Adsorption and desorption of O\textsubscript{2} on Ag surfaces

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A brief review of our measurements of the sticking probability of O\textsubscript{2} on Ag single crystal surfaces is presented. On Ag(110) and Ag(001) the non dissociative chemisorption probability behaves similarly increasing by three orders of magnitude as the oxygen translational energy is increased from 90 to 800 meV. The temperature dependence of the dissociative sticking probability allows to distinguish two different pathways to dissociation: on Ag(110) molecules can dissociate at terrace sites while on Ag(001) only special sites, tentatively identified with kinks, are effective. On Ag(111) the sticking probability is below the experimental sensitivity.

We finally report on the more recent results about the possibility to desorb or dissociate chemisorbed O\textsubscript{2} even at low temperature by collision with hyperthermal Xe atoms. © 1998 Elsevier Science Ltd. All rights reserved

1. Introduction

Understanding energy transfer processes at surfaces is an obliged step for a full description of gas–surface systems and many efforts have been devoted to both theoretical and experimental investigations of the dynamics of gas surface interaction, with particular attention to chemisorption, where chemical bonds are created (between the gas and the metal surface) and broken (the bond between atoms in the molecule, in case of dissociative chemisorption).

Most studies dealt with the H\textsubscript{2}–Cu system, which soon became a prototype for such investigations. Such a choice was due to the absence of a strongly interacting molecular chemisorbed state, to the inefficient transfer of momentum between the molecule and the surface and to the accuracy attainable in computing the multidimensional gas–surface potential for a relatively simple molecule like hydrogen. The dependence of the dissociative sticking probability of H\textsubscript{2} on Cu was measured as a function of translational and internal energy of the molecule and compared to \textit{ab initio} calculations. It was found that hydrogen dissociative adsorption is activated and the activation barrier was found to be a function of the internal vibrational state of the molecule, the barrier being smaller for vibrationally hot molecules.

The attention of the surface science community thereafter moved to more complicated molecules: the O\textsubscript{2}–Ag system was chosen for a series of reasons. There had always been some interest for this system due to its importance for the industrially relevant process of ethylene epoxidation, for which Ag is the only metal catalyst: Barteau and Campbell and Madix had demonstrated that the system presents several adsorption wells, namely a physisorbed state, populated up to about 40 K, a molecularly adsorption state for \(T\) lower than 0.49 K and a dissociated state up to 449 K. When compared to the H\textsubscript{2}–Cu system, it showed some new features, the most important being the presence of a chemisorbed molecular state, despite that it still seemed affordable for a detailed understanding.

We have thus investigated in detail the interaction of oxygen with Ag(110), Ag(100) and Ag(111) by a combined HREELS and molecular beam apparatus. We have measured the sticking probability as a function of energy, polar and azimuthal angle of incidence of O\textsubscript{2}, surface temperature and coverage. Our findings were confirmed by independent observations by Kleyn and coworkers in Amsterdam. Several groups are presently working on this system (we cite here Ertl’s group in Berlin and Franchy’s one in Julich). With the appearance of the first molecular beam experiments, several theoretical investigations were carried, mainly by Bird in Bath, Kosloff in Jerusalem, Zhdanov in Novosibirsk and Tantardini in Milan. More recently we investigated collision induced desorption and dissociation of O\textsubscript{2} on Ag(110) and Ag(001), thus obtaining further insight into energy transfer processes. In this paper we summarize our findings for the sticking probability of O\textsubscript{2} on Ag(110) and Ag(001) and for the cross section of collision induced desorption of O\textsubscript{2} on Ag(001).

2. Experimental

The experimental apparatus is schematically shown in Fig. 1. It consists of a molecular beam and of an Ultra High Vacuum (UHV) experimental chamber, equipped with Electron Energy...
Loss Spectrometer (EELS) and Quadruple Mass Spectrometer (QMS). The molecular beam apparatus consists of three differentially pumped stages: after the nozzle, N, 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 stations, 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 and/or by seeding the \( \text{O}_2 \) molecules in \( \text{He} \). Using typically 4\% concentrations of the heavy component, impact energies \( (E_i) \) up to 0.8 eV for \( \text{O}_2 \) and 2.7 eV for \( \text{Xe} \) could be reached. Beam energy was determined by time of flight with a QMS using a mechanical chopper. The flux was measured by a spinning rotor gauge (SRG). The sticking coefficient can then be measured either directly by the retarded reflector method developed by King and Wells (hence KW in the following)\(^{15}\) or indirectly by monitoring the coverage vs exposure. The coverage is estimated by the intensity of EEL features, calibrated by Thermal Desorption Spectroscopy (TDS) on Ag(001) and by inspection of the Low Energy Electron Diffraction (LEED) pattern on Ag(110), where a \((4 \times 1)\) overlayer forms at 9.14 ml coverage of dissociated oxygen. Details about the experimental apparatus and the surface preparation can be found in our papers.

