Direct observation of mobility and interactions of oxygen molecules chemisorbed on the Ag(110) surface

J. V. Barth,* T. Zambelli, J. Wintterlin, R. Schuster, and G. Ertl

Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, D-14195 Berlin, Germany

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The energetics of thermal motions and interactions of oxygen molecules chemisorbed on a Ag(110) surface were investigated by scanning tunneling microscopy at 60–100 K. Surface mobility is anisotropic, preferably in the [1$\bar{1}$0] direction with an activation energy of 0.22 ± 0.05 eV and a preexponential factor of $1\times10^{13\pm3}$ s^{-1}. Along the [1$\bar{1}$0] direction a repulsive interaction between nearest neighbors of about 0.02 eV and an attraction of 0.04 ± 0.01 eV between next nearest neighbors were derived. Along [001] appreciable repulsion exists between nearest neighbors, while a ''diagonal'' arrangement of molecules is associated with an attraction of 0.02 ± 0.01 eV. The data are indicative for the operation of indirect, substrate-mediated molecule-molecule interactions. [S0163-1829(97)01516-6]

The mobility and the interactions of adsorbed particles are key aspects in surface physics and chemistry. A thorough knowledge of these parameters is indispensable for a better understanding of surface chemical reactions and catalysis. Adsorption of oxygen on metal surfaces is particularly interesting since chemisorbed oxygen is involved in many surface reactions of technical significance. Silver is one of the few metals which allow for a study of the nondissociative chemisorption of molecular oxygen on a metal surface. The molecularly bound oxygen molecules represent the precursors to dissociatively adsorbed oxygen and are thus important for an understanding of the nature of the oxygen metal interaction. In particular, the O_2/Ag(110) system received considerable attention, where molecular adsorption was found in the temperature range between 50 and 150 K.[1–8] Electron energy loss spectroscopy (EELS),[2] angle-resolved photoemission,[5] and near edge x-ray absorption fine structure[6] (NEXAFS) data indicate that the molecules are located in the troughs of the silver lattice with their molecular axis oriented along the [1$\bar{1}$0] direction and with their bond length increased from 1.21 Å of the free molecule to 1.47 Å.[6] Most of the studies agree that the O_2 molecules are bound as a peroxo (O_2^{2-}) species, a view which is confirmed by theory.[9–12]

Nothing is known about the local order, mobility, and the interactions between the adsorbed O_2 molecules. No superstructures were observed by low-energy electron diffraction (LEED). Hence it was concluded that the interaction between the negatively charged molecules is repulsive and that they are randomly distributed on the surface. In this paper we report data from scanning tunneling microscopy (STM) which provide an answer to the above questions. As our STM allows temperature-controlled measurements, the experiments provide kinetic parameters which elucidate the nature of this chemisorption system. In particular, the first direct determination of the activation energy for surface diffusion of chemisorbed molecules and an analysis of their interactions are reported.

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 the beetle type and is cooled by liquid He to temperatures as low as 60 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.[13] The STM data are obtained in the constant-current mode with tunnel currents typically between 0.3 and 1 nA and voltages of 500–1000 mV. 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, 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 O_2 molecule per Ag(110) substrate atom.

