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Physisorption versus chemisorption of oxygen molecules on Ag(100)

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We compare the adsorption of oxygen molecules on Ag(100) at 60 K and at 100 K. At both temperatures, the molecules form islands. Differences between the species adsorbed at the two temperatures in both low-temperature scanning tunneling microscopy and inelastic electron tunneling spectroscopy are attributed to two different adsorption states, a chemisorbed state after 100 K adsorption and a physisorbed state after 60 K adsorption. © *2016 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4945339]

Molecule-surface interactions of non-reactive molecules are often characterized by a two-well potential with a physisorption and a chemisorption well.[1] Physisorbed and chemisorbed molecules differ in their physico-chemical properties, because the electronic structure of physisorbed molecules is much less altered from their gas phase structure than the one of the chemisorbed molecules. For instance, an azobenzene dye that was trapped in its physisorption well via adsorption at 20 K is photoisomerizable in contrast to the chemisorbed species.[2]

Oxygen molecules are of particular importance, because their spin state in the gas phase differs from the one of the chemisorbed molecules.[3] For oxygen molecule adsorption on Ag(111), the existence of a physisorption well has been proposed 30 years ago and discussed intensely.[4–7] Molecules with low incident energy sample the physisorption state first. Based on this idea, some experimentally observed unconventional scattering properties were rationalized in terms of scattering from a dual repulsive well arising from physisorption and chemisorption.[8] The energy dependence of the scattering was attributed to a decreasing trapping probability into the physically adsorbed state with increasing incident energy. This indirect evidence for the existence of physisorbed states was questioned recently by DFT (density functional theory)-based classical dynamics simulations on a six-dimensional potential energy surface.[9] The study confirmed though that a physisorption state at large distance is important for the scattering properties of the Ag(111) surface.

Vibrational energies were measured for oxygen adsorbed on Ag(110).[10] These combined EELS and TDS measurements revealed that only one of the two chemisorbed species dissociates thermally. For this system, unusual inelastic electron tunneling spectroscopy (IETS)[11] data were explained and a paramagnetic nature of the oxygen molecule was revealed.[12] When a molecular state is resonant with the Fermi energy, virtual vibrational excitations are important for the process of inelastic tunneling leading to a decrease in conductance.[13] More recently, calculations related the dissociation with coupling to the surface Rayleigh mode.[14]

For the here investigated system O_2/Ag(100), molecular species are observed below 130 K by HREELS (High Resolution Electron Energy Loss Spectroscopy).[15] The spectra indicated two different adsorption sites of similar binding energy with slightly shifted vibrational energies of 79 and 84 meV. Different sites were identified in a STM (Scanning Tunneling Microscopy) study[16] and possible adsorption sites of chemisorbed molecular oxygen were calculated by molecular orbital calculations,[17] though these might suffer from inaccuracy of the calculations at that time. Already this early study showed that molecular oxygen adsorbs in a hollow site with the oxygen atoms pointing towards bridge sites with a binding energy of 1.99 eV. The binding energy of molecular oxygen adsorbed in a bridge site is lower by 0.07 eV only. The hollow site was confirmed by molecular dynamics (MD) simulations, using the density matrix-based tight-binding (TB) method[18] and more recently by DFT calculations with several functionals.[19] The latter study questioned the assignment of two only slightly different vibrations in HREELS to two distinct adsorption sites. However, this latter study also indicated that there is a second, meta-stable adsorption configuration. In this configuration, the molecule is adsorbed with its axis perpendicular to the surface, also at the hollow site. Molecules in the two adsorption sites differ in their vibrational spectra. The symmetric molecule-metal stretch is expected at 26 meV and at 9 meV for parallel and perpendicular adsorption geometries, respectively. After low temperature adsorption, indeed, molecules of different shapes, elliptical and round, were observed by STM.[20]

In this article, we present real-space and local spectral information of oxygen adsorbed within islands on Ag(100) at two different temperatures gathered by low-temperature scanning tunneling microscopy and inelastic electron tunneling spectroscopy. Adsorption at 100 K and 60 K leads to chemisorbed and physisorbed molecules, respectively, as evident from both the apparent height of the molecules in STM images and their inelastic spectra. Our study presents the first real-space evidence for a physisorbed oxygen molecule.

