

Hot precursors in the adsorption of molecular oxygen on Ag(110)

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Abstract

The molecular adsorption of oxygen on a Ag(110) surface was investigated by scanning tunneling microscopy at 60–70 K, where thermal mobility is suppressed. The data provide evidence for a hot precursor state of the molecules existing prior to their final accommodation in the chemisorption well. The molecules in the precursor state are highly mobile on the surface and can be trapped by collision with the equilibrated species, leading to the formation of pairs or short strings of molecules in the troughs of the Ag(110) surface along $[1\bar{1}0]$

The interaction of gas molecules with solid surfaces has been extensively studied in recent years [1–3]. Particularly interesting is the mechanism of surface chemical bond formation. For its accomplishment dissipation of the binding energy, momentum transfer and charge redistribution are required. The dynamics of these processes are far from being completely understood. Recent scanning tunneling microscopy (STM) experiments revealed transient motions of the atoms formed by the dissociative chemisorption of O₂ on Al(111) [4,5] and Pt(111) [6] surfaces. This effect was attributed to the formation of ‘hot’ atoms which carry the excess energy released in the process of dissociative chemisorption preferentially in a motion along the direction of the molecular axis and hence parallel to the surface. In the case of direct (non-dissociative) chemisorption one expects, however, energy exchange predomi-

nantly along the surface normal. Consequently, the particles should stick where they hit the surface. In the following we present evidence that even in such cases thermalization can be delayed, leading to the intermediate formation of a highly mobile metastable species, which preferentially accommodates by collision with other adsorbed particles. This state will be denoted a ‘hot precursor’ following its original introduction on the basis of indirect experimental evidence [7].

This Letter concerns the adsorption of oxygen molecules on a Ag(110) surface which is studied by STM at $T = 60–70$ K. This system has already been the subject of numerous investigations [8–16], agreeing on the molecular chemisorption in the temperature range between 50 and 150 K. Molecular beam studies demonstrate that the chemisorption well is reached directly (i.e. without involving the physisorbed state) by collision from the gas phase, whereby an activation barrier of about 0.2 eV has to be surmounted [15,16]. Surprisingly, it was also found that the sticking probability is enhanced with increasing $[001]$ momentum (parallel to the surface) of the

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impinging molecules [14–16] – quite opposite to plausible expectations [15]. This aspect will be illuminated below in connection with the present results.

The experiments were performed in an ultrahigh-vacuum (UHV) chamber with a base pressure of 5×10^{-11} Torr, equipped with standard facilities for sample preparation and characterization. The home-built STM employed is of beetle-type and is cooled by liquid He to temperatures as low as 50 K. Higher temperatures are achieved by counterheating the sample with a tungsten filament. The temperatures are measured with a NiCr–Ni thermocouple, attached directly to the sample. The temperature scale was checked with the CO desorption temperature on Ag(110) at 77 K [17]. The STM data are obtained in constant-current mode with tunnel currents typically between 0.3 and 1 nA and voltages of 0.5 to 1.0 V. The Ag(110) single crystal sample was prepared by cycles of Ar⁺ sputtering ($1 \mu\text{A}/\text{cm}^2$, 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, defect-free atomic terraces. Oxygen was adsorbed by backfilling the UHV chamber. Oxygen coverages are given in monolayers (ML), where 1 ML corresponds to 1 O₂-molecule per Ag(110) substrate atom. Exposures are given in langmuir (L, $1 \text{ L} = 1 \times 10^{-6} \text{ Torr s}^{-1}$).

