Application of scanning tunneling microscopy to study adatom diffusion and lateral interactions: sulfur on Re(0001) at low coverage

J. Dunphy, P. Sautet, D.F. Ogletree, M.B. Salmeron

► To cite this version:

J. Dunphy, P. Sautet, D.F. Ogletree, M.B. Salmeron. Application of scanning tunneling microscopy to study adatom diffusion and lateral interactions: sulfur on Re(0001) at low coverage. *Journal of Vacuum Science & Technology A*, 1993, A11, pp.2145-2152. 10.1116/1.578383 . hal-00006087

HAL Id: hal-00006087

<https://hal.science/hal-00006087>

Submitted on 14 May 2020

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Distributed under a Creative Commons Attribution| 4.0 International License

Application of scanning tunneling microscopy to study adatom diffusion and lateral interactions: Sulfur on Re(0001) at low coverages

J. C. Dunphy

Center for Advanced Materials, Material Science Division, Lawrence Berkeley Laboratory, Berkeley, California 94720 and Department of Physics, University of California, Berkeley, Berkeley, California 94720

P. Sautet^{a)}

Department of Physics, University of California, Berkeley, Berkeley, California 94720

D. F. Ogletree and M. B. Salmeron

Center for Advanced Materials, Material Science Division, Lawrence Berkeley Laboratory, Berkeley, California 94720

Scanning tunneling microscopy (STM) imaging was applied to study coverages of less than 0.3 monolayers of sulfur on a rhenium(0001) surface. At coverages near one quarter monolayer sulfur forms a $p(2 \times 2)$ ordered overlayer. Below this coverage islands of $p(2 \times 2)$ ordered sulfur form, indicating an attractive interaction between sulfur atoms at twice the Re lattice spacing. Between these islands the STM images appear noisy. A correlation technique was applied to these images which showed that this noise was actually due to sulfur atoms diffusing on the same time scale as the STM image was acquired. The pair interaction energy between sulfur atoms at twice the Re lattice distance was determined by fitting the results of this correlation technique to an Ising model. The mobility of sulfur on the surface was further investigated by coadsorbing CO. This was found to compress the dilute sulfur overlayer into an ordered structure usually only seen at higher coverages. The transformation was observed by both low energy electron diffraction and STM. An upper limit for the energy required to compress the overlayer was extracted from the adsorption energy of CO. The energy barrier to diffusion was estimated from the average residence time of the diffusing sulfur atoms. These energies compare well with an extended Hückel calculation.

I. INTRODUCTION

Since its development, STM has mainly been used to study surfaces which are static. At the atomic scale most important chemical and physical properties of surfaces occur at rates faster than the time scale of STM imaging, which is limited by the time required to mechanically move a probe over the surface. However in some systems phase changes, chemical reaction, or diffusion occur at rates slow enough for study by STM. For instance, it was possible to directly observe by STM the reconstruction of Cu(100) which occurs upon exposure to oxygen.¹ The chemical etching of a (7×7) reconstructed Si(111) surface by oxygen at high temperatures was observed.² On some systems the rate of diffusion is slow enough so that the hopping of atoms can be observed directly from the changes between images taken sequentially.³⁻⁶ Diffusion occurring at rates faster than the time between two images has been observed in a number of systems.^{3-5,7,8} Since interpretation of the images is complicated by the possibility that the state of the surface may change between the acquisition of two image pixels, few have tried to derive quantitative information from these images. Binnig *et al.* have attempted to measure a diffusion constant of oxygen on nickel from "flicker noise" or spikes in the STM tunneling current which they

interpreted as due to atoms diffusing under the tip.⁷ M. Poensgen *et al.* calculated the density and diffusion rate of kinks from the "frizzling" of steps in their STM images caused by step diffusion.⁸

Here STM is applied to study diffusion and reordering of sulfur on rhenium(0001) which occurs at a rate comparable to time scale of STM imaging. This system has been studied previously by both STM^{9,10} and low energy electron diffraction (LEED).^{11,12} Dynamical LEED calculations of sulfur on metal surfaces¹³ have shown that at low coverages sulfur bonds at the highest coordination site. On rhenium, a dynamical LEED analysis of the $p(2 \times 2)$ structure¹² has shown that the binding site is the threefold hcp hollow site. Below one quarter monolayer sulfur forms a $p(2 \times 2)$ structure. Above one quarter monolayer STM observations show that some of the sulfur coalesces into trimers that coexists with the $p(2 \times 2)$ ordered sulfur. As the coverage is increased further the trimers order into a structure with $(3\sqrt{3} \times 3\sqrt{3})R30^\circ$ periodicity.^{9,10}