STM measurements are performed with a low-temperature STM under ultra-high vacuum conditions (base

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pressure $\leq 2 \cdot 10^{-10}$ mbar).[21] The STM is housed in a UHV chamber with standard facilities for sample cleaning and preparation. The single crystalline Ag(100) surface is cleaned by cycles of Ar$^+$-sputtering at 550 eV (p = $2.5 \cdot 10^{-5}$ mbar, I = 3 μA) and annealing at 900 K for 3 min. The measurements are performed at 5 K in constant current mode. The voltages are applied to the sample with respect to the tip.

For molecule deposition, an oxygen pressure of $1 \cdot 10^{-7}$ mbar to $5 \cdot 10^{-5}$ mbar is established in a separately pumped chamber. The cleanliness of the gas is checked by a quadrupole mass spectrometer. Sixteen pump and refill cycles and eight baking cycles are performed until a gas purity of 99.6% is achieved (oxygen: residual gases ratio of 250:1). The molecules are deposited on the sample, at 60 K or 100 K, by positioning the sample in front of the valve to the oxygen flooded chamber. The valve between both chambers is opened for 10 s for a coverage of 0.006 ML at the low temperature and for up to 2.5 min at the higher temperature.

IET spectra are recorded in a lock-in technique. The lock-in amplifier is set to the first harmonic of a sinusoidal modulation voltage (388.8 Hz, 5 or 7 mV, peak-to-peak) that is superimposed to the bias voltage. The slowly varying surface spectrum, as measured on the same image at several nanometer distance from the adsorbate, is subtracted. The difference is numerically differentiated yielding the second derivative of the current with respect to the voltage. We opt for this method instead of IET spectra recorded with the lock-in amplifier set to the second harmonic, because it reduces the interaction time of the tunneling electrons with the molecules. A short interaction time is important, in particular for the physisorbed molecules, in order to avoid restructuring of the islands, leading to artifacts in the spectra. Numerical differentiation is possible, because the steps in conductivity are clearly discerned in the dI/dV spectrum. The spectra are measured with a set point at −300 mV and (0.5 ± 0.1) nA. The spectra shown are the average of around five spectra measured at the (approximate) center of equivalent islands in order to avoid edge effects.

