Mobility and Trapping of Molecules During Oxygen Adsorption on Cu(110)

B. G. Briner, M. Doering, H.-P. Rust, and A. M. Bradshaw
Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany

(Received 18 September 1996)

Adsorption of oxygen on Cu(110) at 4 K has been investigated by scanning tunneling microscopy. We have observed that weakly bound, "trapped" molecules coexist with pairs of atoms which are preferentially oriented along $[1\bar{1}0]$ and [001]. Molecules and atoms are both adsorbed in hollow sites. Clustering of O_2 at step edges perpendicular to $[1\bar{1}0]$ indicates substantial anisotropic mobility of the molecular precursor. It is concluded that precursor dynamics and multidimensionality of the potential energy surface have a dominant influence on the dissociative chemisorption of O_2 on Cu(110). [S0031-9007(97)02441-1]

PACS numbers: 68.35.Ja, 61.16.Ch, 82.20.Kh, 82.65.My

Chemisorption of oxygen on metal surfaces is of fundamental interest for the understanding of catalytic reactions. The dynamics of adsorption strongly influences the reactivity of an adsorbate-covered surface—only a mobile adsorbate can reach a favorable, chemically "active" site or find an easy path to dissociation. Based on molecular beam experiments it has been suggested (see, e.g., Refs. [1,2]) that chemisorption at low temperature proceeds via molecular precursor states which accommodate to the surface before surmounting the barrier to dissociation. Many experiments on precursor-mediated adsorption are interpreted in terms of motion over a simplified potential energy surface (PES) with only one "reaction coordinate." This model and the assumption that precursors are in thermal equilibrium imply the *sequential* trapping of physisorbed and chemisorbed molecules in local minima of the PES, a phenomenon which has been reported to occur on Ag(110), Pt(111), and Cu(100) [3–5]. There are, however, at least two aspects of adsorption dynamics which can invalidate the concept of sequential adsorption. First, a "hot precursor" may cross the PES by transient motion before it loses its energy to the substrate [6]. Furthermore, the multidimensional PES may possess "valleys" where even a precursor with low kinetic energy can find a crossing path. The importance of a multidimensional model for the PES has recently been emphasized by the first full quantum dynamical calculation of hydrogen chemisorption on Pd(100) [7]. This study has shown that experimental results which are usually taken as indicators for precursor-mediated adsorption can also appear without the presence of a precursor due to steering effects on the six-dimensional PES. Here we report that—in contrast to the notion of sequential adsorption—a weakly bound molecular precursor *coexists* with ordered pairs of dissociated atoms after oxygen adsorption on Cu(110) at 4 K. The static adsorbate distribution serves as a "fingerprint" of chemisorption dynamics and directly reflects the implications of the real, multidimensional PES on the chemisorption process. We find that, depending on their angular orientation, oxygen molecules can be either trapped in a local minimum of the PES or find a channel for dissociation.

All experiments were performed with an Eigler-type scanning tunneling microscope (STM) which operates in UHV at a temperature of 4 K [8–10]. Cu(110) surfaces were prepared by standard sputter-anneal cycles before being transferred into the STM, where surface cleanliness was checked prior to oxygen adsorption. Oxygen (99.998%) was dosed with the sample held in the microscope and the STM tip mechanically retracted. To avoid CO formation, the filaments and ion pump were turned off during oxygen exposure. O_2 impinges on the Cu surface with near grazing incidence ($\sim 5°$) and with a typical thermal energy of 50 meV ($E_{\mathrm{kin}} = 2kT$, $T = 300$ K). Because of the particular design of our STM there is a pressure gradient of several orders of magnitude between the O_2 inlet and the sample position which impedes a proper dosage calibration. Typically, an exposure to 1000 L of O_2 (measured at the leak valve) is needed to obtain a coverage of the order of 0.01 ML on the sample surface. It must be emphasized that this phenomenon is not caused by a low sticking coefficient, since the sticking of oxygen on Cu(110) is facile ($S_0 = 0.6$ at 100 K [11]).

