# Azimuthal Dependence of Sticking Probability of $O_2$ on Ag(110)

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The chemisorption dynamics of $O_2$ and Ag(110) was studied by molecular beams and high resolution electron energy loss spectroscopy by measuring the initial sticking probability $S_0$ as a function of the molecular translational energy $E_i$ and angle of incidence $\theta_i$ along $\langle 001 \rangle$ and $\langle 1\bar{1}0 \rangle$. $S_0$ scales as $E_i \cos^n \theta_i$ with $n = 1.1$ along $\langle 001 \rangle$ and $n = 1.6$ along $\langle 1\bar{1}0 \rangle$. This indicates that parallel momentum has a role in promoting adsorption. The effect is connected to the amplitude of the corrugation seen by the $O_2$ molecule.

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New insight into the dynamics of the adsorption process in chemisorption has been found recently by using molecular beam techniques to study the dependence of the adsorption probability on incident kinetic energy $E_i$, angle of incidence $\theta_i$, surface temperature $T_s$, surface coverage $\Theta$, and internal energy of the beam. The observed features indicate that adsorption is a very complicated phenomenon which can hardly be explained in terms of a simple one-dimensional barrier as was done, for instance, in the pioneering work of Balooch *et al.* [1]. Several different processes do in fact contribute, depending on surface structure and on the chemical nature of the incident molecule: A direct process without activation barrier was observed, e.g., in the case of $H_2$ on Ni(110) [2], while quantum tunneling was found to dominate in the dissociative chemisorption of $CH_4$ on W(110) [3]. In most cases the initial sticking probability scales [4] with normal energy $E_i \cos^2 \theta_i$, but scaling with total energy was reported, e.g., for $N_2$ on W(110) [5]. Quasi-direct dissociation occurs for $O_2$ on Pt(111) [6], while both precursor and direct processes are active for $N_2$ on W(001) [7]. Finally, the internal degrees of freedom of the molecule have a strong influence in the dissociation process as demonstrated for $D_2$ on Cu(111) [8].

In spite of this large amount of experimental work, no dependence of the sticking probability on surface corrugation has so far been reported. Recently an investigation in this direction was performed by Hayden and Lamont [9], who measured the dissociation of $H_2$ on Cu(110), and by Hodgson, Nesbitt, and Lewin [10] for $O_2$ on Cu(110). Both groups observed a substantial insensitivity of the initial sticking probability for scattering along the two high symmetry azimuthal directions.

In this Letter we report on the first evidence for the existence of an effect connected to surface corrugation on $S_0$. The system studied, $O_2$-Ag(110), was chosen since it couples a strong corrugation associated with the nature of the interaction [11] to a large anisotropy of the surface. In addition, Ag(110) has been studied extensively in the past because of the importance of silver as a catalyst for the partial oxidation of ethylene, using several experimental techniques such as thermal desorption spectroscopy

(TDS), high resolution electron energy loss spectroscopy (HREELS), low energy electron diffraction (LEED), x-ray photoemission spectroscopy, ultraviolet photoemission spectroscopy, ion and He scattering, and scanning tunneling microscopy. These studies evidenced the presence of a molecularly chemisorbed state at temperatures lower than $\sim 120$ K and of an atomic state above $\sim 190$ K. A physisorbed precursor state is present at low temperatures (less than $\approx 40$ K) and a recent near edge x-ray absorption fine structure experiment studied its orientation and growth [12]. A semiempirical LEPS (London-Eyring-Polanyi-Sato) potential was developed by Lin and Garrison [13] and more recently Upton, Stevens, and Madix [14], van den Hoek and Baerends [15], and Nakatsuji and Nakai [16] calculated the potential energy surface using *ab initio* methods.

The experimental setup and the method used for determining the initial sticking probability are described in great detail in Refs. [17,18]. Here we limit ourselves to a short description of its essential features. The $O_2$ is provided on the Ag(110) surface with a supersonic molecular beam. The incident energy of the beam is varied from 0.088 to 0.615 eV by seeding in He and by changing the nozzle temperature from room temperature to $T \approx 600$ K. At these temperatures the population of the excited vibrational levels is negligible. The energy distribution is determined by time-of-flight techniques and resulted in $\Delta E/E = 0.2$ FWHM. The angular divergence of the beam is 0.5°.