II. EXPERIMENT

The experiments were performed in a standard surface science UHV chamber with a base pressure of 2×10^{-10} Torr. The chamber was equipped with Auger electron spectroscopy (AES), LEED, an Ar^+ sputtering gun, and the STM. The design of the STM is described elsewhere.¹⁴ Mechanically cut Pt/Rh wire was used for tips. The single

^{a)}Permanent address: Laboratoire de Chimie Théorique, ENS Lyon 46, allée d'Italie, 69464 Lyon, Cedex 07 France and Institut de Recherche sur la Catalyse 2, Avenue A. Einstein, 69626 Villeurbanne Cedex France.

(a)

(b)

(c)

crystal sample could be heated by electron bombardment and cooled by placing the sample holder in contact with a copper block cooled by liquid nitrogen.

The rhenium crystal was cleaned in UHV by Ar^+ bombardment and cycles of heating to 1000°C in the presence of 5×10^{-7} Torr of oxygen. This treatment removed sulfur and carbon contamination. The oxygen was removed by heating the crystal to approximately 1800°C . Once the crystal was clean as verified by AES, it was exposed to H_2S

(d)

(e)

FIG. 1. STM images and models of two structures of sulfur on $\text{Re}(0001)$. The STM images were Fourier filtered to remove noise. (a) A $40 \text{ \AA}$ square STM constant height image of a complete $p(2 \times 2)$ overlayer. (b) A model of the $p(2 \times 2)$ overlayer showing the two types of hollow sites and common separations of hollow sites on the lattice. (c) A $45 \text{ \AA}$ square STM constant height image containing a mixture of the $p(2 \times 2)$ overlayer (atoms appear as small triangles) and the trimers (larger bright triangles) which form the unit structure of the $(3\sqrt{3} \times 3\sqrt{3})R30^\circ$ overlayer. (d) An $85 \text{ \AA}$ square STM image of the $(3\sqrt{3} \times 3\sqrt{3})R30^\circ$ overlayer. (e) A model of the $(3\sqrt{3} \times 3\sqrt{3})$ overlayer on which the unit cell is marked. Each unit cell contains four sulfur trimers.

at 5×10^{-8} Torr for 2–10 min while heating to approximately 700°C . H_2S gas decomposes on the surface, leaving behind sulfur. The crystal was then cooled to room temperature. The large scale ordering of the sulfur overlayer was determined by LEED, and the sulfur coverage determined by AES. If the coverage was higher than desired, some sulfur could be desorbed from the surface by heating to approximately 1000°C for several seconds. Occasionally, annealing for a short period of time at 600°C was

necessary to obtain an ordered LEED pattern. At coverages less than one tenth of a monolayer the LEED pattern was (1×1) . As the coverage was increased to one quarter monolayer (2×2) overlayer spots appeared and became more intense and sharp. Finally, well above one quarter of a monolayer the LEED pattern had $(3\sqrt{3} \times 3\sqrt{3})R30^\circ$ symmetry.

In the CO coadsorption experiments, a background pressure of CO of 5×10^{-9} Torr was produced in the chamber by introducing CO through a leak valve. The LEED pattern of the surface was observed and STM images obtained in this background pressure.

III. RESULTS

A. Sulfur diffusion

STM images of the surface with a coverage of one quarter monolayer sulfur and a $p(2 \times 2)$ LEED pattern show a triangular lattice of maxima. An example of such an image is shown in Fig. 1(a). Within the $\pm 10\%$ accuracy of the STM piezoelectric calibration, the maxima in these images are separated by a distance of twice the Re lattice constant a consistent with a $p(2 \times 2)$ overlayer. A model of this structure is shown in Fig. 1(b). At higher sulfur the STM shows that the surface is covered by trimers of sulfur at nearest neighbor distances intermixed with the $p(2 \times 2)$ ordered sulfur. The trimers appear brighter than the individual sulfur atoms as shown in Fig. 1(c). As the sulfur coverage is increased further the trimers order into a structure with a $(3\sqrt{3} \times 3\sqrt{3})R30^\circ$ LEED pattern. A STM image of this surface and model are shown in Figs. 1(d) and 1(e). On clean surfaces no corrugation due to the underlying Re lattice could be detected, either directly or in the Fourier transform of the image. The corrugation of transition metals is generally very small, of order a few hundredths of an angstrom, and probably below the noise level of our STM.

