

## Existence of a “Hot” Atom Mechanism for the Dissociation of O<sub>2</sub> on Pt(111)

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The dissociation of O<sub>2</sub> on a Pt(111) surface was studied by variable temperature scanning tunneling microscopy at 150–106 K. The two oxygen atoms created by the dissociation appear in pairs, with average distances of two lattice constants. Since thermal random walk sets in only at around 200 K, with a diffusion barrier of 0.43 eV and a preexponential factor of  $10^{-6.3} \text{ cm}^2 \text{ s}^{-1}$ , the distribution of distances at around 160 K evidences nonthermal processes during the dissociation. It is concluded that transient ballistic motion exists, where the short range traveled is in agreement with recent molecular dynamics studies. [S0031-9007(96)00549-2]

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There is a controversial debate about the existence of transient mobility of adsorbed particles on solid surfaces. It concerns the question whether the chemical energy which is released during adsorption is directly dissipated to the heat bath of the solid, or may, at least in part, be transformed into kinetic energy, causing nonthermal motion of the adsorbed particle across the surface, or even inducing chemical reactions [1]. Transient mobility was claimed for metal epitaxy [2], where in certain cases layer-by-layer growth was observed already at temperatures below the onset of thermal diffusion; according to molecular dynamics (MD) simulations [3] energy dissipation should, however, be very efficient in these cases, and the metal atoms should not move by more than one lattice spacing away from the point of impact. Experiments by scanning tunneling microscopy (STM) on the dissociative adsorption of oxygen molecules on an Al(111) surface [4,5] pointed to a “hot atom” mechanism according to which the two oxygen atoms are propelled apart upon dissociation, by distances exceeding 80 Å in a ballistic type of motion before equilibrating with the substrate. Molecular dynamics simulations [6] concluded, however, that, with realistic assumptions about the initial kinetic energy, hyperthermal motion could lead only to separations between the O atoms of less than 16 Å.

We believe that these effects are important for our general understanding of energy dissipation during adsorption. In order to clarify the situation, we have undertaken an STM study on a system for which there was clear evidence for the existence of transient particles from former studies. For the oxidation of CO on Pt(111) a low temperature reaction channel was found [7] in addition to the ordinary reaction between thermalized oxygen atoms and CO<sub>ad</sub> at around 300 K [8]. The interpretation was based on metastable chemisorbed oxygen molecules which had been known from spectroscopic investigations [9] and can be described as superspecies, or peroxolike species [10]. Heating to between 100 and 150 K (depending on the coverage) [11] or UV light radiation [12] causes dissociation (competing with desorption), whereby two “hot”

oxygen atoms are created, which react with CO<sub>ad</sub>, or can stimulate desorption of other coadsorbed particles [13]. Dissociation of the metastable O<sub>2</sub> on the clean surface should therefore lead to a characteristic distribution of O atoms containing information about the possible existence of hyperthermal mobility. Since transient mobility is affected by the corrugation of the interaction potential, part of which is reflected by the diffusion barrier, this quantity was determined, in addition.

The experiments were performed under ultrahigh vacuum conditions with a variable temperature STM that allows us to cool the sample to about 60 K by a liquid helium cryostat connected to the sample holder by a copper braid. Intermediate temperatures are achieved by simultaneous radiative heating from the back of the sample. The Pt(111) surface was prepared by repeated cycles of Ar<sup>+</sup> ion sputtering (1 keV, 2.5 μA), annealing at 1100 K, oxidation of residual carbon contaminations ( $6 \times 10^{-8}$  mbar of O<sub>2</sub> at  $T = 720$  K), and flash desorption of excess surface oxygen. After transfer of the sample to the STM thermal equilibrium is reached within about only 15 min, thereby minimizing readsorption of contaminations.

Figure 1(a) shows the surface after adsorption of oxygen at 163 K. Since at this temperature [11] molecular oxygen on Pt(111) either dissociates or desorbs, the two dark spots are interpreted as two oxygen atoms resulting from the dissociation of an O<sub>2</sub> molecule. The separation between the two atoms is two Pt lattice constants as is directly seen from the Pt lattice visible in Fig. 1(a). The interpretation as atoms is in agreement with the fact that they are imaged dark by the STM, i.e., lower than the surrounding platinum, which is caused by the electronic structure of O<sub>ad</sub> [14] and has been observed also on other metals [4,5]. Images recorded after adsorption at around 60 K, where O<sub>2,ad</sub> exists, show completely different features which can be interpreted as clusters of molecules. Agglomeration indicates that O<sub>2,ad</sub> is mobile even at 60 K, in contrast to the oxygen atoms, which do not show any site exchanges at temperatures around 160 K.