At a sample temperature of 65 K the mobility of chemisorbed O₂-molecules on Ag(110) is so small that only a negligible number of jumps occurs over 100 s [18], the typical period for recording an STM image. Hence a random distribution of adsorbed particles is expected if these are accommodated instantaneously upon chemisorption. The image recorded instantaneously after 30 L O₂ exposure reproduced in Fig. 1a indicates that this is by no means the case. An atomic step is discernible running preferentially along $[\bar{1}\bar{1}0]$ as well as grey depressions ($\approx 0.15 \text{ \AA}$ deep), which are associated with the individual chemisorbed O₂ molecules. The inset in Fig. 1a shows a high resolution image where both the adparticles and the substrate topography are resolved. Either single adsorbates or ensembles containing 2 to 4 molecules are discernible, as illustrated by the model in Fig. 1b. The arrangement of the O₂-molecules in pairs or short strings with an intermolecular distance of 2 *a* ($a = 2.89 \text{ \AA}$ is the next-neighbor distance of Ag surface atoms in the close-

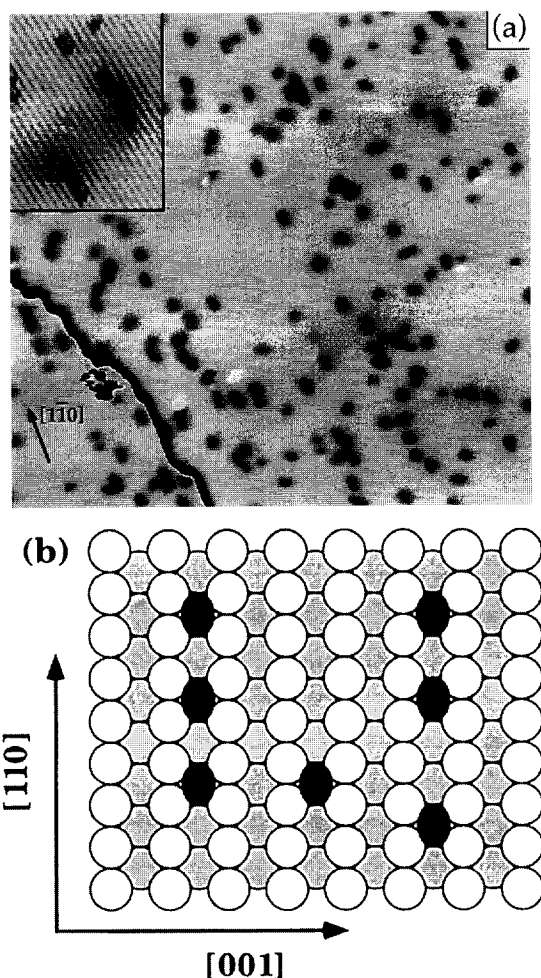


Fig. 1. (a) STM image from an Ag(110) surface with 0.02 ML O₂ at $T \approx 65 \text{ K}$ (recorded immediately after dosing 30 L O₂; $390 \times 340 \text{ \AA}^2$; $U_t = 0.7 \text{ V}$, $I_t = 0.3 \text{ nA}$); inset: atomic resolution image of the Ag lattice with adsorbed O₂ molecules; (b) corresponding model, black: adsorbed oxygen molecules, white (grey): Ag atoms of the surface (second) layer.

packed $[\bar{1}\bar{1}0]$ direction) in the troughs of the surface is the energetically favorable configuration of O₂ molecules in $[\bar{1}\bar{1}0]$ and associated with an attractive interaction energy of 0.04 eV [18]. Since the molecules do not occupy next-neighbor sites of neighboring troughs, the equilibrium saturation coverage of the molecules is concluded to be $\theta_{\text{sat}} = 0.25 \text{ ML}$, in accordance with earlier suggestions [8]. In addition to these structures oval depressions with a somewhat larger corrugation amplitude ($\approx 0.3 \text{ \AA}$,

corresponding to metastable ‘close pairs’ of oxygen molecules with an intermolecular distance of 1 Å in $[1\bar{1}0]$, as detailed below, and some defects, notably ~ 0.5 Å deep black spots, are resolved. The molecules are not attached to atomic step or other defects. In accordance with earlier studies [15], this signals that adsorption in the present system is not promoted by structural defects.