Point defects always appeared as missing maximum, allowing the maxima in the STM images in Fig. 1 to be interpreted as being at location of the sulfur atoms. Sometimes the sulfur atoms in the $p(2 \times 2)$ structure appeared as triangular or Y-shaped maxima. We have been able to attribute the changes in image contrast to changes in the structure of the STM tip, and connect each image appearance to a particular structure of the tip.¹⁵ These tip changes occurred randomly and at intervals varying from a few seconds to several minutes. Our image acquisition time was typically 20 s in the present experiments.

At coverages below one quarter of a monolayer, the surface was covered with islands of the $p(2 \times 2)$ structure such as the one shown in Fig. 2. The islands varied in size from approximately four to twenty atoms. The presence of $p(2 \times 2)$ islands at very low sulfur coverages indicates the interaction between single sulfur atoms, mediated by the substrate, is attractive at a distance of twice the rhenium lattice constant ($2a$) and less attractive or repulsive at nearest neighbor (a) and second nearest neighbor ($\sqrt{3}a$) distances [Fig. 1(b)].

FIG. 2. A 60 Å square FFT filtered STM image of sulfur islands which form at low coverage. Some atoms at the edge of the island appear to have a lower corrugation than those at the center. This is explained by the reduced residence time of the sulfur atoms at the edge of the island.

There are two unusual features of the images of $p(2 \times 2)$ sulfur islands. First, in smoothed images such as Fig. 2 the corrugation of the sulfur atoms making up the islands is not constant. Atoms near the center of the islands have the highest apparent corrugation, while some of those near the edge have a lower corrugation. Secondly, the raw data images such as Fig. 3 contains a large amount of apparent noise in the areas between the islands. This noise is primarily made up of horizontal "frizzes" which extend approx-

FIG. 3. An approximately 20 Å x 20 Å unfiltered STM image showing the raw data image of an area between (2×2) islands. Horizontal frizzes in the image are the fraction of a sulfur atom which is imaged before it moves to another site.

imately the width of an atom in the horizontal direction, but only one to three STM scan lines in the vertical direction.

These features of the images may be explained as an effect of sulfur atoms moving across the surface at a time scale shorter than that required to produce an STM image. The STM tip rasters across the surface in the horizontal direction while scanning slowly in the vertical direction. Therefore, adjacent pixels in the horizontal direction are acquired much closer together in time than adjacent pixels in the vertical direction. If the diffusion rate is not too rapid, a diffusing atom has much less probability to move while it is being scanned over in one line than it does between scan lines. The images of atoms are, therefore, complete in the horizontal direction, but not in the vertical direction. These incomplete images of atoms are shaped like horizontal dashes. Images with features of this type have been observed before,^{3-5,8} and they were also interpreted as diffusing atoms or molecules.

The decrease in the corrugation of some of the atoms at the edge of islands seen in smoothed images can be explained as a result of diffusion. The Fourier filtering used to remove noise from the images spatially smooths the image, blending each scan line into the adjacent ones. If an atom is only present in half of the lines in the raw data, it will appear in all lines in the filtered image, but with a lower corrugation. Atoms at the center of islands are blocked from moving by their neighbors. In contrast, atoms located at the edge of islands are free to move away from the island. At some of these sites an atom is not present in all of the STM scan lines and therefore it appears with a lower corrugation.

The observed diffusion is not caused by the presence of the STM tip. At the gap used in imaging, approximately 50 mV, theoretical calculations of the tunneling gap show that the tip is six Angstroms from the sulfur atoms on the surface.¹⁵ This distance is too long for any direct chemical bond between the sulfur atoms and the tip end atom. A comparison of two images taken simultaneously, one by the tip scanning to the right and the other scanning to the left, shows that they are identical. If the tip were pushing the sulfur atoms on the surface, or catalyzing their diffusion, images produced by the tip moving in opposite directions would not be equivalent.

