Anisotropy of the Oxygen Interaction with Ag Surfaces

M. Rocca

Centro di Fisica delle Superfici e delle Basse Temperature del C.N.R. and Istituto Nazionale per la Fisica della Materia, Dipartimento di Fisica, via Dodecaneso 33, 16146 Genova, Italy

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Abstract

A review of the most recent experimental progress in the investigation of the dynamics of the interaction of dioxygen with Ag single crystal surfaces is given. In such studies the dioxygen molecules are dosed by a supersonic molecular beam, which allows for angle and energy selectivity. Moreover the background pressure remains very low during dosing thus minimizing surface contamination. Energy and angle dependence of the initial sticking probability was investigated for the different low Miller index surfaces. We find that the non dissociative adsorption occurs below 150 K only on Ag(110) and (001) with the same activation barrier. The dependence of the sticking probability on the angle of incidence is anisotropic with respect to surface azimuth for Ag(110) because of the anisotropic surface corrugation. Dissociation is always promoted by chemisorbed O\(_2\) and, when heating the crystal, it prevails over desorption for Ag(110), while the contrary holds for Ag(001). For the latter case we find also evidence for subsurface diffusion at molecular dissociation. The coverage dependence of the sticking coefficient as well as of the TDS spectra are indicative of repulsive interactions between the admolecules, which are particularly strong for Ag(001).

1. Introduction

The dynamics of gas–surface interaction phenomena has drawn increasing attention in recent years as the energy transfer processes and bond breaking mechanisms are limiting steps for diverse catalytic reactions of industrial relevance. An important goal is then to determine which factors, and in particular which form of energy, most affect the outcome of potentially reactive collisions. In principle, such knowledge should be of great value in providing control over reaction yields. Most studies were so far dedicated to H interaction with metals and in particular to H–Cu which was used as a model for the dissociation of a light diatomic molecule on a metal surface [1, 2]. The reasons for this choice were dictated by the absence of a strongly interacting molecular chemisorbed state, by the inefficient transfer of momentum between molecule and surface and by the accuracy by which the relevant gas–surface potential hypersurfaces can be computed for interactions involving H.

The understanding of reactions involving heavier molecules follows eventually, as a far greater number of degrees of freedom may be required to describe the interaction. Oxygen chemisorption on metal surfaces is particularly important and was therefore object of intense investigation [3]. O\(_2\)–Ag arose recently as a model for such processes because of the central role played by oxygen adsorption for the unique selectivity of Ag substrates in the partial oxidation reaction of ethylene to ethylene epoxide [4], and for the large number of highly qualified papers which appeared in literature in particular for O\(_2\) and O adsorbed Ag(110) (see e.g. Refs [5–32]). The other low Miller index surfaces attracted less attention (see Refs [6, 33, 34, 35] for O\(_2\)–Ag(111) and Refs [39, 40, 41, 42] for O\(_2\)–Ag(001)).

These investigations showed that the adsorption of dioxygen on Ag is an activated process and that the interaction potential presents three wells along the reaction coordinate corresponding to physisorption, molecular chemisorption and dissociative adsorption. Moreover oxygen can penetrate subsurface. Only the most recent studies were performed by dosing the O\(_2\) molecules with a supersonic molecular beam, i.e. with selected impact energy and angle of incidence [20–24, 33–37]. In particular two PhD thesis were devoted to the study of this system at the University of Genoa (all three low Miller index surfaces [43, 44]) and one at the FOM in Amsterdam (Ag(110) and Ag(111) [45]).

2. Experimental

A supersonic molecular beam experiment is based on the supersonic expansion of a gas which takes place when it flows through a small orifice (nozzle) with a high enough backing pressure. In the process the thermal degrees of freedom of the gas in the directions ortogonal to the flow freeze and the energy is transferred to translational energy in the direction of the flow. The velocity distribution is therefore much narrower than for a Maxwellian expansion and the angular distribution sharper. A nearly parallel beam can be easily obtained by collimating it. A schematic of the apparatus is shown in Fig. 1. After the nozzle, N, the central part of the beam is screamed out by a skimmer, S. Further collimators (of skimmer type or not) are then placed at the entrance of the differential pumping stadiums, I, II, III and of the main chamber containing the crystal, C. The impact energy of the molecules can be varied either by heating the nozzle (such procedure affects however also the vibrational degrees of freedom of the molecules) or/and by seeding the O\(_2\) molecules in He. The collisions during the supersonic expansion of the gas mixture cause then that the velocities of its components are equilibrated [46]. Using typically 5% concentrations of the heavy component, impact energies (E\(_i\)) up to 0.8 eV could be reached in Genoa and up to 1.6 eV in Amsterdam. Beam energy and flux were determined in our experiment by time of flight with a quadrupole mass spectrometer (QMS) and by a spinning rotor gauge (SRG), respectively [47].