Agglomeration of adsorbed O_2 molecules was observed at even smaller coverages and with in situ STM measurements, also obtained upon adsorption at still lower temperatures, where the surface diffusion of thermally accommodated particles can safely be excluded. Fig. 2 shows the results of an analysis of the relative abundances of ensembles with $n = 1, 2$ and ≥ 3 O_2 molecules at varying coverages. Strings with $n = 3$ are even observed at $\Theta = 0.003$. For this coverage already about 40% of the adsorbed particles form ensembles with $n \geq 2$, and this fraction increases to more than 60% for $\Theta = 0.02$. For $\Theta = 0.003$ the probability of the occurrence of pairs resulting from statistical (random) adsorption would be merely 0.6%, i.e. nearly two orders of magnitude lower than what is actually observed.

At first sight one is tempted to attribute this effect to an increased sticking probability for an incident O_2 molecule in the vicinity of an already adsorbed particle, viz. by a lowering of the activation barrier. In this case the sticking coefficient $S(\Theta)$ is expected to increase with coverage until, with progressing coverage, site blocking will become dominant. Such data were derived in the present experiments simply by counting the density of adsorbed particles as a

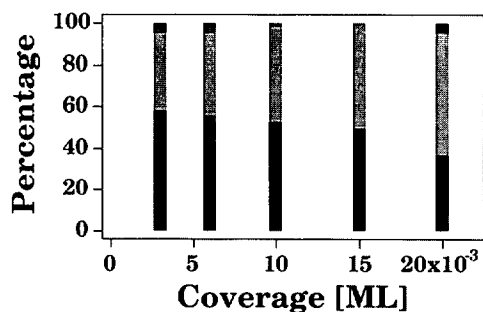


Fig. 2. Relative percentage of single (black), pairs (light grey) and strings (dark grey) of oxygen molecules vs. coverage in STM data upon the adsorption of oxygen at $60 \text{ K} \leq T \leq 67 \text{ K}$.

function of exposure. The initial sticking coefficient (for thermal kinetic energy) was derived to be $S_0 = 1.7 \times 10^{-3}$, while $S(\Theta)$ was found to strongly decrease (with a power of 3.9 of the density of free sites) already at the lowest coverages. These data are in good agreement with previous findings [15,16,19,20] and clearly rule out an enhancement of the sticking coefficient for O_2 molecules impinging from the gas phase near the adsorbed species. The strong decrease in S with Θ indicates an inhibiting effect, where one adsorbed molecule blocks about four adsorption sites, as expected from the saturation coverage.

We are thus left with the idea originally suggested by Harris and Kasemo [7]: after the molecule enters the chemisorption well, the adsorption energy is not released immediately. The adsorbed molecule rather remains in a highly mobile intermediate hot precursor state sliding across the surface. This suggestion is corroborated by scattering studies of the $O_2/\text{Ag}(111)$ system in which transient trapping-desorption without complete thermalization of chemisorbed O_2 molecules was observed [21]. For O_2 -adsorption on the $\text{Ag}(110)$ surface, where the sticking probability is much higher, this phenomenon does not exist. It was suggested that there thermal equilibration of the transient state is preferred to re-desorption [16]. The effect of the surface corrugation is thus twofold: on the one hand, it facilitates the formation of the hot precursor, as indicated by the higher sticking probability and its enhancement with increasing $[001]$ molecular momentum [14,16]. On the other hand, the moving hot precursor, which we associate with temporarily trapped species, can dissipate its energy more efficiently on the more open (110) surface. This effect is presumably related to higher diffusion barriers on $\text{Ag}(110)$ (determined to 0.22 eV in $[1\bar{1}0]$ and ≈ 0.3 eV in $[001]$ [18]). The present results demonstrate that equilibration is even more readily accomplished by collision with another adsorbate of the same mass. The preferential agglomeration at the lowest coverages indicates mean free paths of the hot precursors of the order of 100 Å. The anisotropic (110) surface corrugation potential [18] presumably causes faster motions in $[1\bar{1}0]$ than $[001]$.

