges, as in Fig. 1(f). The growth of these islands indicates considerable diffusion of H$_2$S during aging, even at 4.7 K. If two step edges border a narrow terrace, as in the center of Fig. 1(f), the islands may bridge the terrace. Taken together, these data indicate that H$_2$S adsorbs preferentially at step edges, and the steps can serve to nucleate islands on the terraces. These are reminiscent of observations for H$_2$O on this surface. 20

Simulation of STM images, based on DFT, shows that the molecule’s shape (assuming a static position) is essentially circular, as shown in Fig. 2(c).

For quantitative STM dimensions, calculations show that the measured area per molecule should be about 0.18 nm$^2$ assuming a static position. The measured area of the isolated features in Fig. 1(e) is only slightly larger, about 0.23 nm$^2$, which is probably within the acceptable limit of such a comparison.

We also use DFT to test adsorption of a H$_2$S monomer with the S atom initially near a fcc or a bridge site, using a (2x2) supercell and $\theta_{H_2S}^{rel}$=1/4. These initial conditions result in metastable adsorption with very similar configurations and energies. The S atom is slightly higher, the H atoms are slightly lower than at the on-top site, and $E_a$ is about 0.031 eV less favorable. These metastable adsorption configurations are near the transition states for diffusion of H$_2$S molecules, implying a diffusion barrier of about 0.031 eV. [Strictly speaking, this is a lower estimate. The transition state is a saddle point which should have a higher energy than a nearby metastable adsorption site. However, due to the

B. H$_2$S on terraces: Isolated molecules

At higher $\theta_{H_2S}^{rel}$, before aging, many isolated protrusions can be seen on the terraces as in Fig. 1(e). These features may be isolated H$_2$S molecules. DFT lends some insight about whether this assignment is reasonable. Our calculations indicate that the adsorption energy of a H$_2$S molecule is 0.15 eV. This is in good agreement with Alfonso’s value, 0.17 eV,10 and in reasonable agreement with the value of 0.25 eV derived from experimental temperature-programmed desorption (using major simplifying assumptions).9 The slight difference between the two DFT values, 0.15 and 0.17 eV, is mainly due to the different PAW potential used (and therefore different lattice constant) plus the denser k-point grids in this paper. Regarding the molecule’s configuration, our DFT calculations confirm the results of Alfonso,10 i.e., the fact that in its most stable form, the S atom is nearly at an on-top site, one of the H atoms nearly at a bridge site, and the other H atom nearly at a fcc or hcp site. This configuration is shown in Figs. 2(a) and 2(b).

FIG. 2. ([a] and [b]) Configuration of a H$_2$S monomer on Ag(111) optimized using DFT. The red sphere is a S atom, the green spheres are H atoms, and the gray spheres are Ag atoms. Results are obtained using a five-layer slab and 4x4 supercell. (c) Simulated STM image using the Tersoff–Hamann method.

TABLE I. Sizes and separations of protrusions in STM images. The values are all derived from raw data, i.e., with no image processing. The a-b-c notation for the isolated triangular clusters is defined in Fig. 5(c). Uncertainties equal one standard deviation.

<table>
<thead>
<tr>
<th>Identity/environment of the protrusion</th>
<th>Closest separation between protrusions (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Step edge, low coverage</td>
<td>0.45 $\pm$ 0.06</td>
</tr>
<tr>
<td>Step edge, higher coverage, before aging</td>
<td>0.38 $\pm$ 0.05</td>
</tr>
<tr>
<td>Step edge, higher coverage, after aging</td>
<td>0.38 $\pm$ 0.05</td>
</tr>
<tr>
<td>Isolated pinwheel clusters</td>
<td>0.39 $\pm$ 0.07</td>
</tr>
<tr>
<td>Isolated triangular clusters</td>
<td>0.41 $\pm$ 0.02 AB</td>
</tr>
<tr>
<td>Irregular islands with quasihexagonal internal packing</td>
<td>0.40 $\pm$ 0.05</td>
</tr>
<tr>
<td>($\sqrt{37} \times \sqrt{37}$)R25.3° islands</td>
<td>0.43 $\pm$ 0.16</td>
</tr>
</tbody>
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flatness of the potential energy surface, the difference is hard to discern from numerical calculations. Our calculation of the restricted one-dimension minimal energy pathway shows no higher barrier beyond numerical uncertainties, using a \( \text{H}_2\text{O}_{849}\text{H}_{11003}\text{H}_{11003}\text{H}_2\text{O}_{850}\) supercell. Furthermore, studies of various systems—our own and others\(^{40}\) lead us to expect that the real value does not exceed this estimate by more than 10%.

