Thermal dissociation of chemisorbed oxygen molecules on Ag(110): an investigation by scanning tunnelling microscopy

Thermal dissociation of chemisorbed oxygen molecules on Ag(110): an investigation by scanning tunnelling microscopy

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Abstract
The thermal dissociation of oxygen molecules on Ag(110) was studied by means of scanning tunnelling microscopy. At temperatures around 170 K a fraction of the molecules dissociate to form pairs of O atoms on the unreconstructed surface. The atoms lie in the trenches between the close-packed Ag rows; the intrapair distance is two lattice constants. The O atoms are very reactive with CO at temperatures as low as 70 K. The preferential orientation of the pairs in the [001] direction contrasts with the finding in a previous study (Hahn J R, Lee H J and Ho W 2000 *Phys. Rev. Lett.* **85** 1914) that electron-induced dissociation exclusively leads to [1$\bar{1}$0]-oriented pairs. The trajectories of thermal and electron-induced dissociations must therefore be different. In the temperature range of the dissociation, several additional oxygen features occur on the surface. These include unreacted O_2 molecules, the first nuclei of the added-row reconstruction, and two unidentified O-induced structures.

1. Introduction

Because of the many atomic degrees of freedom, the dissociation of a molecule on a surface is a complex process. Even for a simple scenario like the dissociation of O_2 on a metal surface, a complete multidimensional description of the reaction path is not yet available. Some new insight was provided by scanning tunnelling microscopy (STM), by resolution of the molecular fragments after the dissociation process was completed and the fragments had accommodated on the surface. The distance between the fragments and the direction along which they occur obviously contain information about the atomic trajectories. Such data exist e.g. for the dissociation of oxygen molecules on Al(111) [1–3], Pt(111) [4,5], and Cu(110) [6].

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In this contribution we report on a STM investigation of the O_2 dissociation on Ag(110). The interaction of oxygen with silver surfaces has already been investigated in some detail; the work was motivated by the interest in silver-catalysed oxidation reactions like the formation of ethylene epoxide [7]. The following, overall reaction sequence is generally accepted for the Ag(110) surface [8]. At $T < 40$ K, O_2 physisorbs. At higher temperatures a chemisorbed molecular state is populated, which dissociates or desorbs at $T > 150$ K. Adsorbed O atoms destabilize the Ag(110) surface at temperatures exceeding $\sim$200 K. A reconstruction is formed that consists of –Ag–O– added rows running along the [001] direction [9–11].

Information about the O_2 dissociation process itself is obscured by a number of peculiarities of the Ag(110) surface. Because of the narrow temperature range between the dissociation of the chemisorbed molecules and the formation of the reconstruction, it has not been entirely clear whether these are actually separate processes, i.e., whether the molecules can dissociate without simultaneously inducing the reconstruction. High-resolution electron energy-loss spectra (HREELS), recorded during annealing of an O_2-covered surface [12, 13], showed that the specular intensity dropped sharply at around 150 K and recovered only at $\sim$200 K. The effect was interpreted as a surface disordering resulting from the dissociation of the molecules. The HREELS data did not, however, allow a decision to be made on whether this disordered state was restricted to the adsorbate layer or already involved a local reconstruction. Another complication was revealed by experiments in which, after dissociative O_2 adsorption at 180 K, a CO molecular beam was directed on the Ag(110) surface [14, 15]. CO_2 production could be detected, but the reaction rate showed an unexpectedly complex behaviour as a function of exposure. It was concluded that two atomic oxygen species with slightly different reactivities existed on the surface. Both species appeared to be different from the oxygen atoms in the added-row reconstruction, that only become reactive at $T \simeq 250$ K [16].

The development of a model for the dissociation is particularly hindered by the conflicting evidence about the orientation of chemisorbed O_2. It is mostly assumed that the trajectories of the O atoms during dissociation follow the direction predetermined by the molecular axis. For the Ag(110) surface it had been presupposed in most previous studies that the O_2 molecule adsorbs in the trenches between the close-packed atomic rows, with the molecular axis parallel to the surface and parallel to the atom rows, i.e. having a [1$\bar{1}$0] azimuthal orientation. Evidence for this adsorption geometry came from photoemission [8] and near-edge x-ray-absorption fine-structure (NEXAFS) [17] experiments, and from cluster calculations [18]. By contrast, electron-stimulated-desorption-ion angular distribution (ESDIAD) [19] experiments indicated that the molecule was oriented perpendicularly to the atom rows (i.e. along the [001] azimuth). Recent density functional theory (DFT) calculations [20, 21] revealed energy minima with almost equal energies for both of these azimuthal orientations. A HREELS study indeed identified two chemisorbed molecular states [22], and in a low-temperature STM study [23] observation of two different chemisorbed O_2 species was reported.