The proposed mechanism is substantiated by further STM observations. Fig. 3a,b show STM images recorded from the same area at 67 K shortly after

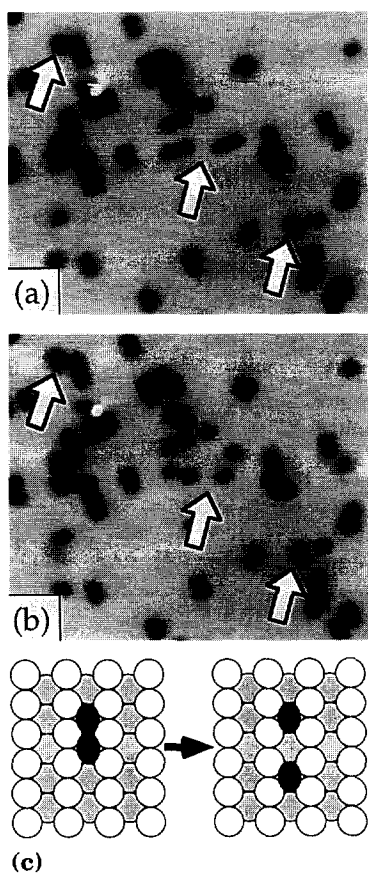


Fig. 3. STM image from Ag(110) with ≈ 0.02 ML O_2 at $T = 67$ K ((a), (b), $\Delta t = 800$ s, each $180 \times 140 \text{ \AA}^2$; $U_t = 0.5$ V, $I_t = 0.3$ nA), transformation of close pairs and movements of single molecules are indicated by arrows; (c) model for close pair transformation, black: adsorbed oxygen molecules, white (grey): Ag atoms of the surface (second) layer.

oxygen exposure (a) and 15 min later (b). A few of the individual molecules experienced thermally activated jumps to neighboring sites in $[1\bar{1}0]$ during this period, reflecting their almost immobile character. In addition, two elongated features arising from close pairs of O_2 molecules (i.e. separated by the metastable distance of 1 a) were transformed into pairs with an equilibrium distance of 2 a. The formation of such close pairs is energetically unfavourable because of the operation of a short-range repulsion [18], but with exposure at low enough temperatures, where thermal diffusion is suppressed, they are formed in up to about half of the regular pairs¹.

This effect is rationalized by the schematic energy

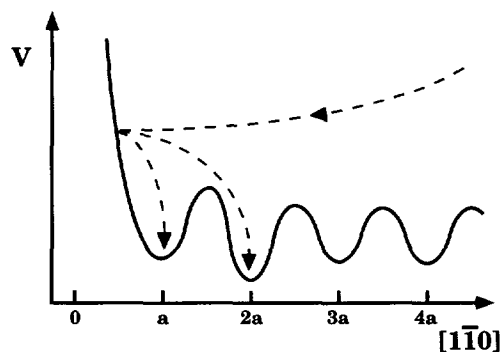


Fig. 4. Schematic potential of two O_2 molecules along $[1\bar{1}0]$ as a function of their mutual distance (full line) and trajectory for pair formation with a hot precursor molecule dissipating its excess energy by collision with an accommodated particle at $x = 0$.

diagram of Fig. 4: after overcoming the activation barrier for chemisorption at the point of impact, the hot precursor molecule slides across the surface until its excess energy is dissipated to the substrate, where it rests as a singleton, or it hits an already accommodated immobile particle, where the energy may become released efficiently allowing for accommodation of the molecule even at an unfavourable neighboring site. From there it may then migrate away on a much larger timescale by regular diffusion. The observation of close pairs is indeed regarded as a strong additional indication for the proposed mechanism of energy dissipation by direct impact onto another adparticle. This process bears similarities with the island formation observed in the course of *dissociative* chemisorption of O_2 on Al(111) [4,5] and step decoration by *physisorption* of Xe on Pt(111) [24].