The equilibrium configuration of a small amount of O_2 molecules on Ag(110) (≈0.02 ML) at 60 K is represented by the image in Fig. 1(a). For this experiment, O_2 was dosed with the sample at 100 K followed by brief annealing to ≈150 K ($T\approx120$ K is sufficient for equilibration). The data were recorded after cool down to 60 K and comprise the typical structural elements also found for higher coverages. The atomic [1$\bar{1}$0] rows of the Ag(110) lattice are clearly resolved (corrugation amplitude: 0.03 Å). In the troughs apparent depressions are found (≈0.15 Å deep), which correspond to individual chemisorbed O_2 molecules. Resolution of the internal structure of the molecules could not be achieved. The majority of the molecules are arranged in strings of n ($n=2,3,4,5$) molecules along [1$\bar{1}$0], with an intermolecular distance of $2a$ ($a=2.89$ Å and $b=4.09$ Å are the surface lattice constants of Ag(110) in [1$\bar{1}$0] and [001], respectively). A structure model is depicted in Fig. 1(b) (STM data not presented here indicate that the molecules occupy the fourfold hollow site on the surface). The observation of these strings of molecules signals the operation of attractive interactions along the [1$\bar{1}$0] direction. More specifically, the preferred separation of $2a$ indicates repulsion between nearest neighbors and attractions between next near-
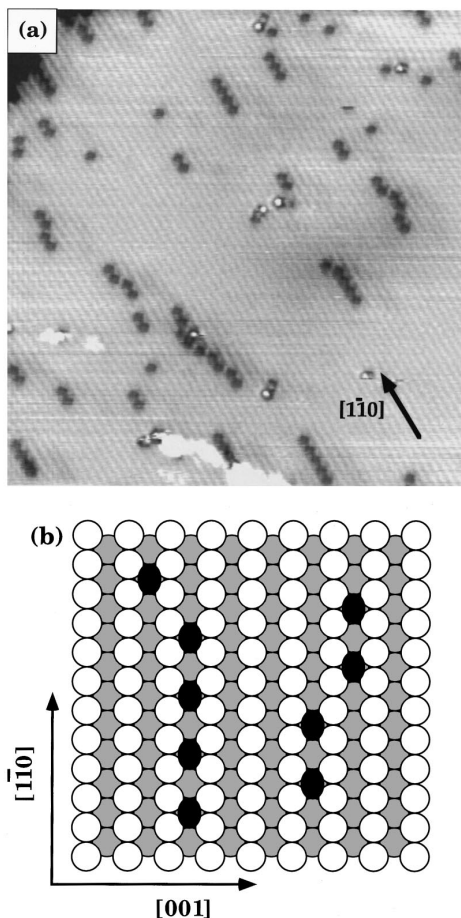
FIG. 1. (a) STM image from a Ag(110) surface with ≈ 0.02 ML O_2 at $T \approx 60$ K (after dosing O_2 at 100 K and flash to 150 K; 270×240 Å^2); (b) ball model for molecular oxygen adsorbed on Ag(110) [white (gray) circles, top (second) layer atoms; black ovals, adsorbed O_2 molecules].

est neighbors along this direction. On the other hand, O_2 molecules were never found in neighboring sites along [001] over the entire coverage range investigated (up to 0.1 ML), indicating pronounced repulsions in this direction.

At $T = 60$ K the arrangement of the O_2 molecules does not change on the time scale of the STM measurement. For temperatures exceeding ≈ 65 K, however, the thermal motion of the molecules on the surface can be directly monitored. This is demonstrated by the images in Fig. 2, where O_2 was adsorbed at 120 K, to ensure an equilibrated initial arrangement. The data were subsequently recorded at $T = 76$ and 80 K in intervals of 200 and 100 s, respectively. Again single molecules and strings of molecules are visible; the atomic Ag lattice is not resolved here. There is also a number of larger black dots, which are single oxygen atoms. This follows from experiments under different conditions which will be presented elsewhere. Since they are immobile in the present temperature range (and apparently do not interact with the molecules) they can serve as markers to identify the scanned areas. It is immediately evident that the patterns formed by the O_2 molecules change between the two measurements (some changes are indicated by arrows). At $T = 76$ K [Figs. 2(a) and 2(b)], a large fraction of the single molecules do not appear at the site where they were observed 200 s earlier, a smaller fraction of diagonally coupled (i.e., adsorbed in the trough next to a string with the preferred

distance $2a$ in [$1\bar{1}0$]) molecules are detached, and one O_2 pair separated. These changes are associated with thermal motions. In a quantitative analysis of larger series of STM patterns, the proportions of the molecules which move in the time interval between the recording of subsequent STM images were determined. (At temperatures below 80 K, where the motions of individual molecules can be traced, long jumps occur frequently, in accordance with expectations for weakly bound gas molecules on a metal surface.[14] They were found to exist over the accessible temperature range of about 10 K, indicating that surface diffusion of the molecules is controlled by a single activation barrier, in contrast to results for strongly bound metallic adsorbates.[15]) The corresponding hopping rate of single molecules at 76 K is $\nu_s = 0.0061$ s^{-1}. In an analogous way, the detachment of diagonally coupled O_2 molecules is determined to be less likely with a rate of $\nu_d = 0.0023$ s^{-1}. The pair dissociation rate ν_p is even smaller: $\nu_p = 0.0002$ s^1, which is only $0.03\nu_s$. The lower rates of the latter processes are in accordance with the attractive interactions between the molecules expected from the equilibrium configuration.