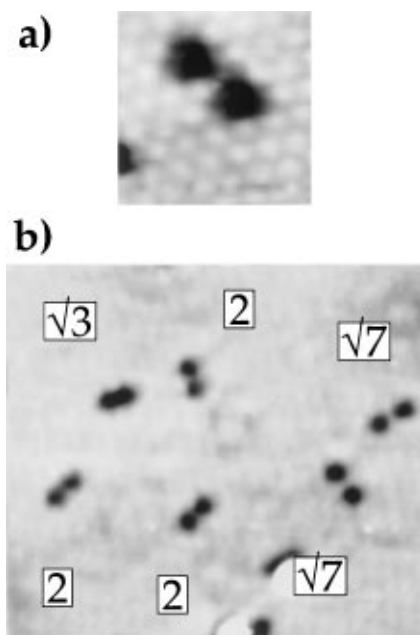


FIG. 1. STM images of Pt(111), recorded after dissociative adsorption of  $O_2$  at around 160 K; black dots are oxygen atoms. (a) 2 L  $O_2$ ,  $19 \text{ \AA} \times 19 \text{ \AA}$ , 163 K,  $-0.2 \text{ V}$ , 28 nA. (b) 1.2 L  $O_2$ ,  $110 \text{ \AA} \times 92 \text{ \AA}$ , 154 K,  $+0.13 \text{ V}$ , 0.8 nA; the distances between the O atoms in the pairs are indicated.

The larger scale image Fig. 1(b), recorded after exposure to 1.2 L [1 L (langmuir) =  $10^{-6}$  torr s] of  $O_2$  at 154 K, shows that the  $O_{ad}$  atoms appear in pairs, which was the exclusive feature observed in this temperature range. After larger exposures small islands begin to appear which consist exclusively of even numbers of atoms. (That the pairs do not cluster already at low coverages, in contrast to the molecules at 60 K, indicates that the molecules which adsorb at around 150–160 K dissociate with a probability greater than that of finding another particle.) It is obvious that the two O atoms from the dissociation of the molecules on Pt(111) remain on closely neighbored sites. As is seen in Fig. 1(b) the distances between the atoms in the pairs vary; there are three pairs with separations of two lattice constants, two with  $\sqrt{7}$ , and one with  $\sqrt{3}$  lattice constant separations.

The atomic model depicted in Fig. 2(a) shows the separations found in the experiments; the relative abundances of the various distances are shown in the histogram Fig. 2(b). Because of symmetry only one  $60^\circ$  lattice segment is shown. The data show that the distances vary between one and three lattice constants, with a maximum number of pairs separated by two lattice constants; the average distance is also about two lattice constants. All atoms sit on identical threefold sites; i.e., given these are fcc sites as was concluded in a former study [15], no hcp sites are occupied. Although a twofold separation is also the most probable one under conditions close to equilibrium (see below), the appreciable abundance of  $\sqrt{3}$  dis-

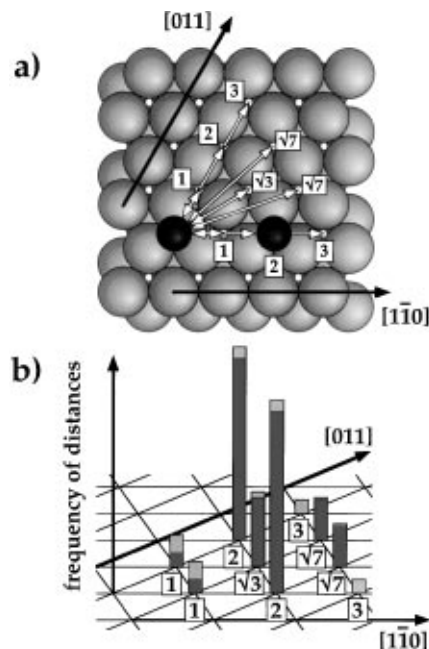


FIG. 2. (a) Model of the Pt(111) surface with two oxygen atoms after dissociation of a molecule (platinum atoms gray, oxygen atoms smaller, dark spheres). (b) Histogram of frequencies of intrapair distances, based on 55 pairs. Average frequencies of 1,  $\sqrt{3}$ , 2,  $\sqrt{7}$ , 3 lattice constant separations were 7.3%, 21.8%, 56.4%, 12.7%, and 1.8%. Gray tops of the bars indicate variations between two data sets at 160 and 163 K.

tances and the, albeit small, number of onefold distances clearly discriminates the histogram from an equilibrium distribution.