The Ag crystal was cleaned *in situ* in an UHV chamber with a base pressure in the lower $10^{-8}$ Pa range, by sputtering with 2 keV Ne ions. After sputtering the crystal was heated to 700 K for at least 1 min. Care was taken not to heat the sample above this temperature to avoid crystal evaporation and reconstruction. Sample cleanliness was controlled by Auger electron spectroscopy and EELS. Such a procedure was repeated several times until no peak due to vibrational modes of adsorbed species was detected by EELS. The sample is mounted on a manipulator which allows us to rotate the crystal with respect to the molecular beam and provides $e$-beam heating and liquid nitrogen cooling. Two dif-

ferential pumping stages separate the expansion chamber of the nozzle beam (base pressure with the beam on $\approx 10^{-1}$ Pa) from the main chamber where the crystal is located. The base pressure in the main chamber varies from $10^{-8}$ Pa with the beam off to $10^{-7}$ Pa with the beam on.

The amount of oxygen adsorbed on the surface is determined as described in Ref. [17] by high resolution EEL spectrometry, after a calibration procedure with LEED. The EEL spectrometer is capable of a resolution of 5 meV with a current of $5 \times 10^{-11}$ A in the direct beam. The spectrometer has been developed and constructed in our laboratory [19] following Ibach's design [20].

A typical energy loss spectrum, recorded after an exposure of 55 sec to a 3.5% $O_2$ beam seeded in helium with the crystal at room temperature, is reported in the inset of Fig. 1. The scattering conditions of the electrons are chosen in order to favor dipole scattering: Incident energy is 1.23 eV and incident angle is 63°. All the measurements presented in this paper were taken under this scattering condition. The ratio $I/I_0$ of loss peak intensity $I$ to the elastically reflected beam $I_0$, recorded as a function of exposure, allows the determination of the initial sticking probability $S_0$. $I/I_0$ is proportional [21] to the number density of molecules captured by the surface $n_s$ and to the square of the dynamic dipole moment $\mu$ of the adsorbate molecules, $I/I_0 = A\mu^2 n_s$, where $A$ is a constant which depends on spectrometer parameters. The relative loss intensity is directly proportional to $n_s$ if the dynamical dipole moment does not depend on coverage. The exposure $n_i$ is determined by measuring the flux $\Phi$ of the oxygen and the exposure time $t$; $n_i$ is given by $n_i = \Phi t \cos\theta_i$, where $t$ is the opening time of a shutter which can flag the beam off.

In Fig. 1 a typical $I/I_0$ vs exposure plot is reported. Both coverage and exposure have been normalized to the surface density of Ag(110), $n_0 = 8.4 \times 10^{14}$ atoms cm$^{-2}$. Thus $\Theta = n_s/n_0$ and $\chi = n_i/n_0$. The coverage, as reported on the right of Fig. 1, was calibrated by assigning the $I/I_0$ value to $\Theta = 0.25$ in correspondence with the appearance on the LEED screen of the $4 \times 1$ structure. Below $\Theta = 0.25$, the proportionality between relative intensity and coverage assumed in the previous equation is satisfied as confirmed by Backx et al. [22], who showed that for coverages below the $4 \times 1$ structure the ratio $I/I_0$ is directly proportional to the oxygen coverage within an experimental accuracy of 13% (given by a 0.8 eV change of the work function measured with a precision of 0.1 eV). A nonlinearity occurs for higher coverages and was explained by dipole-dipole interaction. The value of $S_0$ is obtained by fitting the experimental curve with a polynomial of third order and taking the derivative of the fitting curve for zero exposure. Following this procedure $S_0$ in Fig. 1, for instance, comes out $S_0 = 0.072 \pm 0.008$.

$S_0$ was measured for several incident angles ($\theta_i$ from 0° to 75°) and energies ($E_i$ from 0.088 to 0.615 eV) of
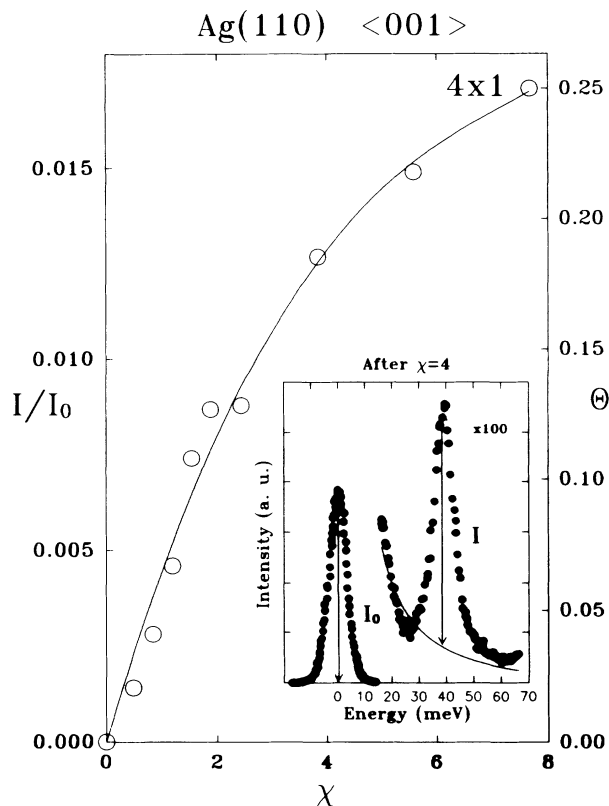