Fig. 1 compares islands formed at the two temperatures. At first sight, the islands look very similar, being branched without any apparent order. However, the apparent height of the islands differs considerably (Fig. 1(e)). Disregarding the bright protrusions (attributed to second layer species), the apparent height of the molecules deposited at 100 K
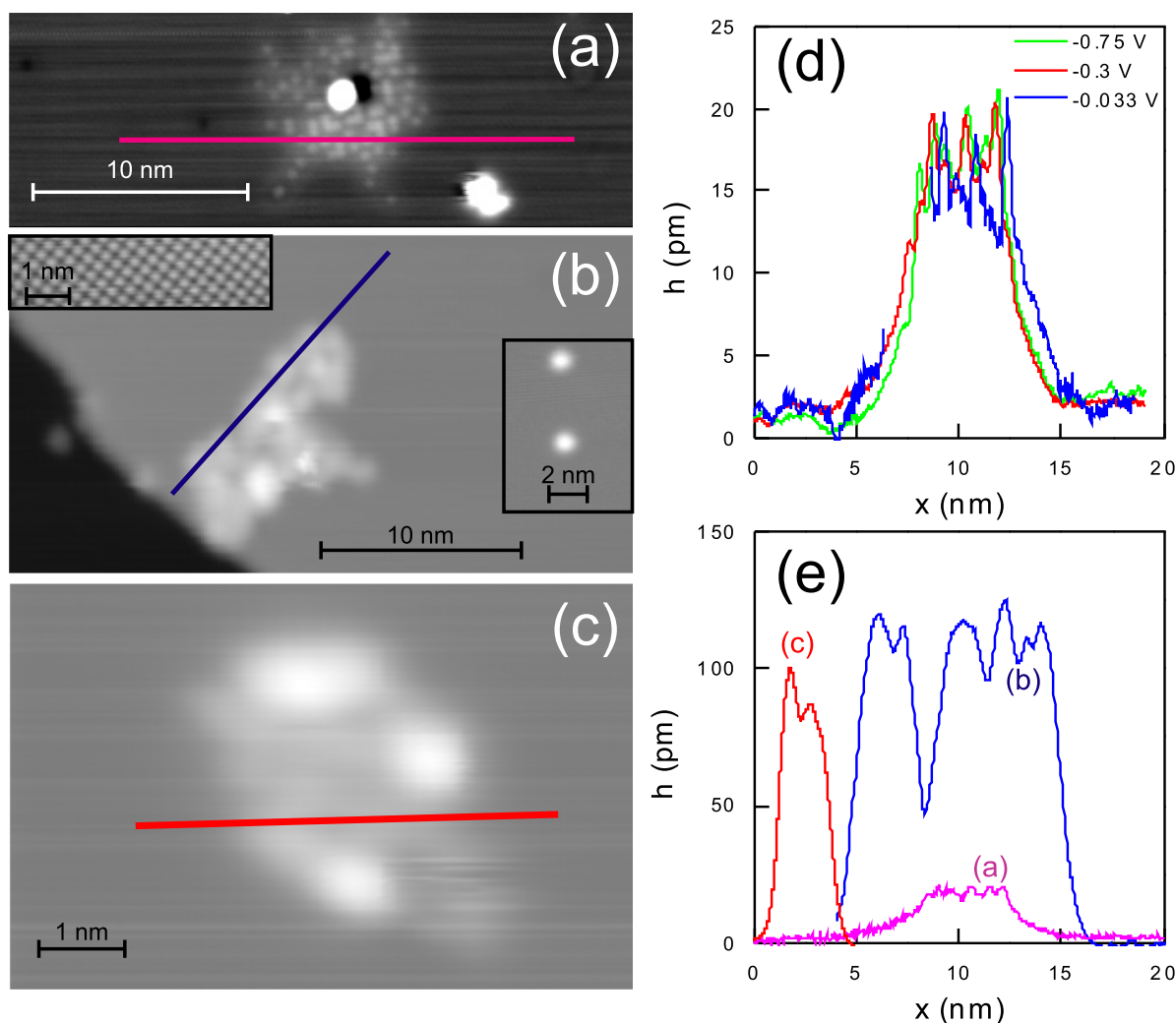

FIG. 1. STM images of oxygen molecules after adsorption at (a) 60 K; V = −300 mV, I = 10 pA, 5 K; ((b) and (c)) 100 K: (b) V = −1.088 V, I = 20 pA; inset left: atomic resolution of surface, V = 4 mV, I = 2.8 nA, 5 K; inset right: single molecules, U = 1.032 V, I = 8 pA, 5 K (c) 100 K; V = −0.34 V, I = 0.1 nA, 5 K; (d) line scans across island as indicated in panel (a) at different voltages (e); line scans across islands as indicated in panels (a)–(c).

is, at more than 100 pm, almost 5 times larger than one of the molecules deposited at 60 K, at less than 20 pm (Fig. 1(e)). This difference in height persists over the voltage range probed. For the molecules deposited at 60 K, there is no change in the range of −0.1 to −0.8 V and a very small reduction in height below 100 V (Fig. 1(d)). For the molecules deposited at 100 K, the variation in apparent height is less than 20% over the voltage range between −1 V and +1 V (Fig. 1(e)). The large difference in apparent height is a first indication for two different species after adsorption at two different temperatures. Note that both apparent heights hardly vary in the accessible voltage range. As apparent heights of molecules depend on both, electronic and geometric effects, the smaller apparent height could indicate both, a smaller molecule-substrate distance or less overlap of the molecular orbitals with electronic states of the surface.