Upon increasing the temperature to 80 K, the motions become faster, as obvious from an inspection of Figs. 2(c) and 2(d). Due to the reduced residence time at a site, the single molecules are not imaged entirely now. Rather they show up only in a limited number of neighboring scan lines, before they hop away during the measurement, leading to the characteristic ''cutoff'' features in the topographs. Now the hopping rates can be obtained from the number of scan lines in which the molecules are imaged on their original sites: The probability that a particle remains at a given site after time τ is $P(\tau) = \exp(-\nu_s \tau)$, where ν_s is the desired hopping rate, τ was chosen such that it corresponds to the time necessary to image a molecule entirely, or, at higher temperatures, a certain fraction of it, for which the number of scan lines times the scanning period (of the fast x direction) was taken. Accordingly, $[1 - P(\tau)]$ is the fraction of molecules that jumped within this time interval and the rates are obtained from a statistical analysis of scan line distributions of series of images. The hopping rate of single molecules at 80 K is thus determined to be 0.18 s^{-1}. This value was determined from data at different scan frequencies, excluding the possibility of tip-induced effects. Hopping frequencies for single O_2 molecules could be determined by this method for temperatures up to 100 K, where the majority of the molecules are imaged only in single scan lines. The data in Fig. 2 also demonstrate that the motion of the O_2 molecules is exclusively in [$1\bar{1}0$]. Anisotropic diffusion is intuitively expected from the O_2 adsorption in the troughs and the symmetry of the surface [cf. the model in Fig. 1(b)]. Evidence for hopping in [001] is found only for temperatures exceeding ≈ 100 K. These findings are in qualitative accordance with the observation of anisotropic diffusion of strongly bound metallic adsorbates on a fcc(110) metal surface.[16]

An Arrhenius plot of the hopping frequencies of single molecules is presented in Fig. 3(a). The data fall on a straight line, the slope of which yields the activation energy for surface diffusion along [$1\bar{1}0$]: $E_s^* = 0.22 \pm 0.05$ eV. The corresponding preexponential factor is determined to be $\nu_0 = 1 \times 10^{13 \pm 3}$ s^{-1}, in accordance with expectations. The
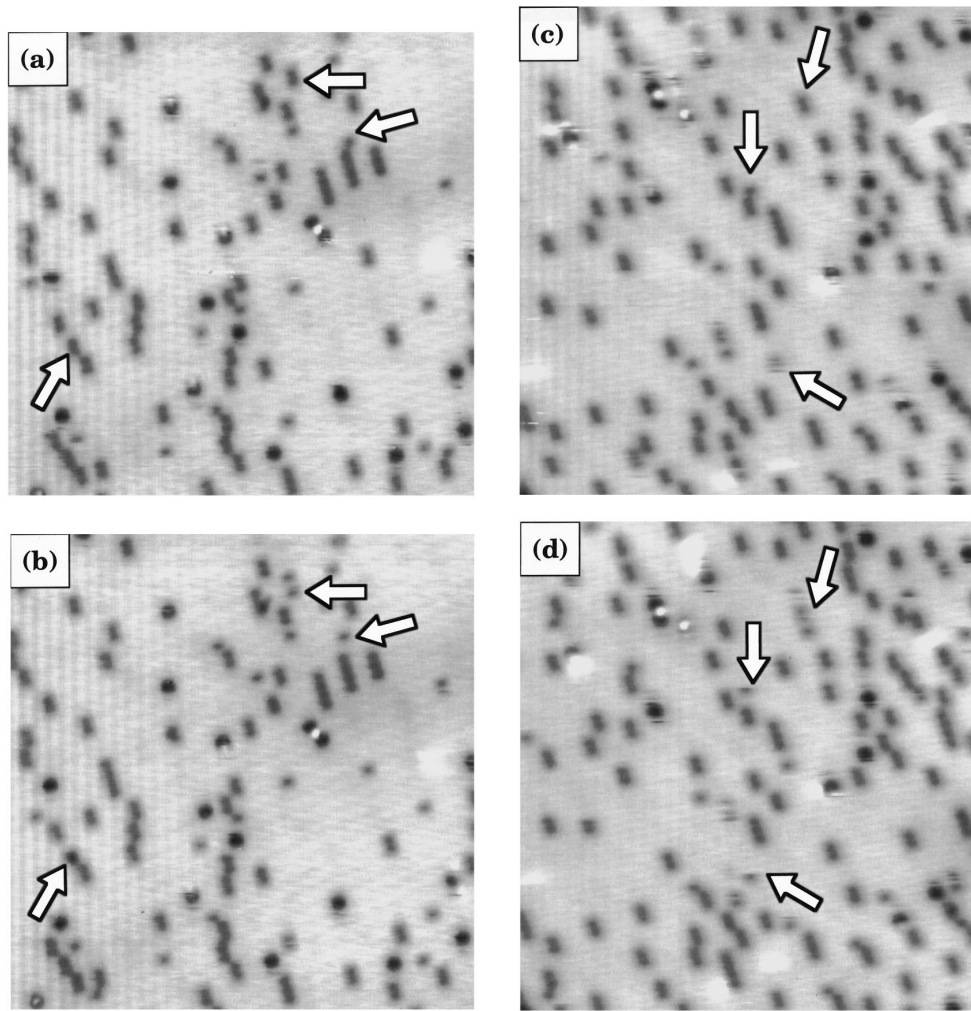
FIG. 2. STM image from Ag(110) with ≈ 0.02 ML O_2 at $T=76$ K [(a) and (b) $\Delta t=200$ s, 250×240 Å^2] and $T=80$ K [(c) and (d) $\Delta t=100$ s, 250×240 Å^2].