FIG. 1. Coverage vs exposure plot as determined by the experimental value of $I/I_0$ after calibration. $\Theta = n_s/n_0$ and $\chi = n_s/n_0$. The surface is exposed to a 3.5% $O_2$ seeded in He beam incident at an energy of 0.32 eV and an angle of 60.0° with an intensity of $(0.59 \pm 0.01) \times 10^{14}$ molecules cm$^{-2}$. The surface temperature is 294 K. $S_0$ calculated as reported in the paper is $0.072 \pm 0.008$. The continuous line is the fit to the experimental data obtained with a cubic polynomial function. The inset reports a typical energy loss spectrum. The spectrum has been recorded after an exposure of 55 sec. The resolution of the spectrometer is 7 meV. The loss at 40 meV is the vibration of atomic oxygen bound to the surface. The ratio $I/I_0$ is directly proportional to the oxygen coverage $\Theta$.

the $O_2$ beam impinging along the high symmetry directions $\langle 001 \rangle$ and $\langle 1\bar{1}0 \rangle$. Figure 2 reports $S_0$ along $\langle 1\bar{1}0 \rangle$ and Fig. 3 along $\langle 001 \rangle$. Some of the data points were recorded more than once. The values reported in Figs. 2 and 3 correspond to the average and the error bars to a mean deviation of 25%. As this error is larger than the uncertainty of 13% discussed above, we assumed this value for the error bar reported in Figs. 2 and 3. We find that $S_0$ scales with an effective energy $E_e = E_i \cos^n(\theta_i)$ and shows the $S$ shape typical of the presence of a barrier distribution, whose height $E_0$ and width $W$ can be estimated, according to Ref. [23], from the fitting function

$$S_0 = \frac{1}{2}\left[1 + \tanh\left(\frac{E_e - E_0}{W}\right)\right].$$

Ag(110) <110>
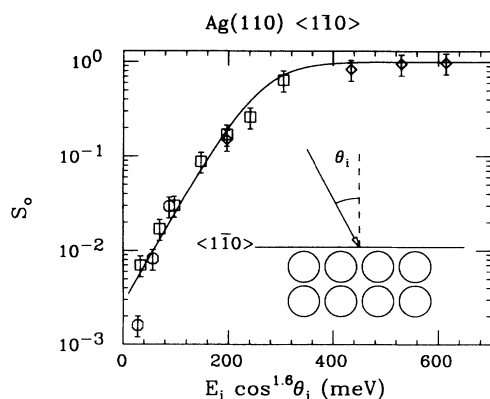


FIG. 2. Initial sticking probability $S_0$ as a function of $E_i \cos^{1.6}\theta_i$. The data are taken along the $\langle 1\bar{1}0 \rangle$ azimuth at 294 K. The same symbol refers to the same incident energy. The measured incident angles range from 0° to 75°. O: $E_i =0.088$ eV; □: $E_i =0.305$ eV; ◇: $E_i =0.615$ eV. The inset shows a sketch of the geometry of the experiment and of the structure of the (110) surface along $\langle 1\bar{1}0 \rangle$.
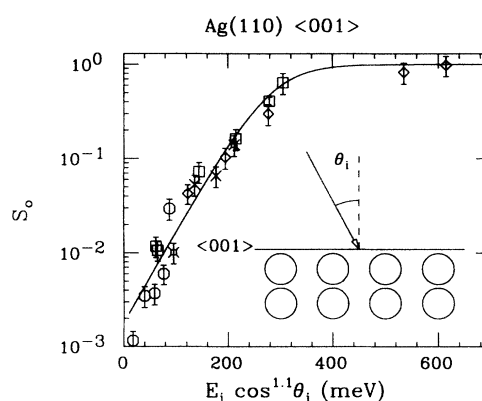
Ag(110) <001>



FIG. 3. Initial sticking probability $S_0$ as a function of $E_i \cos^{1.1}\theta_i$ at 294 K. The data are taken along the $\langle 001 \rangle$ azimuth. The measured incident angles range from 0° to 75°. O: $E_i =0.088$ eV; □: $E_i =0.18$ eV; □: $E_i =0.32$ eV; ×: $E_i =0.470$ eV; ◇: $E_i =0.615$ eV. The inset shows a sketch of the geometry of the experiment and of the structure of the (110) surface along $\langle 001 \rangle$.