The results of the present study demonstrate that the sticking of oxygen molecules on Ag(110) involves the transient formation of a chemisorbed hot precursor. The hot precursors are highly mobile on the surface and can be trapped by equilibrated species. It is suggested that this is a quite general phenomenon which is of relevance also for more

¹ The STM data demonstrate, in addition, that at $T < 70$ K a second metastable state for single molecules exists, in agreement with recent HREELS [22] and theoretical results [23] which transforms into the equilibrium species oriented along $[110]$ once the molecules become mobile.

complex surface reactions as, for example, involved in heterogenous catalysis.

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References

- [1] C.A. Arumainayagam, R.J. Madix, *Prog. Surf. Sci.* 38 (1991) 1.
- [2] C.T. Rettner, M.N.R. Ashfold (Eds.), *Dynamics of Gas-Surface Interactions*, The Royal Society of Chemistry, 1991.
- [3] R.I. Masel, *Principles of Adsorption and Reaction on Solid Surfaces*, John Wiley and Sons, 1996.
- [4] H. Brune, J. Wintterlin, R.J. Behm, G. Ertl, *Phys. Rev. Lett.* 68 (1992) 624.
- [5] H. Brune, J. Wintterlin, J. Trost, G. Ertl, J. Wiechers, R.J. Behm, *J. Chem. Phys.* 99 (1993) 2128.
- [6] J. Wintterlin, R. Schuster, G. Ertl, *Phys. Rev. Lett.* 77 (1996) 123.
- [7] J. Harris, B. Kasemo, *Surf. Sci.* 105 (1981) L281.
- [8] M.A. Barteau, R.J. Madix, *Surf. Sci.* 97 (1980) 101.
- [9] B.A. Sexton, R.J. Madix, *Chem. Phys. Lett.* 76 (1980) 294.
- [10] C. Backx, C.P.M.d. Droot, P. Biloen, *Surf. Sci.* 104 (1981) 300.
- [11] C.T. Campbell, *Surf. Sci.* 157 (1985) 43.
- [12] K.C. Prince, G. Paolucci, A.M. Bradshaw, *Surf. Sci.* 175 (1986) 101.
- [13] D.A. Outka, J. Stöhr, W. Jark, P. Stevens, J. Solomon, R.J. Madix, *Phys. Rev. B* 35 (1987) 4119.
- [14] L. Vattuone, C. Boragno, M. Pupo, P. Restelli, M. Rocca, U. Valbusa, *Phys. Rev. Lett.* 72 (1994) 510.
- [15] L. Vattuone, M. Rocca, C. Boragno, U. Valbusa, *J. Chem. Phys.* 101 (1994) 713.
- [16] A. Raukema, D.A. Butler, A.W. Kleyn, *J. Phys. C: CM* 8 (1996) 2247.
- [17] L.D. Peterson, S.D. Kevan, *J. Chem. Phys.* 95 (1991) 8592.
- [18] J.V. Barth, T. Zambelli, J. Wintterlin, R. Schuster, G. Ertl, *Phys. Rev. B*, in press (1997).
- [19] L. Vattuone, M. Rocca, C. Boragno, U. Valbusa, *J. Chem. Phys.* 101 (1994) 726.
- [20] H.A. Engelhardt, D. Menzel, *Surf. Sci.* 57 (1976) 591.
- [21] A. Raukema, A.W. Kleyn, *Phys. Rev. Lett.* 74 (1995) 4333.
- [22] F. Bartolucci, private communication.
- [23] P.A. Gavril, D.M. Bird, J.M. White, *Phys. Rev. Lett.* 77 (1996) 3933.
- [24] P.S. Weiss, D.M. Eigler, *Phys. Rev. Lett.* 69 (1992) 2240.