In this latter investigation the molecules could be induced to dissociate in a controlled way by the current from the STM tip. It was found that only one of the two molecular species dissociated under these conditions. After applying voltage pulses with the tip over the molecule, pairs of O atoms were detected that were exclusively oriented along [1$\bar{1}$0]. It was thus concluded that the reactive molecular state must have had this orientation before the dissociation. The other molecular species could be induced to rotate into the reactive species, likewise by means of the tunnelling current.

We have investigated the thermal dissociation of the O_2 molecules. We find that the distribution of the O atoms is different from that resulting from the current-induced dissociation. Furthermore, other species were identified that may account for some of the previously observed complications in the Ag(110)/oxygen system.
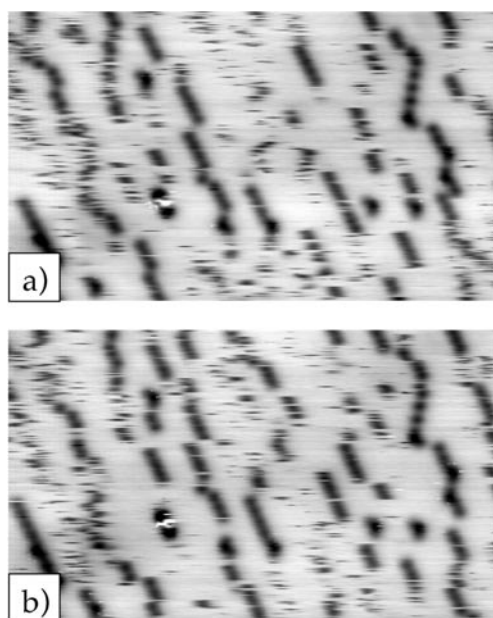
Figure 1. STM images of the Ag(110) surface covered with molecular oxygen at $T = 110$ K (O_2 coverage: 0.03 ML; 200 s between the two frames). Because of their high mobility at this temperature, single oxygen molecules appear as 'dashes' in the individual scan lines; 250 Å × 240 Å, −0.6 V, 1 nA.

2. Experimental details

The experiments were performed in an ultrahigh-vacuum (UHV) chamber (base pressure 5×10^{-11} Torr) equipped with standard facilities for sample preparation and characterization. The STM employed was of the beetle type. The sample was attached to a holder that was connected to a liquid He cryostat, allowing one to cool the sample to about 60 K. Temperatures between 60 and 300 K were maintained by simultaneous irradiation with a hot filament. The temperature was measured with a NiCr–Ni thermocouple, which was directly attached to the sample. The temperature scale was calibrated with respect to the temperature of desorption of CO from Ag(110), reported to be 77 K [24]. The STM measurements were performed in the constant-current mode, with tunnelling currents typically between 0.3 and 1 nA and voltages between 0.5 and 1 V. The Ag(110) single-crystal sample was prepared by cycles of Ar^+ sputtering (1 μA cm^{-2}, 700 eV, 10 min at 300 K) and annealing at 750 K, until no contaminations could be detected by Auger electron spectroscopy, and STM resolved large terraces with low contents of residual defects. Oxygen was dosed by backfilling the UHV chamber. Oxygen exposures are given in Langmuirs (1 L = 10^{-6} Torr·s), oxygen coverages in monolayers (ML), where 1 ML corresponds to one particle per Ag surface atom. Additionally, photodissociation experiments were performed. The sample was irradiated by UV light from a 100 W high-pressure Hg arc lamp through a regular UHV window (cut-off wavelength: $\simeq$300 nm). The illumination angle was $\simeq$70° with respect to the surface normal. To reduce sample heating, infrared radiation was absorbed using a water filled quartz cell.