B. CO coadsorption

During the investigation of sulfur diffusion at low coverages it was found that the $p(2 \times 2)$ ordering of the surface at lower coverages was unstable when exposed to CO. Figure 4 shows a sequence of LEED patterns which were taken over a period of time during which the surface was exposed to CO. First the surface was shown to be stable for several hours in the absence of CO. No significant change in the LEED pattern occurred during this time. CO at a pressure of 5×10^{-9} Torr was then introduced into the chamber. Over five minutes the $p(2 \times 2)$ spots on the LEED pattern faded and lines connecting the spots formed in a six pointed star pattern [Fig. 4(b)]. This pattern eventually faded, leaving the rhenium (1×1) spots and a dif-

FIG. 4. Evolution of the LEED pattern of the S covered Re surface during exposure to 5×10^{-9} Torr of CO. (a) Initial $p(2 \times 2)$ LEED pattern; (b) After 5 min of CO exposure. (c) After 10 min; (d) After 15 min the LEED pattern is diffuse with $(3\sqrt{3} \times 3\sqrt{3})R30^\circ$ spots; (e) The LEED pattern after 35 min; (f) After annealing for several seconds at 800 K to desorb the CO the LEED pattern returns to $p(2 \times 2)$.

fuse background. After 15 min a diffuse $(3\sqrt{3} \times 3\sqrt{3})R30^\circ$ pattern appeared [Figs. 4(c) and 4(d)]. No further changes in the LEED pattern occurred [Fig. 4(e)] despite continued exposure to CO. Heating the surface to 800 K for several seconds reversed the transition back to a $p(2 \times 2)$ pattern as shown in Fig. 4(f). The sulfur coverage on the surface, as measured by AES, was unchanged during the transition.

The speed of the transition between the $p(2 \times 2)$ and the $(3\sqrt{3} \times 3\sqrt{3})R30^\circ$ LEED patterns depended on both sulfur coverage and the CO pressure in the chamber. At lower sulfur coverages and higher pressures, the surface re-ordered more quickly. At coverages very close to one quarter of a monolayer (a full coverage of 2×2) the structure was more stable.

The same transition process was studied by STM. After atomic resolution was attained on a $p(2 \times 2)$ ordered surface, CO was leaked into the chamber at a pressure of 1×10^{-8} Torr and the surface imaged while exposed to CO. As has been reported by others¹⁶ CO molecules were not resolved by the STM. However the effect of the CO on the surface was observed. Initially the $p(2 \times 2)$ overlayer appeared to have few defects. However as time progressed an increased number of defects in the sulfur overlayer were found. These defects regions consisted of what appeared to

FIG. 5. A 55 Å square FFT filtered STM constant height image of the $p(2 \times 2)$ overlayer after exposure to CO. Part of the area in this image still has $p(2 \times 2)$ ordered sulfur. The other part is a combination of apparently clean Re where CO is adsorbed and some trimers of sulfur atoms (brighter spots) which are the units that make up the $(3\sqrt{3} \times 3\sqrt{3})R30^\circ$ overlayer normally only seen at higher sulfur coverages.

be mixtures of trimers of sulfur and apparently clean areas of the surface. An example of such a defect is shown in Fig. 5. By counting atoms and trimers of atoms the average coverage of sulfur on the surface surrounding these defects was found to be within 10% of the original quarter monolayer. Only the ordering of the sulfur has changed.

IV. DISCUSSION

A. Correlation function

While information on the diffusing sulfur is contained in the STM images, it is difficult to see this directly. As some of the sulfur adatoms are moving at a rate faster than the STM imaging, it is impossible to know the exact location and motion of all atoms in the image. However, the average positions of atoms relative to each other is contained in the image data. A spatial pair correlation function was used to extract this information. This function is the average product of the tunnel current value at pixels in an image or part of an image separated by a particular vector,

$$C(\mathbf{r}, t) = \frac{1}{N} \sum_{\mathbf{r}_0, t_0} I(\mathbf{r}_0, t_0) I(\mathbf{r}_0 + \mathbf{r}, t_0 + t). \quad (1)$$