For a quantitative comparison to thermal mobility measurements were performed also at higher temperatures. Figure 3(a) shows the surface after adsorption of 10 L of  $O_2$  at 205 K. In contrast to temperatures between 150 and 160 K there are many single atoms, and the islands, which show a  $(2 \times 2)$  arrangement of atoms, contain even as well as odd numbers of atoms. This is attributed to the onset of thermal mobility in this range of temperatures. The distribution of atoms in Fig. 3(a) is therefore considered to be close to equilibrium; a  $(2 \times 2)$  structure is the thermodynamically stable structure of  $O_{ad}$  on Pt(111) [16]. In contrast to the low temperature results  $\sqrt{3}$  separations are observed only scarcely (see, e.g., the row of three atoms in the upper right corner of the first image of the series). Onefold distances were not found at all.

Comparison of the four images which were recorded successively on the same area shows that many of the atoms undergo site exchanges on the time scale of the image series. This is illustrated in the fourth image by arrows pointing to those atoms that have jumped from their positions in the preceding image. Quantitative analysis of about 50 frames revealed the average hopping time  $\tau$  from which the random walk diffusion constant was obtained by means of the Einstein-Smoluchowski relation

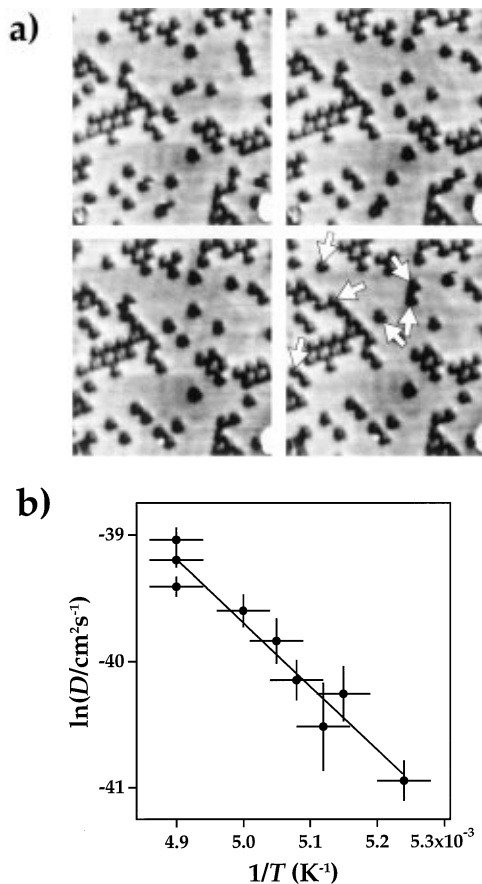


FIG. 3. (a) Series of successive STM images Pt(111) surface after exposure to 10 L  $O_2$ ; black dots are oxygen atoms; the Pt lattice is weakly resolved.  $93 \text{ \AA} \times 92 \text{ \AA}$ , 205 K, +0.5 V, 2.3 nA, time for one image 12.5 s. (b) Arrhenius plot of diffusion constants between 191 and 205 K.

$D = l^2/4\tau$  [ $l$  is the lattice constant of Pt(111) =  $2.77 \text{ \AA}$ ]. Since the atoms in the islands are subject to interactions with  $O_{ad}$  neighbors only, those atoms were counted that have no neighbors within two lattice constants. This analysis was performed for several temperatures between 191 and 205 K; the result is shown in the Arrhenius plot of Fig. 3(b). The data fall on a straight line, from the slope of which the diffusion barrier  $E_{diff}^*$  is  $0.43 \pm 0.04 \text{ eV}$ ; the preexponential factor  $D_0$  equals  $10^{-6.3 \pm 1.0} \text{ cm}^2 \text{ s}^{-1}$ . The value for  $E_{diff}^*$  is in the expected range between 10% and 20% of the adsorption energy of 3.7 eV (with respect to the energy of a free oxygen atom) [17]; the difference to the much larger  $E_{diff}^*$  values of 1.2–1.5 eV found by field emission microscopy [18] is attributed to the known incompatibility between random walk results and macroscopic diffusion measurements.  $D_0$  is smaller than the expected value of  $10^{-3} \text{ cm}^2 \text{ s}^{-1}$  which may, however, be due to the error caused by the relatively small temperature range over which the atomic motion could be followed. With the experimental numbers for  $E_{diff}^*$  and  $D_0$  the hopping time is extrapolated to be between 4 and 32 h in the temperature range of 150–160 K, which is an order of

magnitude longer than the time scale on which the atomic distributions were analyzed. Consequently, the distances larger than two lattice constants that are found at these temperatures cannot be caused by thermal motion. An oxygen atom, jumping from a distance of two to a distance of  $\sqrt{7}$  lattice constants, would even have to overcome a larger barrier than an individual oxygen atom because of the attractive interactions on  $(2 \times 2)$  sites. For distances shorter than two lattice constants the jump rates may be larger, because repulsive interactions at these separations increase the potential energy of the O atoms, thus lowering the barrier. A portion of the pairs with onefold or  $\sqrt{3}$ -fold separations may, therefore, have transformed into pairs with twofold separations. Nevertheless, the fact that distances of one lattice constant are detected at all and distances of  $\sqrt{3}$  lattice constants to a much greater extent than at around 200 K evidence nonthermal processes at 150–160 K.