Before discussing this origin further, we substantiate our interpretation by the IET spectra presented in Fig. 2, because recent work about the adsorption strength of a molecule showed that it is reflected in its inelastic electron tunneling (IET) spectrum.[22] Thus, the spectroscopy is performed on islands. IET modes of *meta*-chlorobenzene on the reconstructed Au(111) surface chemisorbed at the elbow sites have a larger intensity than the ones of the molecule physisorbed on hcp or fcc sites. In addition, they are shifted in energy in accordance with chemisorption mainly through the chlorine bond.[22] Though at lower coverage, single molecules exist on the surface (Fig. 1(b), inset), these are induced to diffusion during spectroscopy. Spectra for both types of oxygen molecules investigated here are point symmetric indicative for a vibrational origin of the maxima/minima. The mere existence of maxima in the spectra confirms that the molecules do not dissociate during adsorption as IET spectra of oxygen atoms on Ag(100) are featureless in the region up to 250 meV.[23]

There are two differences between the spectra. The spectra are inverted and the peak position differs. Concerning the inversion, the spectra are inverted with a peak on the positive side in the spectrum for low temperature adsorption, and a dip in the one for 100 K adsorption. We discuss this

difference in view of the established two contributions to the tunneling current.[24] While the opening of the inelastic channel at the vibrational energy increases the conductivity, the conductivity of the elastic channel decreases. Often the change in inelastic channel dominates, leading to a peak at the positive side of the IET spectrum and a dip at its negative side. A dip on the positive side of the Fermi energy implies that the conductivity change in the elastic channel dominates over the one in the inelastic channel. Such a large conductivity decrease of the elastic channel is possible, if an electronic level is close to or crosses the Fermi level.[13] While the electronic levels do not shift towards the Fermi level for physisorbed molecules, chemisorption might lead to an orbital shift that is large enough to let one of the frontier orbitals cross the Fermi level. The broadening and shift of the orbitals were calculated at different levels of theory for chemisorption of O_2 on Ag(110),[12] Al(111),[25,26] and Pd(100).[19,27] Indeed, some parts of the 2π-orbitals shift across the Fermi energy on these surfaces. Thus, the inverted symmetry of the spectrum after 100 K adsorption supports chemisorption at 100 K.

Concerning, the position of the maxima, the Gaussian fits to spectra after 100 K adsorption yield maxima at −(41 ± 3) meV while fits to spectra after 60 K adsorption yield maxima at a lower energy of (28 ± 2) meV. The internal stretch mode measured by HREELS at around 80 meV is not observed.[15] The authors of Ref. 15 attributed an energy loss at 30.5 meV to external Ag–O_2 vibrations. Both broad peaks observed here cover this frequency. We thus attribute them to external vibrations of the molecule. Their broadness and some shoulders suggest that several external vibrations contribute to the maximum.