A rough, nudged elastic band calculation of the minimal energy diffusion path yields a diffusion barrier of 0.036 eV, very close to the difference in adsorption energies between the metastable and stable configurations, 0.031 eV. This is a very small diffusion barrier, suggesting that the potential energy surface is quite smooth, and that thermal diffusion at low temperature is not unreasonable. This will be discussed more fully in Sec. IV.

C. \( \text{H}_2\text{S} \) on terraces: Pinwheel and triangular clusters at low \( \theta_{\text{H}_2\text{S}}^{\text{rel}} \)

Under the same conditions where the steps are decorated at low \( \theta_{\text{H}_2\text{S}}^{\text{rel}} \) [Figs. 1(c) and 1(d)], wide terraces also exhibit clusters. These clusters are very uniform, as shown in Fig. 3(a), with a diameter of 3.0 ± 0.2 nm\(^2\). All the clusters exhibit internal protrusions arranged in a chiral pinwheel pattern, which is evident at high magnification in Figs. 3(b) and 3(c). It is faintly visible in the raw image [Fig. 3(b)] but is more pronounced in the differentiated image [Fig. 3(c)]. Within experimental uncertainty, the individual protrusions in the pinwheel clusters have the same separation as the step-edge protrusions, i.e., 0.39 ± 0.07 nm (see Table I). The pinwheel clusters do not transform or coarsen, over a period of tens of hours in UHV at 4.7 K. The coverage of pinwheel clusters under these conditions is 0.0033 nm\(^{-2}\), which is very low compared with the density of Ag atoms, 14.4 nm\(^{-2}\). Thus, it is conceivable that these clusters nucleate at defects or impurities, although if that is the case, the nucleation center exerts no influence on the molecular structure within the cluster.

The \( \text{H}_2\text{S} \) pinwheel clusters can dissociate under certain tunneling conditions. They undergo increasing dissociation in the sequence in Fig. 4, leaving many small fragments finally in Fig. 4(c). The small fragments, which we call triangular clusters, are shown at closer view and are also represented schematically in Fig. 5. Each triangular cluster consists of three unequal protrusions [labeled (a)–(c) in the schematic].

These asymmetric triangular clusters share the same orientation. This was a reproducible observation. In other words, dissociation of a pinwheel cluster always produces
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We do not believe that the parallel alignment of the triangular H$_2$S clusters reflects an artifact in the imaging process itself, i.e., a multiple tip. Morgenstern and co-workers observed (but not identical) triangular features, for ~0.05 bilayers H$_2$O and D$_2$O on Cu(111) and Ag(111) at 17 K. They initially suggested that these features were trimers of H$_2$O molecules. However, upon further investigation and by comparison with DFT, they later identified the feature as a nine-molecule cluster, i.e., a nonamer. The nonamers consist of a hexamer of “bilayer ice” with three additional H$_2$O molecules at the periphery, hydrogen-bonded to the alternating, lower H$_2$O molecules of the hexamer. STM of these triangular features on Ag(111) showed a peak-to-peak distance of 0.56 nm and an internal angle of 60°, with each protrusion at the same height. In contrast, the triangular clusters of H$_2$S represented in Fig. 4 are smaller, the protrusions form an irregular triangle, and the protrusions are not at the same height. For example, the lengths of the sides of the triangle [as defined in Fig. 5(c)] are $\overline{AB}=0.41 \pm 0.02$ nm, $\overline{BC}=0.52 \pm 0.02$ nm, and $\overline{CA}=0.49 \pm 0.03$ nm—all significantly smaller than the 0.56 nm of H$_2$O. Given that the S–H bond of H$_2$S in the gas phase is 40% longer than the O–H bond of H$_2$O (and that the hydrogen bond is weaker), one would not expect a hexamer or nonamer of H$_2$S to be smaller than the corresponding cluster of H$_2$O. Therefore, it is unlikely that our triangular clusters are hydrogen-bonded hexamers or nonamers.

Using DFT, we searched for clusters that might be compatible with the data. Clusters are necessarily stabilized by short-range, attractive interactions. For large intermolecular separations (0.9–6 nm), periodically arranged H$_2$S molecules actually repulse one another since $E_a$ decreases steadily with increasing coverage, from 0.15 eV at $E_a = 1/16$, to 0.085 eV at $E_a = 1/3$. Next examining shorter intermolecular separations, we find a dimer with $E_a = 0.35$ eV, implying an attractive interaction of about $0.35 - (2 \times 0.15) = 0.05$ eV. The distance between the two S atoms is 0.39 nm (0.38 nm in-plane). Its configuration is shown in Fig. 6(a), and its predicted shape in STM is shown in Fig. 6(b).