The sticking coefficient can then be measured either directly by the retarded reflector method developed by King and Wells [48] (hence KW in the following) or indirectly by monitoring the coverage vs. exposure. For KW experiments
two flags are needed: SH1 in the second stadium of the beam and SH2 in the main chamber in front of the sample. A typical K–W measurement is shown in Fig. 2. When removing SH1 at time $t_1$, leaving SH2 closed, the beam enters the main chamber and the partial pressure of $\text{O}_2$ (measured with another QMS not in line of sight with the surface) rises to a level, $P_1$, determined by the flux and by the pumping speed in the chamber. When also SH2 is removed at time $t_2$, the beam is allowed to strike the clean surface. A drop in the partial pressure to $P_2$ is then observed because the $\text{O}_2$ molecules are gettered by the reactive surface. The relative magnitude of the observed drop is a measure of the sticking coefficient, provided that the diameter of the beam is smaller than the size of the crystal. The integral of the missing $\text{O}_2$ pressure with time is proportional to the surface coverage, $\Theta_{\text{O}_2}$, and to the flux. For the alternative approach thermal desorption spectroscopy (TDS) is usually used to monitor the coverage [1]. Any other surface sensitive spectroscopy can however be employed as well. In our experiment we used high resolution electron energy loss spectroscopy (HREELS). The sticking was then evaluated by analysing the loss intensity (hence EELS method) associated to the $\text{O}^{--}\text{O}$ stretch vibration at 80 meV, indicative of the $\text{O}_2$ coverage, and of the $\text{O}$-substrate vibration at 40 meV, indicative of the dissociated oxygen coverage. Details about the experimental apparatus and the surface preparation can be found elsewhere [47, 23]. It suffice to say here that the surface has to be prepared by ion sputtering and heating in situ and that cleanliness and order conditions were verified by Auger Electron Spectroscopy and HREELS, and Low Energy Electron Diffraction, respectively.

3. Results

3.1. Initial sticking coefficient

The normal energy dependence of the initial sticking coefficient $s_0$ is shown in Fig. 3. Similar curves were measured for $\text{O}_2$–Ag(110) [21, 23] and were confirmed by the independent investigation in Amsterdam [45]. As one can see the data scale with normal energy, $E_n = E_i \cos^2 \theta$, as indeed expected for a flat surface. $s_0$ grows by 3 orders of magnitude between $E_n = 20$ meV and $E_n = 0.8$ eV indicating that the process is activated. Above $E_n = 0.8$ eV, $s_0$ saturates at the value of 0.6 as demonstrated by Raukema and Kleyn for Ag(110) [45]. Such value is very near to a 2/3 ratio and could be indicative of a steric factor, i.e. that only molecules arriving with a their axis tilted by an angle larger than some critical value are able to stick.

$s_0$ decreases monotonously at low $E_n$, although under such conditions trapping in the physisorption well is
expected to become important. An increase of $s_o$ was indeed observed for most systems when lowering $E_i$ below $\approx 100 \text{ meV} \ [49, 50]$. Such effect is absent to our knowledge only for $O_2$-Ag and $N_2$-Fe(111) \[51\]. Both systems are characterized by activated non dissociative chemisorption but no clear understanding exists so far for the different behavior of e.g. $O_2$ on Pt, where trapping has a strong influence on $s_o(E_i)$. Moreover physisorbed $O_2$ is known to convert to chemisorbed $O_3$ (peroxide) at large coverage of the physisorbed specie \[52\]. In the latter conditions a molecular dynamics study showed that the axis of the molecules lies nearly parallel to the surface pointing along \langle 100 \rangle, while for dilute conditions the \langle 110 \rangle direction is preferred. As the chemisorbed molecules are also oriented along \langle 110 \rangle \[13\] one could guess that the 90° rotation necessary to pass from one state to the other for large coverages might help in overcoming the barrier \[52\]. Such mechanism cannot explain however the absence of the effect for Ag(001) where the orientation of the admolecules in both states is expected to be more random.