activation energy for surface diffusion in $[00\bar{1}]$ cannot be determined exactly, since the motions in $[1\bar{1}0]$ obscure an analysis of the data. However, motions in $[001]$ become observable at $T\approx100$ K in the STM data. This indicates a hopping frequency of the order of 10^{-4} s^{-1} in $[001]$ at this temperature, from which an energy barrier of ≈0.3 eV is estimated (assuming a preexponential factor of 1×10^{13} s^{-1}).

Diffusion barriers are expected to be of the order $\frac{1}{5}$ of the binding energy.[17] This means for the present system that the binding energy of the O_2 molecules should be around 1 eV. This value is considerably higher than the binding energy obtained from an analysis of thermal desorption (TD) data (0.4 eV).[4] It was argued, however, that the TD analysis of the present system is obscured by dissociation of O_2, which was found in the same temperature range.[3] The estimate of ≈1 eV is, however, in rough agreement with theoretical results, where a binding energy of 0.78 eV was calculated for the peroxo species on Ag(110).[11]

In the following the interactions of the chemisorbed molecules are discussed. The potential energy in $[1\bar{1}0]$ for two O_2 molecules is sketched in the diagram in Fig. 4, which reflects the repulsion between nearest neighbors and attraction between the next nearest neighbors. This diagram is

constructed from the activation energies determined from the STM observations. The dissociation of a pair of oxygen molecules can be interpreted as a surface diffusion process, where an increased barrier has to be surmounted. Dissociation rates ν_p obtained from an analysis of series of subsequent images at three temperatures are included in Fig. 3(b). The corresponding activation energy is $E_p^*=0.26\pm0.05$ eV [using $E_p^*=-kT\ln(\nu_p/\nu_0)$; $\nu_0=1\times10^{13\pm3}$ s^{-1}]. In an analogous way the detachment rates ν_d and the corresponding activation energy for detachment of diagonally coupled O_2 molecules was evaluated to $E_d^*=0.24\pm0.05$ eV. Hence we conclude that the next nearest neighbor attractive energy along $[1\bar{1}0]$ is $E_p^*-E_s^*=kT\ln(\nu_s/\nu_p)=0.04\pm0.01$ eV, and that along the diagonal is $E_d^*-E_s^*=0.02\pm0.01$ eV. (The error bars of these values are smaller than those of the absolute energies; they are derived from the ratios of the rates, where the preexponential factors cancel. Since in the two cases hopping events of entire pairs or strings were counted, respectively, a factor of $\frac{1}{2}$ is included in the preexponential factor, due to the fact that the molecules can hop only in one direction. For the pairs this cancels, however, because both molecules can jump.)