For a H$_2$S trimer, $E_a$ is around 0.52 eV, implying 0.07 eV total attraction between molecules. We find three trimer configurations that have the same energy, to within a few meV, and these are shown in Figs. 7(a)–7(c). They have several features in common. First, they have two hydrogen bonds (S–H⋯···S bonds) that link the molecules. Second, one molecule in each trimer is similar to an isolated H$_2$S molecule, with its S–H bonds nearly parallel to the surface and the S almost directly above a Ag atom. Third, each of the other two molecules has a S–H bond pointing down toward the surface. Fourth, the isolated-like molecules are always closer to the surface than the downward-pointing molecules, with the S atoms being 0.28–0.29 and 0.38–0.42 nm above the Ag atom plane, respectively. Fifth, the S–S separations in the S–H⋯···S bonds span a wide range, from about 0.34 to 0.57 nm in-plane, or about 0.37–0.57 true distance. Sixth, the S–H⋯···S bond angles are $161°$–$178°$, i.e., the hydrogen bonds are nearly linear. Finally, the predicted STM images are shown in Figs. 7(d)–7(f). In all trimers, the isolated-like molecule appears lower and slightly broader than the other two. In summary, these seven features are common to all the minimum-energy trimers that we have found.

There are also some differences among the trimers found in DFT. In the first two types [Figs. 7(a) and 7(b)], the isolated-like molecule is at the center, and it contributes all the hydrogen to the S–H⋯···S bonds. Both these types of
trimers are nearly isosceles triangles. In the third type, shown in Fig. 7(c), the isolated-like molecule is at one end of the trimer (top of figure) instead of in the center. Of the three trimers, the third type fits the experimental shape best because it is the most irregular. The S–S distances for this trimer, from DFT, are 0.34, 0.36, and 0.54 nm (projected onto the surface plane). These can be compared to the observed values of 0.41 ± 0.02, 0.49 ± 0.03, and 0.52 ± 0.02 nm in the triangular clusters. Only one of the three values matches exactly. Nonetheless, the DFT calculations make it plausible to interpret the triangular clusters as some type of noncyclic H$_2$S trimer.

In trimers (a)–(c), molecules with S–H bonds pointing toward the Ag surface occupy a variety of sites. Referring to Fig. 7, these sites range from semi-on-top—as in the top molecule of trimers (a) and (b), and the middle molecule of trimer (c); to a nearly perfect twofold bridge site—as for the bottom molecule of types (a) and (c); to a nearly perfect threefold hollow site—i.e., the bottom molecule of type (b). This, plus the wide range of S–S separations, indicates that the intermolecular hydrogen bonds give rise to preferred local configurations, but these configurations are quite flexible and adaptable. The isolated-like molecule is more site-specific than the other two because it is always found in an on-top site. In other words, the potential energy surface for the downward-pointing molecules is very smooth indeed.

### D. H$_2$S on terraces: Extended islands at higher $\theta_{\text{H}_2\text{S}}$

Initially after adsorption at $\sim$30 K and at higher $\theta_{\text{H}_2\text{S}}$, the molecules form large and irregularly shaped islands that coexist with many small, isolated protrusions. The islands themselves have protrusions arranged in an irregular hexagonal-like packing, as shown in Fig. 8. The protrusions in these islands have the same nearest-neighbor separation, 0.40 ± 0.05 nm, as the protrusions along the step edges in Figs. 1(c) and 1(d), and in the pinwheel clusters in Figs. 3(b) and 3(c). We hence assign them as H$_2$S molecules that are fixed in place by H-bonding with other molecules. These islands coexist with isolated protrusions on terraces which, as discussed already, are assigned as individual H$_2$S molecules.

With aging at 4.7 K, the features on the terraces change to those shown in Fig. 9. The individual H$_2$S molecules disappear. The islands with quasihexagonal packing of H$_2$S molecules also disappear, indicating that they must be metastable. They are replaced by islands that differ in several respects. One difference is found at the edges of the islands: instead of being irregular, the edges of the new islands sometimes consist of linear segments (facets), as shown in Fig. 9.