The K–W sticking data for the “open” Ag surfaces are summarized vs. $E_i$ in Fig. 4: in (a) for Ag(001) and in (b) and (c) for the two high symmetry directions of Ag(110), respectively. By inspection one can see that the data in (a) and (b) are identical within experimental error. In both cases we observe overall scaling with $E_i$ although the points at $E_i = 390 \text{ meV}$ and normal incidence are clearly higher than the points recorded at the same $E_i$ but for $E_i = 800 \text{ meV}$. This is an example of energetic corrugation as was recently suggested by Darling and Holloway for the easier case of the $H_2$-surface interaction \[53\]. An energetic corrugation of the surface causes a dependence of $s_o$ on $E_i \cos\theta_i$ with $n > 2$, i.e. given a certain velocity of the molecules in the vertical direction, $s_o$ is larger if less energy has to be dissipated. The data recorded for Ag(110) along \langle 001 \rangle, see Fig. 4(c), show the same behavior at large $E_i$ but the spread becomes much larger when $E_n$ is decreased. Such spread can be eliminated assuming a dependence with $E_{eff} = E_i \cos\theta_i$ with $n \approx 1$ indicating that also parallel momentum helps in overcoming the barrier. As demonstrated by Darling and Holloway a geometric corrugation could indeed cause the effect because of the steering action of corrugation on the impinging molecules. The physical picture behind this is that the translational energy is most effective in overcoming the barrier when the molecules impinge along the local normal to the

![Fig. 3. Dependence of the non dissociative sticking coefficient vs. $E_i$ for Ag(001).](image)

![Fig. 4. Retarded reflector measurements of the sticking coefficient of $O_2$ on (a) Ag(001), (b) Ag(110) \langle 110 \rangle, (c) Ag(110) \langle 001 \rangle vs. $E_i$. As one can see the data coincide for the flat Ag(001) surface and for the flat \langle 110 \rangle direction of the one dimensionally corrugated Ag(110) surface.](image)
Such effect dominates at low impact energy where the steering is most effective.

To be more quantitative the functional dependence of \( s \) on impact energy and angle is generally described by the functional form:

\[
s(E_{\text{eff}}) = \eta \int_0^{E_{\text{eff}}} e^{-(E_{\text{eff}} - E_0)^2/W^2} dE_{\text{eff}}
\]

which allows to estimate the average height of the distribution of barriers to adsorption, \( E_0 \), and its width, \( W \). \( E_0 \) and \( W \) come out to be \( 368 \pm 50 \text{ meV} \) and \( 167 \pm 25 \text{ meV} \), respectively, identical within experimental error for all surfaces and directions as expected from the picture given by Darling and Holloway [53].

The average barrier found in the present experiment is thus much higher than the value determined by TDS [6]. Such finding is connected with the fact that with the beam we are averaging over the whole unit cell and over all possible orientations of the impinging molecules. In a TDS experiment on the contrary the adsorbed molecules have the time to search for the lowest energy path, which allows them to leave the surface.

At room temperature very similar curves were measured, except that the absolute values of \( s \) are shifted by the dissociation probability \( P_{\text{diss}} \). Dissociative adsorption is thus always promoted by the molecularly chemisorbed state. At low coverage such values came out to be 0.63 on Ag(110) and \( 4.4 \times 10^{-3} \) on Ag(001). The value for Ag(110) decreases with crystal temperature, \( T \), as expected by the competition between desorption and dissociation; for Ag(001) on the contrary it increases with \( T \). Such anomalous dependence is indicative that dissociation on Ag(001) is induced by thermally activated defects [36], while on Ag(110) it takes place also on the atomically flat terraces. Indeed it was recently proven by STM that for Ag(110) at room temperature the supply of Ag adatoms necessary to form the Ag–O adrows of the \((n \times 1)\) reconstructions is not rate limiting for the dissociation reaction. The oxygen molecules can therefore dissociate and eventually search for the Ag adatoms necessary to stabilize them. On Ag(001) on the contrary O₂ molecules on the terraces desorb.

For O₂–Ag(111) a low but finite value for \( s \) (\(< 10^{-5} \) for \( E_i \approx 0.5 \text{ eV} \)) was found by the group in Amsterdam [37], while our data indicate that no sticking occurs within the sensitivity of our EELS method (\(< 10^{-6} \)) [35]. The latter result was recently confirmed by the group of K. Jacobi in Berlin [38] who saw no adsorption signal after an exposure of \( 10^5 \text{ L} \) of O₂ dosed by backfilling the chamber. \( s \) must therefore be \(< 10^{-8} \) assuming an EELS sensitivity to chemisorbed O₂ of \( 10^{-3} \text{ ML} \). We thus conclude that no chemisorption takes place for Ag(111) under clean conditions. To explain the data of Raukema and Kleyn [37] and the previous literature [6] we propose that water contamination was responsible for the enhanced surface reactivity as oxygen adsorption can be stabilized by H₂O [54].