3. Results

The situation before the dissociation is shown in figure 1. We have characterized this state in a previous publication [25] and give only a summary here. The molecules, which are imaged
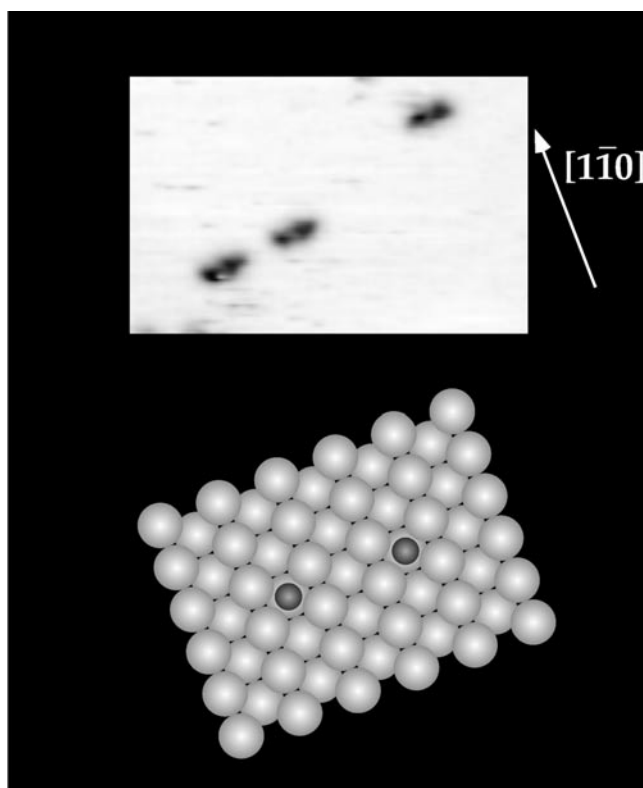
Figure 2. A STM image, recorded after adsorption of 30 L of O_2 at 124 K, annealing at 175 K for 60 s, and recooling to 115 K. The image shows pairs of O atoms, oriented perpendicularly to the $[1\bar{1}0]$ direction. 160 Å × 100 Å, −1.1 V, 0.2 nA. The exact positions of the atoms in the trenches (fourfold hollow or long bridge; see the model) could not be determined. The azimuthal orientation of the substrate was extracted from images recorded under other tip conditions, for which the close-packed rows of Ag atoms became just visible. The substrate orientation can also be identified from the added-row reconstruction in figures 3 and 5 that marks the [001] direction. (In all figures the orientations of the sample with respect to the STM are more or less the same.)

as dark dots, tend to form chains along the close-packed, $[1\bar{1}0]$, direction. Other data show the expected adsorption positions between the atomic rows [25], but the internal structure of the molecular features and hence the azimuthal orientation could not be clearly identified. At 110 K (figure 1) the molecules are mobile, explaining the sharp, cut-off appearance of many features that are caused by hopping events. The changing distribution in successive frames (figures 1(*a*) and (*b*)) also reflects this mobility. The molecular arrangements are somewhat stabilized by attractive interactions that mainly act along the $[1\bar{1}0]$ direction, and by weaker forces diagonally across the rows.

The dissociation experiments were performed by dosing the surface with oxygen at temperatures around 110 K and annealing at higher temperatures. STM data were taken after recooling to ∼110 K. Figure 2 shows a small-scale image, recorded after annealing at 175 K for 60 s. Three pairs of dark dots are visible that are interpreted as pairs of oxygen atoms from the dissociation of the O_2 molecules. Under most tunnelling conditions these features appear dark, which is typical for adsorbed O atoms [4]. The absence of thermal mobility proves that the features cannot be unreacted O_2 molecules that would be mobile at
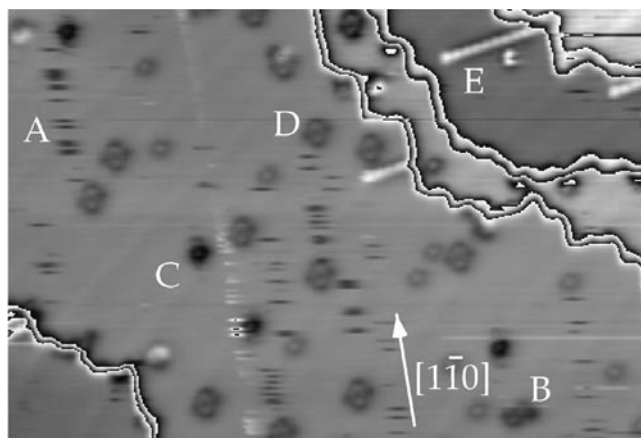
Figure 3. A STM image of Ag(110) covered with various oxygen species (110 K). The O_2 precoverage was 0.02 ML, the annealing time 60 s at 175 K. 310 Å × 210 Å, −0.8 V, 0.3 nA.