The red-shift of the spectrum for 60 K adsorption to lower energy as compared to the spectrum for 100 K adsorption is consistent with a weakening of the bond to the surface as expected for physisorbed molecules in contrast to the chemisorbed ones. Preliminary theory shows a similar amount of shift between parallel and perpendicular adsorption geometries from 25 to 8 meV (Ref. 19, cf. Introduction), though the absolute values differ. This suggests that physisorbed
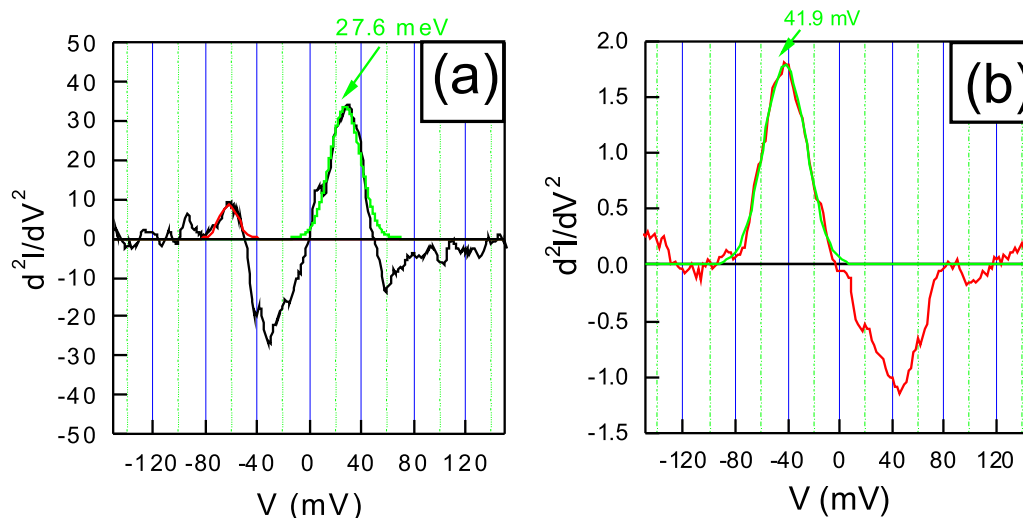

FIG. 2. IET spectra of (a) Molecules adsorbed at 60 K (b) Molecules adsorbed at 100 K.

molecules are adsorbed with their axis perpendicular to the surface and chemisorbed ones in parallel.

Having confirmed that the two adsorption temperatures lead to two different adsorption states of the molecules, we finally discuss possible origins of their different apparent heights in the STM image in terms of phase and amplitude differences between direct and molecular tunneling channels assuming that the tunneling flow of electrons between the tip and the sample can be decomposed into different tunneling channels.[28–30] If there was no hybridization of orbitals due to adsorption, the 2π-orbital would be at the Fermi level, and hence that orbital would open the dominant channel for tunneling. However, if the molecule lies parallel to the surface, the overlap between the tip and the 2π orbital is very small and actually zero, if the tip is right on the bisecting plane perpendicular to the molecular bond. Thus, only hybridization with, e.g., the 1π orbital would enhance the overlap, since this orbital is symmetric. The stronger bonding of the oxygen orbital with the substrate mixes the orbitals and consequently increases the overlap between the tip and the frontier orbital. If the bonding between the substrate and the molecule is weak as in physisorption, the molecular orbitals remain more like those of a free molecule. Hence, the anti-symmetry of the frontier orbitals makes the tip-molecule overlap very small, which would weaken the current through the molecule. This reasoning holds, if both, the physisorbed and the chemisorbed molecules were adsorbed in parallel to the surface.

If we further assume that the physisorbed molecule is not adsorbed with its molecular axis in parallel, but perpendicular to the surface, the π orbitals would have a nodal plane perpendicular to the surface also leading to a much smaller tunneling signal. A weaker signal is expected from the physisorbed species than from the chemisorbed species in both cases, consistent with our experiment.

In conclusion, we present the first real-space evidence of two adsorption states of oxygen molecules on a metal surface, a physisorbed one and a chemisorbed one. The apparent height is much smaller for the physisorbed than for the chemisorbed species. Moreover, IET spectra differ in structure and mode position consistent with the physisorbed and the chemisorbed species. We thus demonstrate that oxygen may be trapped on Ag(100) in its physisorption well by low-temperature adsorption at 60 K and below. Spin-resolved STM should be able to determine, whether or not the spin state of the gas phase molecule is conserved during adsorption.

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