### 3.2. Coverage dependence of \( s \)

As one can see in Fig. 2 the sticking coefficient decreases strongly with exposure, i.e. with dioxygen coverage, \( \Theta_{\text{O}_2} \). The initial dependence of \( s(\Theta) \) is thereby linear up to \( \Theta_{\text{O}_2} \approx 0.1 \) for Ag(110) [24] \( \Theta_{\text{O}_2} \approx 0.2 \) for Ag(001) [55]. In the large coverage limit on the other hand an exponential decrease is found. Such dependences are indicative of strongly repulsive interactions between the admolecules, expected indeed in view of the relatively large charge transfer from the substrate, \( \approx 1 \text{ e}^- \) for both O_{ad} and O_{2ad}. The effect is larger for Ag(001) probably because of the worse screening properties compared to the more corrugated Ag(110) surface. Indeed the TDS spectra for O₂ on Ag(001) show a strong downshift of the desorption threshold with \( \Theta_{\text{O}_2} \) [56]. Quantitative simulations of the phenomenon are in progress [52].

### 4. Oxygen induced substrate reconstructions

At room temperature on Ag(110) oxygen adatoms are bound in adrows with Ag atoms forming \((n \times 1)\) reconstructions with \( n \) as large as 7 or 8 [5, 32]. On the contrary no LEED superstructure is observed for chemisorbed molecules on both Ag(001) and Ag(110) and for dissociative chemisorption on Ag(001). An interesting effect is observed upon dissociation for Ag(110) [22]. As shown in Fig. 5(a) the elastic reflectivity drops by more than one order of magnitude at 150 K, in spite of the partial desorption of adsorbed O₂ (according to Barreau and Madix about \( 2/3 \) of the admolecules desorb at such high coverages [7]). Dissociation is evidenced by the disappearance of the loss at 80 meV associated to the O–O stretch vibration and the appearance of a loss at 40 meV corresponding to the vibration of O-adatoms against the surface (see Fig. 5(b)).

The drop in reflectivity is associated with an increase of the intensity of the diffuse off-specular background (see Fig. 5(b)). The elastic reflectivity is recovered only above \( T = 200 \text{ K} \), at which temperature diffuse extra LEED spots appear indicating that adrows have formed while the 40 meV peak becomes narrower and gains in intensity indicating that the inhomogenous broadening mechanisms become less important. This finding is in nice agreement with the STM pictures recorded at room temperature by Pai et al. [31], who
find that the Ag adatoms needed for the formation of the added row chains are readily grabbed from the flat Ag terraces. Pits are formed eventually when the oxygen flux exceeds the mobility of Ag as the adatom supply from steps becomes insufficient to fill the pits. At room temperature the critical conditions occur for an O$_2$ partial pressure of 10$^{-5}$ mbar. The same explanation holds for our measurements, the disorder being induced in our case by the absence of mobile Ag adatoms at 150 K which might fill the pits caused by the grabbing process.

5. Subsurface oxygen migration

Subsurface migration of O atoms to subsurface sites was first suggested to occur by C. Backx et al. [10] who noticed an unbalance in the initial adsorption–desorption experiments for a freshly sputtered surface. No EELS signal could be attributed to subsurface oxygen in accord with the large screening of the dynamical dipole moment for a subsurface site. On Ag(001) we noticed however [57] that upon dissociation a peak at 130 meV forms which is more difficult to be sputtered away than ordinary oxygen adatoms (which vibrate at 33 meV on Ag(001)). Such loss cannot be due to the formation of superoxide because it persists up to $T = 350$ K. For the same reason it cannot be due to the formation of carbonates, which are known to desorb at 450 K on Ag(110) [58]. For carbonates moreover a much richer EEL spectrum was observed for Ag(110). Finally the peak is due to oxygen as it shifts when $^{18}$O is replaced by $^{16}$O. The peak was therefore associated to subsurface oxygen which forms at the transient of molecular dissociation. To be observable with EELS in dipole scattering the subsurface atoms must however lie either very near to the surface or their motion must be coupled to the one of substrate atoms. The latter effect is probably occurring in case of Ag(001) as the most probable subsurface site, the octahedral interstitial, lies directly below the Ag atoms in the first layer.

6. Conclusions

In conclusion we have shown that the O$_2$–Ag system deserves its model role for heavier molecules interacting with a clean surface. The system is simple enough to be understood in detail and yet complicated enough to give rise to an interesting variety of new phenomena.

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