this temperature. That the O atoms are not mobile is as expected from their higher adsorption energy compared to that of the chemisorbed O_2 molecules. A striking result is that the O pairs are not oriented along the expected [1$\bar{1}$0] direction, but perpendicular to this direction, along [001]. Some oblique orientations around the [001] direction were observed, too, but of the 315 oxygen pairs identified in this study no pair oriented along [1$\bar{1}$0] was found. The distances between the two atoms are mostly two [001] lattice spacings. The atoms reside on sites in the trenches of the Ag(110) surface, but it could not be determined from our data whether they occupy long-bridge or fourfold hollow sites.

We find that the adsorbed O atoms readily react with CO at temperatures as low as 70 K. This agrees with previous investigations [14, 15], where reaction was detected at the lowest temperature of the study, 100 K. The O atoms in the added-row reconstruction only become reactive at $T \simeq 250$ K [16]. It can be concluded that the thermal dissociation of O_2 actually leads to a well-defined atomic state on the unreconstructed surface. The high reactivity can, in turn, be regarded as a characteristic of oxygen atoms that are not involved in the surface reconstruction. The reactivity is so high that the O atoms cannot be kept on the surface for very long. We found that their number halved in ∼30 min because of reaction with the residual gas of the UHV chamber, despite pressures well below 1×10^{-10} Torr and sample temperatures of ∼110 K. Because typical STM experiments took similar or longer times, the number of O atoms observed was generally lower than expected for the O_2 coverage. The STM images did not reveal indications of two different atomic O species as had been claimed on the basis of molecular beam measurements [14, 15]. From these it had been concluded that a more reactive and a less reactive species existed with respect to CO_2 formation with CO. Because the reactivities only differed by one order of magnitude, such a difference would not have been noticed in our reaction experiments with CO.

The result with regard to the dissociation is complicated by several other features that occurred reproducibly during annealing of the O_2-covered surface in the same temperature range. Figure 3 shows an example of a STM image recorded after annealing at 175 K. Five different features are marked that are interpreted as follows. The dark dashes (A) appear quite similar to the structures in figure 1 and are identified as O_2 molecules. That dissociation is not yet complete at temperatures as high as 175 K is consistent with the relatively large range of dissociation temperatures—between 145 and 175 K—that is reported in the

literature [12, 13, 26]. Because the coverage of molecules is small—most of them have disappeared by dissociation or desorption—they no longer form the chains typical for O_2 at higher coverages (figure 1). At still higher temperatures, molecules could no longer be detected. The feature B is one of the O-atom pairs just described. That O atoms do not occur more frequently in figure 3 is caused by the above-mentioned reaction with the residual gas and the formation of other features. The coverage of O pairs varied depending on the time elapsed after the annealing, the precise background pressure, and the precise annealing temperature.

Another, known feature is the chains of bright dots (E), running in [001] direction. The period along the chains is one [001] lattice spacing. These features are identical to the added-row reconstruction formed by –Ag–O– chains above the first layer of Ag atoms [9–11]. The reconstruction thus starts to form at ∼170 K. Its formation requires that Ag atoms detach from steps and diffuse across the terraces [10, 11]; this process obviously sets in at this temperature. That the reconstruction rows mostly originate at steps is typical for the formation of this structure at low temperatures [11].

There are two additional features, 'black dots' (C) and 'rhombs' (D), which we have not been able to definitely identify with known adsorbate structures so far. However, there are several observations that restrict possible explanations. The 'rhombs', features oriented along [1$\bar{1}$0] and displaying some internal structure, do not react with CO at the low temperatures studied here. The only species reacting between 70 and 170 K are the O-atom pairs. Because low-temperature reactivity can be regarded as a signature of O atoms adsorbed on the unreconstructed Ag(110) surface [14, 15], we rule out the possibility that the rhombs simply represent adsorbed O atoms. This conclusion is supported by the fact that, for most tip conditions, the imaging of the pairs and of the rhombs is quite different. Moreover, the pairs are occurring already at annealing temperatures <170 K, whereas the rhombs first appear at temperatures slightly higher than 170 K, suggesting different formation mechanisms. The fact that at 170 K the first added-row nuclei also occur may be taken as an indication that the formation is connected to the same effect, the detachment of Ag atoms from the atomic steps. The rhombs may therefore represent some reconstructive arrangement of O and Ag atoms. Because they appear quite different to the added rows in STM, and because they do not form nuclei for this surface phase, the atomic structure must, however, be different from that in the added-row reconstruction.