Figure 1 shows a 340 Å × 340 Å topography image of the Cu(110) surface after oxygen dosage at 4 K. To highlight the adsorbates all atomic terraces are reproduced with the same grey scale. *Two different adsorbate-related features* can clearly be distinguished in Fig. 1. First, we find closely spaced pairs of depressions (marked p) which are interpreted as *dissociated oxygen atoms*. This assignment is in accordance with other STM studies of atomic oxygen on metals, where the adsorbate could also be imaged as a holelike feature [12,13]. Most of the pairs are aligned parallel to the close-packed rows of the substrate lattice. Besides the pairs we observe randomly distributed single protrusions (marked m). As will be substantiated below, these features are attributed to a weakly bound *molecular precursor*. Apart from the two isolated adsorbate species, we find that clusters (marked

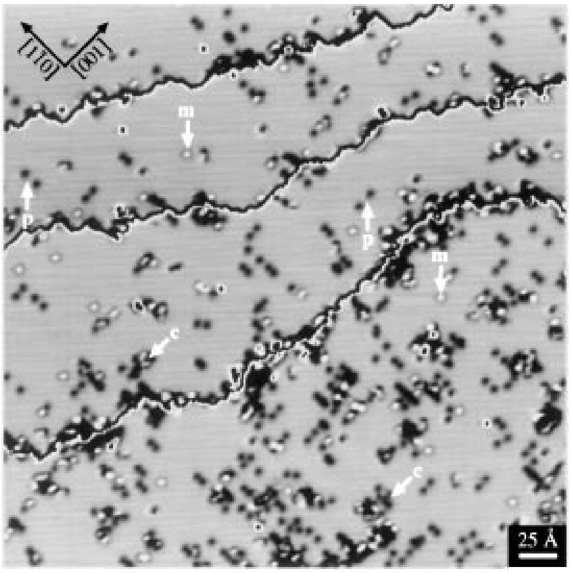

FIG. 1. Cu(110) after O_2 adsorption at $T = 4$ K. Field of view: 340 Å × 340 Å, $V_B = -0.2$ V, $I_T = 100$ pA. The same grey scale is used on all atomic terraces. Adsorbate-related features are marked [pairs (p), single protrusions (m), clusters (c)].

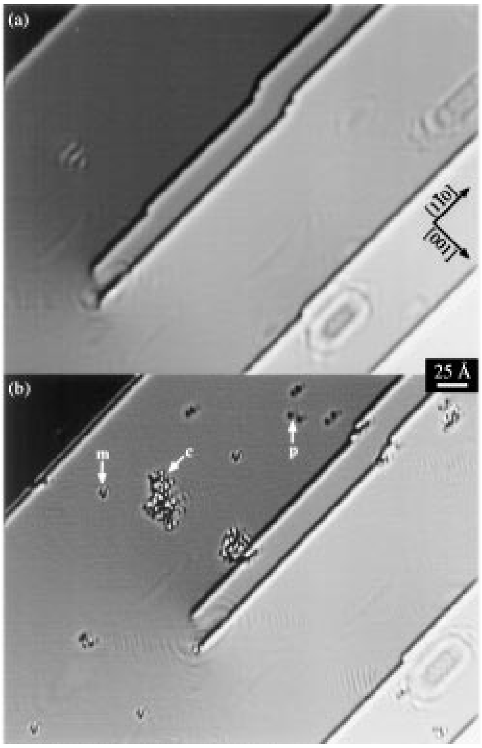

FIG. 2. Same area on Cu(110) *before* (a) and *after* (b) O_2 exposure at 4 K. Field of view: 370 Å × 280 Å, $V_B = -0.1$ V, $I_T = 400$ pA. A partial high-pass filter is applied to enhance the local contrast. Adsorbates are labeled as in Fig. 1.

c) grow either in the middle of larger terraces or at step edges perpendicular to $[1\bar{1}0]$.

Small amounts of surface impurities could easily be mistaken for oxygen adsorbates. Therefore it is crucial to ensure that all observed features really are oxygen related. For this purpose we image the *same* surface area on Cu(110) before and immediately after O_2 dosage. The bare surface [Fig. 2(a)] is entirely free of impurities and Cu adatoms. It displays a screw dislocation and several racetracklike subsurface defects [14] which serve as convenient markers. After O_2 exposure, all expected features (pairs, protrusions, clusters) appear on the surface [Fig. 2(b)]. Here the protrusions are imaged slightly differently compared to Fig. 1. We have found that the appearance of the precursor-related features strongly depends on the sample bias voltage V_B and on the state of the tunneling tip, while the pairs are imaged as depressions over a wide range of tunneling conditions. The results shown in Fig. 2 preclude residual surface contamination as a possible source of the observed adsorbate features. However, it could be argued that some adsorbates are carbon monoxide molecules since CO is known to appear as a frequent by-product during oxygen exposure. Although the STM does not provide a means for chemical identification of adsorbates, it can still be applied to discriminate between impurities and oxygen adsorbates by probing their respective adsorption geometries. CO has been found to adsorb on Cu(110) in an on-top configuration with respect to the substrate atoms in the topmost layer [15–17]. The adsorption sites for O_2/Cu(110) are shown in Fig. 3, a high-resolution STM topograph which displays two pairs of depressions (O atoms) and one protrusion (O_2 molecule). Evidently both species sit in hollow sites of the Cu lattice. It can therefore be established that no CO contamination