Second is the internal structure, which exhibits a $(\sqrt{37} \times \sqrt{37})$ R25.3° unit cell. This is shown in more detail in Fig. 10. The rows of protrusions highlighted by the rectangle in Fig. 10(b) have a lateral separation of 0.43 ± 0.16 nm, similar to that of other features (cf. Table I). Perhaps the most prominent features are dark triangles, which have alternating orientations, as shown in the inset in Fig. 9(b).
Our DFT calculations show that two types of molecules can form upon adsorption at 20 K for low $\theta_{H_2S}$ (pinwheel clusters), and upon adsorption at 30 K for high $\theta_{H_2S}$ (irregular hexagonal islands). In addition, the latter clusters can rearrange over a time scale of about 20 h at 4.7 K into $(\sqrt{37} \times \sqrt{37})R25.3^\circ$ islands, and simultaneously, individual H$_2$S molecules disappear. This requires that individual molecules can diffuse, while clusters can dissociate and/or rearrange at these temperatures, over the corresponding experimental time scales. Is this plausible? The clearest situation may be the aging experiment since there T and $\theta_{H_2S}$ are both constant. From Fig. 1(e), a fair estimate is that a molecule must travel a distance of at least 1 nm during aging, corresponding to about 12 hops for a random walker. Assuming a frequency factor of $10^{14}$ s$^{-1}$, which is toward the high end, allows an estimate of the upper limit of the diffusion barrier, $E_d$, of 0.02 eV. This value would also be consistent with the fact that the adsorbate structures are static on the time scale of STM imaging (2 h) at 4.7 K. As discussed in Sec. III B, we have calculated from DFT that the diffusion barrier is 0.03 eV. Hence, both experiment and DFT support a small barrier of a few tens of meV.

Let us compare this with diffusion of H$_2$O on Ag(111). The upper limit of $E_d$ for H$_2$O on Ag(111) has been estimated, from experimental data, at 0.2 eV. From DFT, an alternate estimate for $E_d$ is given by the difference in adsorption energies between the most-favorable site and next-most-favorable site, as discussed in Sec. III B. This difference is 0.050 eV from the present work, and 0.04 eV from others. If we focus on values of $E_d$ for H$_2$O and H$_2$S derived only from our calculations (to make the comparison as consistent as possible), then the two values of $E_d$ are fairly close: 0.050 and 0.031 eV, respectively. This similarity in $E_d$ parallels the similarity in adsorption energies for isolated H$_2$O and H$_2$S: 0.14 and 0.15 eV, respectively, from our calculations.

### B. Molecular interactions

From the experimental data, the lateral separation of protrusions in clusters on terraces, or along step edges, is consistently close to 0.4 nm (see Table I). The nearest-neighbor S–S separations in crystalline H$_2$S are 0.40 and 0.42 nm. (This is considerably longer than the O–O separation in crystalline H$_2$O, 0.28 nm.) Therefore, we suggest that protrusions separated by 0.4 nm are individual molecules, at least some of which are linked by hydrogen bonds.

Our DFT calculations show that two types of molecules should be expected in H-bonded clusters: Molecules similar to isolated, adsorbed H$_2$S, and molecules with one S–H bond pointing down into the surface. The latter are farther from...
the surface than the former, and are predicted to be higher (brighter) in STM images, regardless of whether these molecules are hydrogen acceptors [as in Figs. 7(a) and 7(b)] or hydrogen donors [Fig. 7(c)]. The molecules with one S–H bond pointing toward the surface have especially low site-specificity. The DFT calculations indicate that clusters of three molecules, linked by two hydrogen bonds, are stable relative to isolated molecules. The triangular clusters observed in experiment (Fig. 5) might be such clusters.

Larger clusters and islands also form. While we are not able to propose specific models at this time, the fact that the potential energy surface is very smooth makes coincidence lattices and metastable structures very plausible. One such extended structure has a \((\sqrt{37} \times \sqrt{37})R25.3^\circ\) unit cell. The same unit cell has been reported for \(\text{H}_2\text{O}\) on Pt(111), and a hydrogen-bonded structure was proposed.\(^{47-49}\) However, the proposed structure does not match the features in our STM images, indicating that the molecular arrangement within the unit cell may be different for \(\text{H}_2\text{S}\) than for \(\text{H}_2\text{O}\). Indeed, one would expect the molecular arrangement to be different, given the large difference in the O–O and S–S bond lengths in the solid ices (0.40–0.42 and 0.28 nm, respectively).

V. CONCLUSIONS

\(\text{H}_2\text{S}\) forms a rich variety of structures on Ag(111) at low temperature and at submonolayer coverage. The molecules decorate step edges, exist as isolated entities on terraces, and aggregate into clusters and islands, under the various conditions of our experiments. The typical molecular separation in the clusters and islands is 0.4 nm, the same as that in crystalline \(\text{H}_2\text{S}\). The potential energy surface for adsorption and diffusion is very smooth.

Note added in proof. We recently became aware of a paper describing a new model for the \((\sqrt{37} \times \sqrt{37})R25.3^\circ\) structure of \(\text{H}_2\text{O}\) on Pt(111) on STM images and DFT calculations.\(^{50}\)

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