The C features ('black dots') represent another characteristic, however still unexplained, type of structure. They are imaged quite differently to O atoms and do not react with CO (1–100 L) between 70 and 180 K, again ruling out adsorbed O atoms.

Larger coverages of black-dot features were observed after exposure of the O_2-covered surface to CO at 100 K. Under these conditions, O_2 can directly react with CO to give CO_2 [27], but at the same time considerable numbers of black-dot features appear on the surface (these experiments will be published elsewhere [28]). A similar result was obtained by UV irradiation of the O_2-covered surface. O_2 on Ag(110) can be photochemically dissociated as was found in a previous HREELS investigation [29]. Figure 4(*a*) shows a surface that was precovered with 0.03 ML of O_2 and then irradiated with UV light for 100 s. The surface displays a number of black dots (the C features from figure 3), together with the characteristic, cut-off features of unreacted, mobile O_2 molecules. Irradiation for 300 s (figure 4(*b*)) led to complete disappearance of the molecules. In contrast to thermal dissociation, no structures other than the black dots are observed. That no O-atom pairs are observed is explained by the pressure increase during the irradiation, leading to their quick removal by reaction. The absence of added-row elements is as expected from the low temperature at which Ag atoms can no longer detach from the step edges. The same explanation may account for the fact that the rhomb features are absent. Annealing such a surface exclusively covered with black dots at 300 K
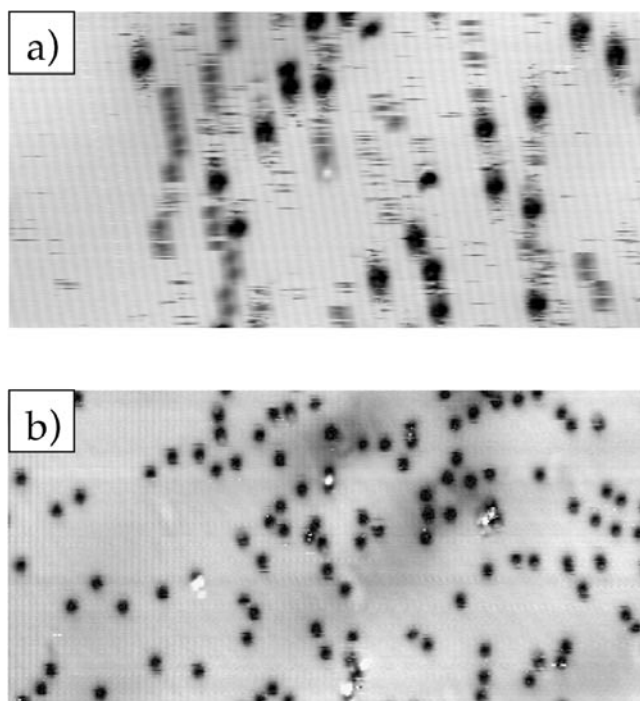
Figure 4. (*a*) A Ag(110) surface that was covered with 0.03 ML O_2 at 110 K and irradiated with UV light for $\sim$100 s. Dark-spot features appear that coexist with molecular oxygen; 240 Å $\times$ 120 Å. (*b*) Complete removal of molecular oxygen after 300 s of UV irradiation, after which only dark-spot features remain on the surface; 480 Å $\times$ 240 Å, -0.8 V, 0.1 nA.
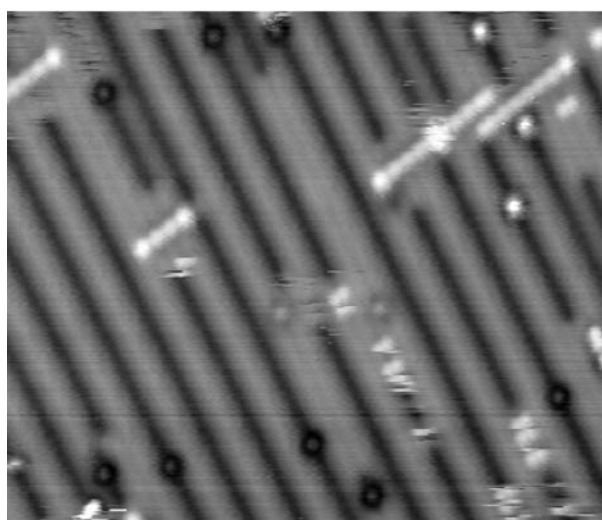