Occupation of nearest neighbors sites in $[1\bar{1}0]$ is not excluded for the molecules and could be observed upon adsorp-
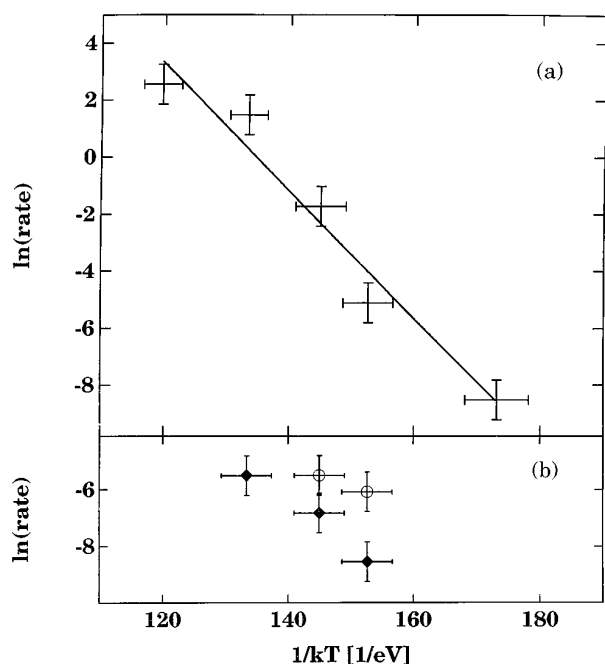
FIG. 3. Arrhenius plots of the (a) hopping rates for single and (b) detachment and pair dissociation rates for diagonally coupled (○) and pairs (◆) of oxygen molecules, respectively.

FIG. 4. Schematic potential diagram in the $[1\bar{1}0]$ direction for an O_2 molecule interacting with another molecule located at the origin; E_s^* (E_p^*) corresponds to the activation energy for single molecule surface diffusion (pair dissociation).

tion at the lowest temperatures as a metastable structure. The dissociation rate of such pairs was found to be close to the hopping frequency of single molecules, corresponding to an activation energy of $\approx 0.22 \pm 0.05$ eV. Hence such metastable pairs are observable on the same time scales as single O_2 molecules. However, their formation from separate molecules was only scarcely observed. An example is illustrated by the STM data in Fig. 2: a pair of oxygen molecules in the lower left of Fig. 2(a) merges into an oval depression in Fig. 2(b) (indicated by an arrow). In the next frame the initial pair was resolved again. The observed formation rate from two O_2 molecules at equilibrium distance is of the order of 10^{-5} s^{-1} at 76 K, from which an activation energy of $\approx 0.28 \pm 0.05$ eV is estimated. The energy barrier for their formation is thus significantly higher than that for dissociation of the equilibrium pairs with a repulsive interaction energy for the two O_2 molecules with a distance of $1a$ in $[1\bar{1}0]$ of $\approx 0.02 \pm 0.02$ eV, as sketched in Fig. 4. The magnitude of the repulsive interaction energy in the [001] direction cannot be extracted from the present data. Since under all conditions
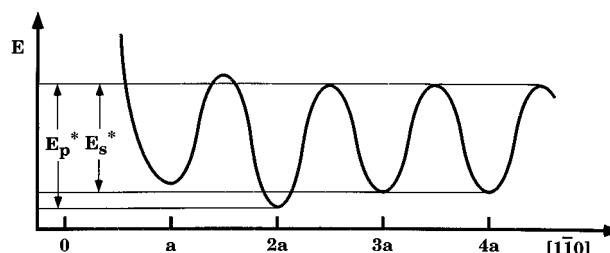
a minimum separation of neighboring molecules of $2b$ in [001] was maintained, and since no molecules or strings in neighboring troughs with a distance of merely $1a$ $[1\bar{1}0]$ were found, the magnitude of these short-range repulsions exceeds that of the attractions significantly.

Interactions between adsorbates on metal surfaces are usually classified in direct (van der Waals, electrostatic, bond formation) and indirect, substrate-mediated (elastic or electronic) interactions.[18] Electrostatic interactions are certainly present—O_2 adsorption causes a sizable work function increase—and must be repulsive. Since we find a net attraction, other interactions must be stronger, and the interactions are not dominated by electrostatics. Bond formation can be ruled out because of the large equilibrium distances and hence small orbital overlap. van der Waals interactions are in the same order of magnitude as the attractive energy found here: $(O_2)_2$ van der Waals molecules have a heat of formation of 0.023 eV and an average molecular distance of 4.8 Å,[19,20] similar to the $2a$ distance observed here. However, for a linear end-to-end arrangement of oxygen molecules, as is the case here, calculations indicate an interaction energy of only 0.006 eV,[20] too low to explain the observations. This suggests the presence of additional attractive O_2-O_2 interactions that are mediated by the substrate lattice. Their strength and range over about two lattice constants are characteristic for indirect electronic (''through bond'') interactions as suggested already in early theoretical models of the chemisorption bond.[21–23]

*Permanent address: Institute de Physique Expérimentale, Ecole Polytechnique Fédérale de Lausanne, PHB-Ecublens, CH-1015 Lausanne, Switzerland. Electronic address: johannes.barth@ipe.dp.epfl.ch

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