For $n = 2$, $E_e$ corresponds to the energy associated with motion normal to the surface as expected from a completely uncorrugated interaction potential. Values of $n < 2$ are expected for a corrugated surface. Along $\langle 1\bar{1}0 \rangle$ the best fit parameters are $E_0 =0.26$ eV, $W =0.09$ eV, and $n =1.6$ with $\chi^2 =0.57$; along $\langle 001 \rangle$ we find $E_0 =0.28$ eV, $W =0.09$ eV, and $n =1.1$ with $\chi^2 =0.65$. $E_0$ can be compared with the value of 63 meV measured by Campbell [24] by thermal desorption. The difference is connected to the different definitions of barrier height. In the present case $E_0$ is the average value of the distribution of barriers, while the desorption experiment probes the lowest energy path [25]. This barrier is between the physisorption and the molecular adsorption state.

The anisotropy in the sticking probability is present also at low crystal temperatures where no dissociation takes place as shown in Fig. 4, where $S_0$ is reported vs $\theta_i$ along both high symmetry directions for $E_i =605$ meV at $T =83$ and 278 K. In this case $S_0$ was measured by the method of King and Wells [26] to prove the absence of effects caused by systematic errors of the EELS method. Moreover, the EELS method is quite inaccurate at low temperature, where no calibration is possible as $O_2$ forms no ordered structures [27]. The method of King and Wells is, on the other hand, less sensitive so that only data with high sticking probability can be recorded. The observed effective energy scaling along both directions implies that the parallel momentum of the incident $O_2$ molecule is important in promoting the adsorption. The similarity of the behavior for dissociative and molecular sticking indicates that the mechanism causing the anisotropy of $S_0$ acts already before dissociation takes place. It requires a strong corrugation of the gas-surface potential of a precursorlike state in which the molecule is temporarily trapped: In fact in the case of Cu(110) where no

azimuthal dependence of the sticking coefficient was observed [10], no precursor is present.

The precursor state therefore plays the dominant role in converting the translational energy. The observed anisotropy implies as a consequence that the dissociation occurs in the troughs of Ag(110). This consideration is supported by the calculations of Upton, Stevens, and Madix [14] who found that chemisorption takes place in the troughs at the long bridge site with the $O_2$ molecule oriented preferably along the $\langle 1\bar{1}0 \rangle$ direction. Such a state was observed at low crystal temperature [28].
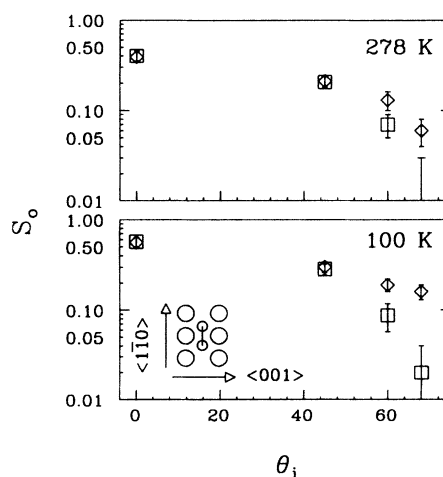


FIG. 4. Initial sticking probability $S_0$ as a function of the incident angle $\theta_i$ for the same experimental conditions along the $\langle 1\bar{1}0 \rangle$ and $\langle 001 \rangle$ azimuths measured using the King and Wells method for different surface temperatures. The inset shows the surface geometry and the scattering directions. The figure shows the site of the molecular precursor. It is placed in the grove between two atoms with the axis along the $\langle 1\bar{1}0 \rangle$ azimuth.

As a consequence of these observations we suggest the following mechanism for the dissociation process: the $O_2$ overcomes the barrier and is temporarily trapped in the $O_2^{2-}$ state also at room temperature; the lifetime of this state must be considered much shorter than the time required to perform the experiment in order to escape our observation; in this time the molecule moves along the surface and part of the available translational energy is transferred into O-O stretching motion. The stretched molecule can meet the bond length required for the adsorbed state thus favoring adsorption which is followed by dissociation. The coupling between translational and vibrational energy is more effective along $\langle 001 \rangle$ than along $\langle 1\bar{1}0 \rangle$ because the potential of $O_2^{2-}$ $Ag(110)$ is more corrugated. On the contrary, because of the weaker corrugation, the energy transfer mechanism is less efficient along $\langle 1\bar{1}0 \rangle$. In this direction, in fact, the sticking probability scales with $n = 1.6$, a value closer to $n = 2$ observed for uncorrugated systems. It is not surprising that no azimuthal anisotropy was reported for $H_2$ and $O_2$ on $Cu(110)$ [9,10]: In these systems no molecular precursor is present.

In conclusion, we have reported on the first experimental evidence of azimuthal anisotropy in chemisorption of a gas molecule with a surface. We have given evidence that the effect is connected to the strong anisotropy of the potential of the molecular precursor state.

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