Figure 5. A STM image of Ag(110) at 110 K, after dosing with 200 l O_2 at 110 K and annealing for 60 s at 180 K. In this experiment the background pressure was higher than usual, resulting in stripes along [1$\bar{1}$0] that are interpreted as the (1 $\times$ 3)OH structure. 200 Å $\times$ 170 Å, -0.8 V, 0.3 nA.

led to the added-row reconstruction. This observation means that the black dots must contain oxygen in some form, even if its nature remains unclear. Considering the fact that they do not react with CO and the known property of Ag of dissolving oxygen in the bulk, one may speculate about a subsurface oxygen species, the energy for its formation possibly coming from the dissociation process.

Further possible explanations for the two unknown features are contaminants that may be present under the conditions of the low-temperature experiments. One possibility is a reaction of adsorbed O atoms with CO_2 to give carbonate. CO_3 can form on the oxygen-covered Ag(110) surface under various conditions [30], and the reaction of CO_2 with the added-row reconstruction at 300 K was recently investigated by STM [31, 32]. However, carbonate decomposes to give CO_2 and O atoms only on annealing to temperatures between 460 and 485 K [30, 33], whereas both the C and the D features (figure 3) have already disappeared upon annealing at 300 K. CO_3 is therefore not very likely.

Another obvious possibility is adsorbed hydroxyl. OH readily forms on Ag(110) from water from the residual gas by the reaction $O + H_2O \rightarrow 2OH$ [34, 35]. Experiments performed under poorer UHV conditions than in the other experiments indeed indicate OH on the surface. After dosing with 200 l of O_2 at a base pressure of 3×10^{-10} Torr and annealing, the O-atom pairs seen in figure 2 could no longer be observed. After annealing at 180 K under such conditions the STM image of figure 5 was recorded. Except for a few bright elements of the added-row reconstruction, the surface predominantly shows dark stripes oriented perpendicularly to the reconstruction, i.e. along the $[1\bar{1}0]$ direction. The distances between the stripes are mostly three [001] lattice spacings. The structure is therefore very probably caused by OH that is known to form (1×3) and (1×2) surface phases on Ag(110) at $\sim$200 K [35]. Further heating to 300 K leads to the added-row reconstruction, which is consistent with the interpretation of the stripes as OH (OH decomposes into O and H_2O by the reverse formation reaction). OH thus appears different to both the rhombs and the dark dots. The latter features are present in figure 5, but display a central bright dot at these tip conditions, and they are clearly different from OH features. A hydroxyl contamination is thus also not a very likely explanation for the unknown structures in figure 3.

4. Discussion

The STM data show that, upon annealing an O_2-covered Ag(110) surface at temperatures around 170 K, a fraction of the adsorbed molecules actually dissociate on the unreconstructed surface. Although several other oxygen features occur in the same temperature regime, this finding agrees with the conventional picture in which the adsorbed molecules dissociate at $T > 150$ K before the added-row reconstruction forms in a second step.

The pairs of O atoms observed afterwards display intrapair distances of two lattice constants, which had similarly been found for thermal O_2 dissociation on Pt(111) [4] and Cu(110) [6], and for electron-induced dissociation on Pt(111) [5] and Ag(110) [23]. The preferential orientation of the pairs along the [001] azimuth is surprising, however. It contrasts with the usually assumed orientation of the O_2 molecules, and it is different from the case for Cu(110) where about 2/3 of the O pairs occurred along the $[1\bar{1}0]$ direction [6]. Most striking, however, is the difference with respect to the electron-stimulated dissociation on Ag(110) that exclusively led to $[1\bar{1}0]$-oriented pairs [23]. Because of the high reactivity of the O atoms with the residual gas we cannot rule out the possibility that, before recording the STM scans, some $[1\bar{1}0]$ pairs had also existed. Nevertheless, the distribution of the O pairs remains distinct from that resulting from the electron-induced dissociation. This can have either of two causes. Either the reaction paths of the thermal and the stimulated dissociation start from differently

oriented molecular states, or, if the starting configurations are identical, one of the two reaction paths must involve a rotation of the molecule. In any case, the present case is a clear example of different trajectories for thermal and electron-induced dissociations.