N is the number of products in the sum, and $I(\mathbf{r}, t)$ is the current value at a pixel in the image at position $\mathbf{r}$ at time t . In a STM image, t is a function of $\mathbf{r}$ since it is only possible for the tip to be at one point in the image at a time. The value of this average product or correlation function is a measure of how well pixels at a particular distance and time separation are correlated. On a well ordered surface, pixels separated by vectors close to the lattice vectors of the overlayer should be well correlated, because the overlayer

FIG. 6. A $70 \times 70 \text{ Å}^2$ unfiltered STM image (A) of diffusing sulfur atoms and the corresponding correlation image (B). The correlation image shows that the diffusing sulfur is a lattice gas which maintains a local $p(2 \times 2)$ order over several lattice distances.

atoms are well correlated at this distance. This spatial correlation function can be represented as a two dimensional map or image which we will call a correlation image.

One would expect that the correlation function has a maximum at each $\mathbf{r}$ which is a lattice vector separating two hcp hollow sites. The size of this maximum is proportional to the probability of overlayer atoms being separated by this lattice vector at the time separation between which the two pixels were acquired. For a STM image, one is limited to a given t for each vector $\mathbf{r}$, but since lattice vectors rotated by 60° are equivalent, several time separations for each lattice vector are available in the data.

The correlation function was calculated for a number of experimental images and sections of experimental images. A representative correlation image, together with the original data, is shown in Fig. 6. When an image with many of the frizzes of diffusing atoms is used as input, the correlation image shows that the surface is unexpectedly well ordered. The image shows clearly that the sulfur is diffusing between low energy sites as a lattice gas. The correlation image has maxima on a $p(2 \times 2)$ lattice, not the (1×1) lattice of hcp hollow sites that would be expected if the sulfur atoms were not interacting. The diffusing sulfur atoms are most likely to be separated by lattice vectors of the $p(2 \times 2)$ lattice, even when they are separated by many lattice constants. At small odd multiples of a there are minima in the correlation plot, signifying that it is unlikely to have atoms separated by this distance. The first of these minima is the lowest, due to the repulsive interaction of sulfur atoms at this short distance. Although the atoms are diffusing, they maintain a local $p(2 \times 2)$ order which extends at least several unit cells over the surface. This order is maintained even on parts of the surface where there appear to be no stationary sulfur atoms.

The size of the maxima in the correlation image, as a function of their position away from the center, is a direct measure of the probability of the atoms being spaced by that particular lattice vector. The experimental curve in Fig. 7 shows a cross section through several of the maxima of a correlation image. The central maximum is the corre-

FIG. 7. Cross section of a correlation image and the expected cross section in the two limiting cases of no interaction (dashed line) and a large interaction (dotted line) between sulfur atoms. In both cases the sulfur atoms are assumed to be only on a $p(2 \times 2)$ overlayer lattice as found experimentally. The experimental cross section is between the two limits.

lation of each atom with itself. Each atom of the surface contributes to this peak, and thus its height is proportional to the coverage. Peaks at a distance of $2a$ receive a contribution from each pair of atoms separated by $2a$ in the image. Their height is proportional to the probability of $2a$ neighbors on the overlayer lattice. Peaks at large distances represent the probability of finding two atoms at a large distance from each other at the same time. Since atoms far from each other should not be well correlated, and since the probability of each atom being present is proportional to the coverage, this peak height is proportional to the square of the coverage.

The strength of the interaction between sulfur atoms on the surface determines the height of these peaks as a function of distance. If there were no interaction between overlayer atoms, the probability of pairing at multiples of $2a$ would be the square of the coverage for any separation distance, as indicated in the dashed curve in Fig. 7. If there is an attractive interaction between atoms separated by this distance, one would expect an increased number of pairs. In the limiting case in which the attraction is so strong that all the sulfur atoms are on islands, a cross section of the correlation image would appear like the dotted line in Fig. 7. The actual experimental data is in between the two limits indicating a weak attractive interaction.