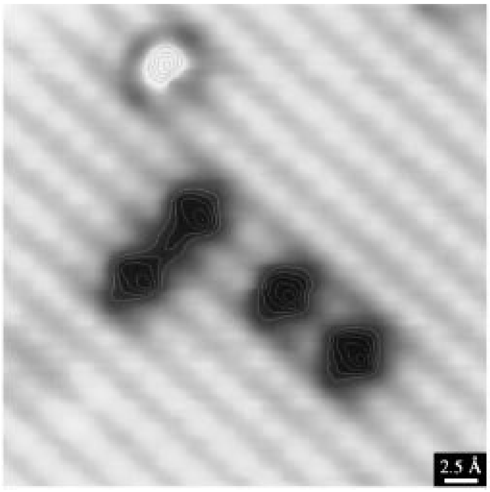

FIG. 3. High-resolution STM image of molecular and atomic oxygen on Cu(110). Field of view: 37 Å × 37 Å, $V_B = -0.2$ V, $I_T = 400$ pA. Contours are added to highlight the shape of the adsorbates and the position of the local topographic extremal points.

is present in Fig. 2 and that the observed protrusions are indeed molecular oxygen. The adsorption site for O atoms confirms the result reported for an active oxygen species which has been found on Cu(110) after room temperature exposure to O_2 [18].

The formation of adsorbate clusters points to a significant lateral mobility of the molecular precursor (the high initial sticking coefficient of O_2 on Cu(110) [11] precludes an explanation of cluster growth in terms of selective sticking at the edges of preadsorbed islands). Precursor mobility requires a weak adsorbate-substrate interaction, a property which can be qualitatively probed with the STM by using it as a tool for atomic scale manipulation [19]. This is illustrated in Fig. 4(a), an image similar to Fig. 2(b) which has been recorded with an increased tunneling current of 1 nA. In response to the stronger tip-adsorbate interaction the molecules which are immobile in Fig. 2(b) slide along the close-packed rows and appear as diagonal traces. Although the image is rastered horizontally, all molecules stay in the troughs of the substrate. Obviously, the hopping barrier for the molecules is much smaller along $[1\bar{1}0]$ than perpendicular to the close-packed rows. A high-resolution image of a sliding molecule [Fig. 4(b)] and a schematic illustration of the sliding process [Fig. 4(c)] reveal that the tip-adsorbate interaction is repulsive and short range. At the low sample bias of $V_B = 6$ mV, the O_2 molecule is imaged as a circular feature ($d \approx 6$ Å) with a dark core and asymmetric bright lobes. As the image is scanned horizontally from top to bottom, the STM first reproduces the upper semicircle of the molecular feature. When the center of the semicircle (i.e., the true position of the molecule) is reached the adsorbate recoils, making one hop along $[1\bar{1}0]$. Subsequently, a displaced slice of the same semicircle is observed. The constant length of the jump distances in Fig. 4(b) corroborates the observation of one well-defined adsorption site for the molecular precursor.

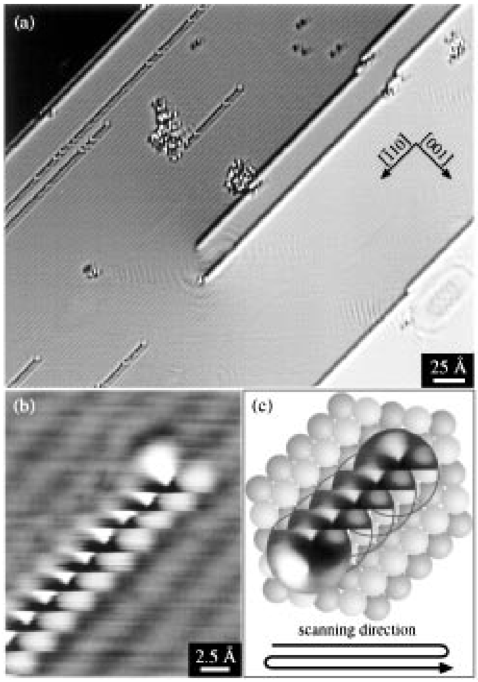

FIG. 4. (a) Same as Fig. 2(b), recorded with increased tunneling current (370 Å × 300 Å, $V_B = -0.1$ V, $I_T = 1$ nA). O_2 molecules slide along $[1\bar{1}0]$ (diagonal traces). (b) High-resolution image of a molecular trace (20 Å × 24 Å, $V_B = 6$ mV, $I_T = 1$ nA). (c) Schematic sketch illustrating the repulsive tip-molecule interaction.