For chemisorbed O_2 molecules on Ag(110), recent DFT calculations [20] revealed adsorption energies of 0.51 and 0.55 eV for the [1$\bar{1}$0] and [001] azimuthal orientations, respectively (with flat-lying molecules in fourfold hollow sites). Within the accuracy of the calculations the two orientations thus appeared equally likely. The authors suggested that this finding could be reconciled with previous NEXAFS experiments [17, 36], if one assumes that the procedure of preparation of the chemisorbed state determines which of the two molecular states is populated. Adsorption at elevated temperatures, where the chemisorbed state forms directly, would lead to the [1$\bar{1}$0] orientation, whereas adsorption at physisorption temperatures and annealing would result in a mixture of the two orientations. Combined HREELS/temperature-programmed-desorption (TPD) experiments [22] were interpreted along the same lines and showed, in addition, that only the directly chemisorbed state dissociates upon annealing, whereas the other one desorbs. A previous STM study on O_2/Ag(110) [23] confirmed the existence of two chemisorbed states. Because the O_2 adsorption temperature of 110 K in the present experiments clearly is in the chemisorption regime it appears more likely that in our case the molecules were [1$\bar{1}$0] oriented.

In this case, in order to explain the [001] direction of the O-atom pairs resulting from the dissociation, one has to assume that the molecule rotates on the reaction path of the thermal dissociation. A more complicated trajectory than the one simply following the direction of the molecular axis is actually not unreasonable. At the dissociation temperature of ~150 K the O_2 molecules can easily overcome the diffusion barrier in the trenches of the Ag(110) surface of 0.22 ± 0.5 eV [25], which is much lower than the calculated dissociation barrier of ~0.6 eV [20]. Even the higher diffusion barrier perpendicular to the Ag atomic rows, of ~0.3 eV [25], is traversed at a rate of ~10^3 s^{-1}. One can therefore envisage trajectories where the O_2 molecule is first displaced from its original site, e.g. to the top of the atomic rows, before the O–O bond breaks. Another indication of more complicated reaction paths comes from the above-mentioned DFT calculations [20]. Making the usual assumption that the atomic trajectories follow the O–O axis of the molecule, dissociation barriers of 0.62 and 0.76 eV were found for the [1$\bar{1}$0] and [001] orientations, respectively. These values are larger than the calculated O_2 adsorption energy, so the molecule would preferentially desorb, rather than dissociate. By contrast, TPD experiments [22] showed that, for low coverages, the majority of molecules dissociate (molecular desorption becomes stronger at higher coverages when site exclusion comes into play [26]). This discrepancy may be resolved by the fact that the calculations were limited to surface-parallel trajectories. By lifting this restriction and allowing for other, lower-symmetry paths, one may find smaller dissociation energies.

5. Summary

STM data recorded after thermal dissociation of chemisorbed oxygen on Ag(110) show pairs of O atoms, with the two atoms adsorbed in the trenches of the (110) surface and with intrapair distances of two lattice constants. Quite surprisingly, the O-atom pairs are oriented along the [001] direction, which disagrees with expectations based on the most likely orientation of the chemisorbed molecules along [1$\bar{1}$0]. The finding of an [001] orientation also contrasts with the result from STM experiments in which dissociation was induced by means of the tunnelling current from the tip [23], which led to [1$\bar{1}$0]-oriented pairs. The trajectory of the thermal dissociation must hence be different from that of the electron-induced dissociation. Because the molecules, at the temperature of the thermal dissociation, are almost freely mobile in the

potential energy profile of the Ag(110) surface, it is proposed that the dissociation trajectory may deviate from that predetermined by the O–O axis in the stable position of the molecule.

In addition to the O-atom pairs we found several other oxygen features in the temperature range of the O_2 dissociation that complicate this picture. At 175 K, intact molecules were still detected, and at the same time the first nuclei of the added-row reconstruction occurred. Two other features were observed that are induced by oxygen, but could not be identified further. The intermediate drop of the elastic peak intensity observed in HREELS in this temperature range [12, 13] may possibly be explained by this variety of oxygen species, that appears like a disordered surface at high coverages.

Acknowledgments

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