B. Ising model

The simplest possible model for the interaction between the diffusing sulfur atoms is an Ising model.¹⁷ In this model, atoms are only allowed to be on the sites of a lattice, in this case the $p(2 \times 2)$ overlayer lattice. The total energy is the sum of a pair interaction energy and a chemical potential energy for each atom. The total pair interaction energy is simply the product of a pair interaction energy E_{12} and the number of pairs separated by a distance of $2a$. The chemical potential energy term controls the equilibrium coverage.

FIG. 8. Graph of the results of Ising model and experimental data. The horizontal axis represents the sulfur coverage or the ratio of the number of sulfur atoms to first layer rhenium atoms. The vertical axis is the frequency of formation of pairs of atoms at the $2a$ distance. This axis is normalized to the square of the coverage such that the result is one in the zero interaction energy case in which pairs form randomly. The results of the Ising model are displayed as contours of constant interaction energy spaced at intervals of $0.25kT$. The experimental results based on pair correlations of images with different sulfur coverages are shown as dots. The five experimental points at low coverage follow these contours, but the contours fall below the two higher coverage points due to inaccuracies in the theoretical model at high coverage. From the fit of the five low coverage experimental points to the Ising model, the attractive interaction energy between sulfur atoms at the $2a$ distance was determined to be 24 ± 5 meV.

This model may be solved analytically using the Weiss molecular field approximation.¹⁷ Since the $\text{Re}(0001)$ surface is a triangular lattice, the calculation was done on a group of three overlayer nearest neighbor sites. All the other nearest neighbors of these atoms on the overlayer were taken to have the average occupation. The frequency of pair formation was calculated as a function of average coverage and pair interaction energy E_{12} , and normalized to the non-interacting case where this frequency is proportional to the square of the coverage.

The results of this model are shown in a contour graph, Fig. 8, of pair interaction energy as a function of coverage and normalized pair frequency. The experimental results from the correlation function are also shown as points. From the fit of the experimental results to the theoretical curves, the pair interaction energy for sulfur atoms is found to be -24 ± 5 meV.

There are several limitations to the mean field approximation Ising model and the way in which the data is fitted to it. The error bars on the data are wide because there are statistical fluctuations due to the limited size of the STM images. Only the interaction at the $2a$ distance is considered in the model and the atoms are not allowed to come closer than $2a$ to each other. While, at higher coverages, shorter range and many body interactions must be considered to explain the variety of structures formed by sulfur on rhenium,⁹ the atoms are widely separated at the low coverage of the $p(2 \times 2)$ structure so interactions beyond the nearest neighbor are not likely to be significant.

The molecular field approximation assumes that the overlayer is homogeneous which is inaccurate when large islands form in the overlayer. This approximation is valid

at low coverages and energies, but causes an underestimate of the frequency of pairs at higher energies and coverages. An exact solution of the Ising model,¹⁸ which is possible only at a coverage of one eighth of a monolayer, shows that islands will form in the overlayer for attractive interactions above 28 meV at room temperature. Since this energy is very close to the interaction energy determined by this experiment, the model is not accurate for this system at coverages above approximately one eighth of a monolayer. Due to this limitation of the theoretical model, the two highest coverage experimental points do not fit well with the model and were not used in the determination of the interaction energy.

C. Diffusion behavior

The residence time for atoms which are not attached to an island can be determined from the shape of the central maxima in the correlation images or from the size in the y -scan direction of the dashes in the raw data. This turns out to be approximately two STM scan lines or 100 ms. An estimate of the energy barrier to diffusion can be calculated from this measurement. Since the residence time was measured at only one temperature, the exact pre-exponential term cannot be determined. Using a standard pre-exponential of 10^{14} s^{-1} the mean number of diffusions per second between two sites is given by the Einstein equation:¹⁹

$$n = 10^{14} \exp\left(-\frac{E}{kT}\right). \quad (2)$$

Taking into account the number of possible sites an atom may diffuse to, this formula gives a diffusion energy barrier of $0.79 \pm 0.1 \text{ eV}$. Since the residence time and pre-exponential factor determine E through a logarithmic dependence, errors of one order of magnitude in these parameters imply only a 0.06 eV change in E .