We suggest that tip-induced sliding actually simulates the transient motion of the "hot" molecular precursor immediately after adsorption, This hypothesis is in accord with the observed cluster distribution. Since anisotropic hopping barriers largely restrict the precursor mobility to the $[1\bar{1}0]$ direction, it can be expected that clusters agglomerate at step edges perpendicular to this direction. Experiments also show that clustering at step edges perpendicular to $[1\bar{1}0]$ does not depend on the azimuth of the incoming beam. Obviously, less time is required to randomize the initial momentum of an adsorbed particle than to equilibrate its kinetic energy with the substrate. Clusters are imaged mainly as depressions, and for small clusters, individual oxygen atoms can be resolved. Therefore it is proposed that pairs of O atoms act as nuclei for cluster growth. It must be emphasized that at 4 K we do not observe any thermal diffusion (on a time scale of hours). Consequently, clusters cannot grow by attachment of already dissociated pairs but only by trapping of mobile molecules which seem to experience an enhanced dissociation probability upon collision with a cluster. A comparison of the tunneling parameters which are needed to displace an O_2 molecule with similar manipulation experiments involving either physisorbed Xe or chemisorbed CO [19] suggests that the O_2 molecule is physisorbed. However, this question cannot be conclusively answered, since it is conceivable that a chemisorbed precursor is equally easy to displace if the diffusion barrier along $[1\bar{1}0]$ is low enough.

In Fig. 5 we show a bar chart which represents the orientation and intrapair separation of chemisorbed oxygen pairs. It is immediately clear that the angular orientation of the pairs is highly anisotropic. We find that from a total of 296 pairs, 205 are aligned parallel to the close-packed rows. While it is still quite probable to find pairs which lie perpendicular to $[1\bar{1}0]$ (72 pairs), obliquely oriented pairs remain the exception. For pairs aligned with either $[1\bar{1}0]$ or [001] the most probable intrapair separation corresponds to 2 lattice constants. The surprisingly small number of pairs with nearest neighbor separation points to a repulsive interaction at short distances. On the assumption that the part of the chemisorption energy which becomes available for lateral motion is equally distributed among the two oxygen atoms [20], these pair statistics suggest that dissociation happens preferably over the hollow site. Based on the result shown in Fig. 5,

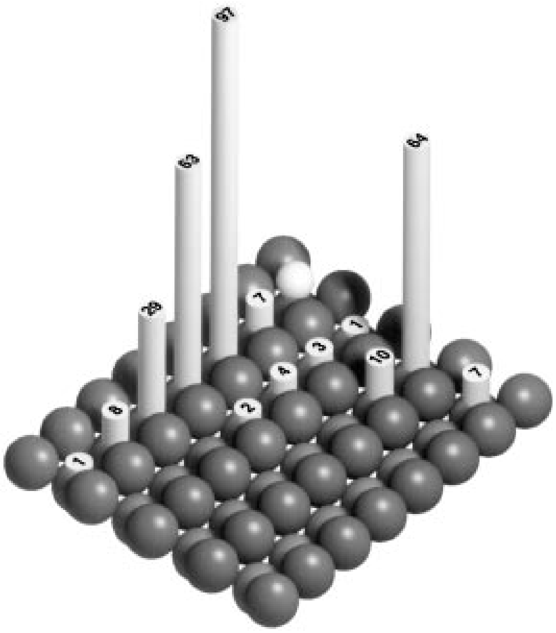

FIG. 5. Statistics of intrapair separation and orientation for dissociated oxygen on Cu(110). The lightly shaded sphere represents the position of one atom in a pair and marks the origin of the diagram.

we propose that the dissociation probability is enhanced (i.e., there are "easy paths" across the PES) for flat-lying molecules with their axis oriented either parallel or perpendicular to $[1\overline{1}0]$. This conclusion hinges upon the assumption that the static pair orientation reflects the initial momentum of the oxygen atoms after dissociation, an assumption which is justified by the observation that the nondiffusive mobility of dissociated atoms is restricted to very short distances (1–2 lattice constants). The observation of very limited "ballistic" motion of oxygen atoms confirms a recent experimental study for O_2/Pt(111) [13], and it is also in qualitative accord with a molecular dynamics simulation for O_2/Al(111) [20]. It is reasonable to infer from Fig. 5 that the precursor is not aligned in either the $[1\overline{1}0]$ or [001] azimuth, although the exact orientation of the molecular axis cannot be deduced directly from the STM images. Theoretical modeling of the observed "internal structure" of O_2 [Fig. 4(b)] may provide a means to decide whether the molecules are flat lying or their axis is rotated out of the substrate plane.