We conclude that the dissociation of the chemisorbed molecules causes a nonthermal, transient motion of the two oxygen atoms. Without such an effect the two atoms would always be found on neighbored lattice sites, in contrast to the data. We confirm therefore the claims about hot atoms that originated from observations of nonthermal processes on Pt(111) [7,12,13], but these reactions must take place on a rather short range, of about two lattice constants.

The possibility of transient motion after dissociation of  $O_2$  has been treated theoretically in an MD investigation by Engdahl and Wahnström [6]. Trajectories were calculated for hot oxygen atoms, with a parallel kinetic energy of 3.5 eV, on a surface with a diffusion barrier of 0.3–0.4 eV. The resulting mean displacement of  $8 \text{ \AA}$  per atom was shown to be limited not primarily by energy transfer to the substrate (via phonon excitation), but by scattering of the O atoms at the corrugated potential, causing equipartition of the parallel kinetic energy between the different translational degrees of freedom within only 0.2 ps. Although the total  $E_{kin}$  is transferred to the substrate at a slower rate (after 0.2 ps it is still 1 eV, i.e., larger than  $E_{diff}^*$ ), it does not result in further net displacement. Since we know the energetics for  $O_2$ /Pt(111) and the geometry of the initial state quite well, a comparison to the present case can be performed: The distance between the oxygen atoms in the flat lying [19] supermolecule or peroxolike molecule is 1.3–1.4  $\text{ \AA}$  [10,19]. Upon stretching of the O-O bond over a certain limit the two oxygen atoms feel a mutual repulsion (the chemisorbed molecule is only metastable), which accelerates them in opposite directions, mostly parallel to the surface. The maximum kinetic energy thus gained is given by the energy for dissociative adsorption of  $O_2$  (2.2 eV [17]) plus the barrier of 0.07 eV [17] separating the atomic and molecular potentials, both values with respect to the free molecule. Since for the nonthermal reaction with  $CO_{ad}$  both O atoms were found to react [7],

we assume that the energy is shared equally between the two atoms, resulting in 1.1 eV per atom. The O-O distance at which the maximum kinetic energy is reached is probably at around one Pt lattice constant since the equilibrium measurements show that the interaction changes from strongly repulsive at one to weakly repulsive at  $\sqrt{3}$  lattice constants. A value of about 1 eV is consistent with the fact that the CO<sub>ad</sub> oxidation with thermalized oxygen requires an activation energy of 1.0 eV [20], which must be brought up also by the hyperthermal atoms, and with experiments in which the hot oxygen atoms were found to transfer 0.7 eV to coadsorbed noble gas atoms [13]. We have therefore a considerably smaller energy than that used in the MD calculation but about the same diffusion barrier and therefore potential corrugation. It is therefore expected that scattering should stop the motion of the hot atoms practically at the first Pt atoms encountered. The distance traveled by a 1.1 eV O atom on a 0.1 ps scale is only about one lattice constant. The small separations observed for Pt(111) are therefore in agreement with such a mechanism, which is confirmed in a recent theoretical study [21].

The result for Pt(111) is in striking contrast to the large separations between oxygen atoms that were observed for Al(111) [4,5]. Part of the difference may be explained by the much larger binding energy, and thereby  $E_{\text{kin}}(t = 0)$ , of O on Al(111), for which a recent calculation [22] found 5.0 eV per atom with respect to free O<sub>2</sub>. However, even with a similarly large energy (3.5 eV) the quoted MD calculation did not reproduce the experimentally observed distribution of oxygen atoms on Al(111). The discrepancy is in fact even larger since a diffusion barrier of 0.3–0.4 eV had been used, whereas the actual value is close to about 1 eV [5,22]. The mechanism for Al(111) is still an open question. It has been suggested that the hot oxygen atoms do not fly parallel to the surface but describe a “canon ball” trajectory [21,22], or that one of the two atoms is completely ejected. This is a known effect for F<sub>2</sub> on Si(100) [23] and would, thermodynamically, be allowed also for O<sub>2</sub>/Al(111).

In conclusion, we find that dissociation of O<sub>2</sub> on Pt(111) actually creates hot atoms, confirming former claims. This leads, however, to only a very limited transient motion, by distances of about two Pt lattice constants between the two O<sub>ad</sub> atoms, which is in good agreement

with a mechanism derived from recent MD simulations. Nevertheless, this effect may give rise to transient enhanced reactivity, in agreement with previous speculations [1], which might be of quite general relevance for heterogeneous catalysis.

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