This result compares well with the results of an extended Hückel calculation. In this calculation a three layer thick seventy atom cluster of rhenium atoms was used as a substrate. The height of the sulfur atoms was such that their distance to the nearest rhenium atom was set equal to the sum of the covalent radii. A correction was made for the effect of the edges of the cluster.²⁰ The relative energy of sulfur atoms adsorbed at hcp and fcc hollow sites, the top site, and a bridge site were calculated. Relative to the hcp hollow site, the fcc hollow had an energy 0.1 eV, the bridge site had an energy 0.74 eV, and the top site energy was 1.6 eV. Therefore, the lowest energy path between two hcp hollow sites is over a bridge site to an fcc hollow and then over a second bridge site. The highest energy along this path is at the bridge sites. The energy of these sites (0.74 eV) compares quite well to the experimentally determined energy barrier.

D. CO induced restructuring mechanism

As both LEED and STM results show, coadsorption of CO onto the sulfur covered surface causes a reordering of the sulfur overlayer to produce sulfur trimers in which the

atoms occupy nearest neighbor sites. Sulfur is known to block the adsorption of CO on Re even in the relatively dilute $p(2 \times 2)$ overlayer.¹³ In order for CO to adsorb onto the surface, the sulfur overlayer must be compressed, opening up areas at which CO may adsorb. The large dark area in Fig. 7 may be interpreted an area where CO has adsorbed compressing the sulfur into trimers.

The compression of the sulfur overlayer by CO is surprising as our early correlation function results showed that the interactions between the sulfur atoms at a distance less than $2a$ is repulsive. The correlation function of the diffusing sulfur had a deep minima surrounding the central peak indicating that sulfur atoms were rarely separated by these distances as they diffused over the surface. At higher coverages, however, the sulfur does form trimers. Clearly the energy to overcome the first nearest neighbor repulsion is provided by the sulfur adsorption energy. A similar mechanism must occur when CO is adsorbed on the surface. The adsorption energy of CO must be high enough to provide the energy to overcome sulfur repulsion allowing them to form trimers. As the adsorption energy of CO is much less than that of sulfur, it will provide an upper bound to the energy required to form trimers. We can analyze the energy balance of the reordering induced by CO based on known energies.

The adsorption energy of CO on the Re surface has been measured to be 1.0 eV per molecule.²¹ The maximum saturation coverage of CO at low pressures is 0.49 monolayers,²² or approximately one CO molecule per two Re surface layer atoms. Therefore, the energy gained by freeing a Re surface atom of sulfur so that it can adsorb CO is 0.5 eV. In the $p(2 \times 2)$ structure there are 4 surface Re atoms per sulfur while in the $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure there are only 2.25 surface Re atoms. Therefore each sulfur atom moved to the more compact structure frees 1.75 Re surface atoms releasing 0.87 eV of energy when CO adsorbs on this area. If the reduction in surface free energy per sulfur atom required to form a trimer is less than this value, the process will be energetically favorable. Based on this model, we can give a maximum decrease in adsorption energy per sulfur atom of trimer formation of 0.87 eV. This is larger than the energy derived from the sulfur thermal programmed desorption (TPD) data of Kelly *et al.*¹¹ They find a desorption peak which appears at a coverage above one quarter monolayer and has an adsorption energy 0.56 eV less than the sulfur desorption peak from the $p(2 \times 2)$ structure.

An extended Hückel calculation, similar to the one described previously, was used to determine the energy of formation of trimers on the surface. The difference in energy between sulfur atoms adsorbed separately and in a trimer was calculated. It was found to be 1.1 eV. This is slightly higher than the maximum difference found in our experiments of 0.87 eV. The higher value may be explained by the neglect of Re restructuring in our Hückel calculation. Relaxations of the real surface would be expected to lower the energy.

Similar effects of the interaction between adsorbates and coadsorbed CO have been observed in the case of $p(2 \times 2)$

sulfur²³ and $p(2 \times 2)$ Se²⁴ on Pt(111). In both these systems CO coadsorption compressed the other adsorbate into a higher coverage structure.