For a long time the physical reality of the precursor concept has remained doubtful [2]. Although many results of molecular beam experiments have been interpreted as indirect evidence for the existence of precursors [for Cu(110), see [11]], a recent theoretical study [7] has questioned the validity of such an interpretation. Observations of O_2 on Ni(111), Ag(110), Pt(111), and Cu(100) [3–5,21] have left it unclear whether precursors still play an important role under conditions where oxygen *can* dissociate. The present results establish the existence of a molecular precursor under such conditions. We conclude that *molecular mobility and trapping* strongly influence the adsorbate distribution in the system O_2/Cu(110), while *atomic mobility* is only of secondary importance.

[1] S. T. Ceyer, Annu. Rev. Phys. Chem. **39**, 479 (1988).

[2] K. D. Rendulic and A. Winkler, Surf. Sci. **299/300**, 261 (1994).

[3] K. C. Prince, G. Paolucci, and A. M. Bradshaw, Surf. Sci. **175**, 101 (1986).

[4] A. C. Luntz, J. Grimblot, and D. E. Fowler, Phys. Rev. B **39**, 12 903 (1989).

[5] T. Yokoyama, D. Arvanitis, T. Lederer, M. Tischer, L. Tröger, K. Baberschke, and G. Comelli, Phys. Rev. B **48**, 15 405 (1993).

[6] J. Harris and B. Kasemo, Surf. Sci. **105**, L281 (1981).

[7] A. Gross, S. Wilke, and M. Scheffler, Phys. Rev. Lett. **75**, 2718 (1995).

[8] P. S. Weiss and D. M. Eigler, in *Nanosources and Manipulation of Atoms under High Fields and Temperatures,* edited by V. T. Binh *et al.,* NATO Advanced Study Institutes, Ser. E, Vol. 235 (Kluwer Academic, Dordrecht, 1993), p. 213.

[9] J. Buisset, Ph.D. thesis, Wissenschaft und Technik Verlag, Berlin, 1996.

[10] H.-P. Rust, J. Buisset, E. K. Schweizer, and L. Cramer, Rev. Sci. Instrum. **68**, 129 (1997).

[11] A. Hodgson, A. K. Lewin, and A. Nesbitt, Surf. Sci. **293**, 211 (1993).

[12] H. Brune, J. Wintterlin, J. Trost, G. Ertl, J. Wiechers, and R. J. Behm, J. Chem. Phys. **99**, 2128 (1993).

[13] J. Wintterlin, R. Schuster, and G. Ertl, Phys. Rev. Lett. **77**, 123 (1996).

[14] The fringes around the stadiumlike defects are topographic. We interpret them as atomic scale manifestation of stress due to the presence of a subsurface impurity. An interpretation in terms of standing waves is precluded, since the fringes fit the lattice period, and the surface state on Cu(110) is centered around $\bar{Y}$ (i.e., standing waves would appear parallel to $[1\overline{1}0]$).

[15] P. Hofmann, K.-M. Schindler, S. Bao, V. Fritsche, A. M. Bradshaw, and D. P. Woodruff, Surf. Sci. **337**, 169 (1995).

[16] M. Doering, J. Buisset, H.-P. Rust, B. G. Briner, and A. M. Bradshaw, Faraday Discuss. (to be published).

[17] The observant reader may have noticed a small number of unpaired depressions with a light rim in Fig. 1. These adsorbates are CO molecules which have already been present on the surface before oxygen exposure and can be identified because of their different adsorption site.

[18] J. Buisset, H.-P. Rust, E. K. Schweizer, L. Cramer, and A. M. Bradshaw, Surf. Sci. **349**, L147 (1996).

[19] D. M. Eigler and E. K. Schweizer, Nature (London) **344**, 524 (1990); J. A. Stroscio and D. M. Eigler, Science **254**, 1319 (1991).

[20] C. Engdahl and G. Wahnström, Surf. Sci. **312**, 429 (1994).

[21] M. Shayegan, J. M. Cavallo, R. E. Glover, and R. L. Park, Phys. Rev. Lett. **53**, 1578 (1984).