V. CONCLUSIONS

We have studied the dynamics of sulfur ordering on Re(0001) surface with the STM. At low coverages sulfur diffuses across the Re surface. Even though the time scale of the diffusion was small compared to the rate of imaging, we were able to use a spatial correlation function to extract information from the STM images. The sulfur was found to diffuse as a lattice gas between hcp hollow sites while maintaining $p(2 \times 2)$ order. Fitting the results to an Ising model we determined that there is an attractive interaction of 24 ± 5 meV between pairs of sulfur atoms separated by $2a$ on the surface. Sulfur displacement inside the $p(2 \times 2)$ islands could be induced by CO coadsorption. The adsorbed CO compressed the sulfur overlayer, effectively increasing the local coverage. The sulfur overlayer restructured to form first trimers and then trimers ordered into a $(3\sqrt{3} \times 3\sqrt{3})R30^\circ$ structure which is usually only seen at higher sulfur coverages.

ACKNOWLEDGMENTS

This work has been supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Science Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098. P. S. acknowledges the support of NATO.

¹F. Jensen, F. Besenbacher, E. Lægsgaard, and I. Stensgaard, Phys. Rev. B **42**, 9206 (1990).

²A. Feltz, A. U. Memmert, and R. J. Behm, Chem. Phys. Lett. **192**, 271 (1992).

³R. M. Feenstra, A. J. Slavin, G. A. Held, and M. A. Lutz, Phys. Rev. Lett. **66**, 3257 (1991).

⁴Chr. Günther and R. J. Behm (unpublished).

⁵V. M. Hallmark, S. Chiang, J. K. Brown, and Ch. Wöll (preprint).

⁶E. Ganz, S. K. Theiss, I. S. Hwang, and J. Golovchenko, Phys. Rev. Lett. **68**, 1567 (1992).

⁷G. Binnig, H. Fuchs, and E. Stoll, Surf. Sci. Lett. **169**, L295 (1986).

⁸M. Poensgen, J. F. Wolf, J. Frohn, M. Giesen, and H. Ibach, Surf. Sci. Surf. Sci. **274**, 430 (1992).

⁹R. Q. Hwang, D. M. Zeglinski, D. F. Ogletree, A. Lopez Vazquez-de-Parga, G. A. Somorjai, and M. Salmeron, Phys. Rev. B **44**, 1914 (1991).

¹⁰D. F. Ogletree, R. Q. Hwang, D. M. Zeglinski, A. Lopez Vazquez-de-Parga, G. A. Somorjai, and M. Salmeron, J. Vac. Sci. Technol. A **9**, 886 (1991).

¹¹D. G. Kelly, A. J. Gellman, M. Salmeron, G. A. Somorjai, V. Maurice, M. Huber, and J. Oudar, Surf. Sci., **204**, 1 (1988).

¹²D. Jentz, G. Held, M. A. VanHove, and G. A. Somorjai (to be published).

¹³J. M. MacLauren, J. B. Pendry, P. J. Rous, D. K. Saldin, G. A. Somorjai, M. A. Van Hove, and D. D. Vvedensky, *A Handbook of Surface Structures* (Reidel, Dordrecht, 1987).

¹⁴D. M. Zeglinski, D. F. Ogletree, T. P. Beebe, Jr., R. Q. Hwang, G. A. Somorjai, and M. Salmeron, Rev. Sci. Instrum. **61**, 3769 (1990).

¹⁵J. C. Dunphy, D. F. Ogletree, M. Salmeron, P. Sautet, and M.-L. Bocquet, Ultramicroscopy, **42-44**, 490 (1992).

¹⁶T. Gritsch, D. Coulman, R. J. Behm, and Ertl, Phys. Rev. Lett. **63**, 1086 (1989).

¹⁷X. Reif, *Statistical and Thermal Physics* (McGraw-Hill, New York, 1965), pp. 428-434.

¹⁸J. Stephenson, J. Math. Phys. **5**, 1009 (1964).

¹⁹A. Zangwill, *Physics at Surfaces* (Cambridge University Press, Cambridge, 1988), p. 362.

²⁰P. Sautet and J.-F. Paul, Catal. Lett. **9**, 245 (1991).

²¹J.-W. He and D. W. Goodman, J. Phys. Chem. **94**, 1502 (1990).

²²R. Ducros, J. Fusy, J. Jupille, P. Pareja, and S. Tatarenko, Appl. Surf. Sci. **29**, 179 (1987).

²³B. J. McIntyre, J. C. Dunphy, D. F. Ogletree, and M. Salmeron (to be published).

²⁴M. Kiskinova, A. Szabo, and J. T. Yates, Vacuum **41**, 82 (1990).