The self-built EEL spectrometer was designed following the recent development in Julich.\(^{20}\) It has a double monochromator and analyzer and can achieve a resolution up to 3.5 meV in specular. Figure 2 shows EELS spectra for \( \text{O}_2 \) chemisorbed on Ag(001) after oxygen dosing (bottom) followed by different \( \text{Xe} \) doses. As one can see two moieties are present at the low crystal temperature of the experiment \((T = 100 \text{ K})\), tentatively assigned to molecular oxygen chemisorbed at two different adsorption sites.\(^{21}\) The cross section for removal of molecular oxygen (desorption plus dissociation) can be determined from the behaviour of the loss intensity around 80 meV vs \( \text{Xe} \) exposure, while the cross section for dissociation can be determined by the increase with \( \text{Xe} \) exposure of the intensity of the 34 meV loss. The same method allows to determine the sticking coefficient by monitoring the intensity of the loss feature (80 meV for molecular oxygen and 34 meV for atomic oxygen on Ag(001); 80 meV and 40 meV, respectively, for Ag(110)) as a function of the exposure time. Repeating the same experiment at different \( \text{O}_2 \) energies and angles of incidence a complete description of the adsorption dynamics can be attained.

### 3. Initial sticking coefficient

A typical measurement of the energy and angle dependence of the initial sticking coefficient \( S_i \) is shown in Fig. 3 for non dissociative adsorption of \( \text{O}_2 \) on Ag(001).\(^{11}\) Similar curves were measured for both dissociative and molecular adsorption for \( \text{O}_2–\text{Ag} (110) \)\(^{16}\) and were confirmed by the independent investigation in Amsterdam.

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**Figure 1.** Schematics of the experimental apparatus for chemisorption studies as described in the text.

**Figure 2.** Sample EELS spectra as function of exposure to Xe for Oxygen on Ag(001). \( \text{Xe} \) atoms of energy 2.7 eV impinge normally onto the Ag(001) surface at 100 K. The peak at 30 meV is due to the \( \text{O}_2 \) surface vibration, the peaks at 79 meV and 84 meV are due to the internal stretch vibration of \( \text{O}_2 \) in two different sites. The growing peak at 34 meV is due to dissociated oxygen.
Two surfaces. On Ag(001) the initial dissociation probability $P_{diss}$, given by the ratio of the dissociative sticking probability ($S_d(T)$) and the initial trapping probability ($S_i(100K)$), does not depend on $E_i$ decreases with increasing sample temperature and is still high at room temperature (about 0.63) while on Ag(001) it drops down as soon as the desorption temperature of molecular oxygen is overcome and increases slightly with increasing sample temperature to reach a value as low as 4.4 $10^{-3}$ at room temperature. We shall come back to this intriguing point later. On Ag(110) the sticking probability was below our experimental sensitivity ($S_i < 10^{-5}$).

For both Ag(110) and Ag(001) surfaces $S_i$ decreases monotonously with decreasing $E_i$ at room temperature and even at liquid nitrogen temperature, although under such conditions trapping in the physisorption well is expected to become important. An increase of $S_i$ was indeed observed for most systems when lowering $E_i$ below $\approx 100$ meV. Such an effect is absent to our knowledge only for O$_2$–Ag and N$_2$–Fe(111). Both systems are characterized by activated non dissociative chemisorption but no clear understanding exists so far for the different behaviour of e.g. O$_2$ on Pt, where trapping has a clear influence on $S_i(E)$.

3.1. Anisotropy in the sticking coefficient. The breakdown of normal energy scaling for Ag(110) is observed when oxygen molecules impinge along the ⟨001⟩ azimuth while for the less corrugated ⟨110⟩ direction, data are not incompatible with normal energy scaling. We have checked this important point by independent KW measurements. Such a method can be applied only when the sticking probability is larger than 3–4 $10^{-2}$, but has the strong advantage not to need any external calibration. The KW sticking data for O$_2$ on Ag(110) are summarised vs angle of incidence $\theta_i$ in Fig. 5. As one can see the sticking probability depends on the azimuthal direction, being larger when the molecules impinge along the more corrugated ⟨001⟩ azimuth. A similar effect is found for dissociative adsorption, consistently with the precursor role played by molecular chemisorption. The physical explanation is that the translational energy is most effective in overcoming the barrier when the molecules impinge along the local normal to the surface, an effect which dominates at low impact energy when the steering is most effective. Such effect was recently simulated by Darling and Holloway for the easier case of the H$_2$–surface interaction. They distinguished between geometric and energetic corrugation, the former causing an effective energy dependence of $S_i$ as $E_{i,a} = E_i \cos^2 \theta_i$ with $n < 2$, the latter with $n > 2$. Given a certain velocity of the molecules in the vertical direction, $S_i$ is thus expected to be larger if less energy has to be dissipated for a geometrically flat but electronically corrugated surface while in presence of geometric corrugation parallel momentum helps in overcoming the potential energy barrier. Indeed both effects are present for O$_2$–Ag: the electronic corrugation dominates thereby for $E_i > 0.4$ eV and is isotropic with
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Figure 4

$S_9$ vs $u_i$ at $T = 99$ K measured by the King and Wells method for two values of $E_i$. Data points indicated by $\square$ refer to molecules impinging along $\langle 110 \rangle$, data points indicated by $\bigtriangleup$ to molecules impinging along $\langle 001 \rangle$. The anisotropy is smaller at $E_i = 800$ meV because at high energy the energetic corrugation becomes important and counteracts the effect of geometric corrugation.

3.2. Temperature dependence of the sticking coefficient. The sticking coefficient for Ag(110) decreases with crystal temperature, $T$, as expected from the competition between desorption and dissociation; for Ag(001) on the contrary it increases with $T$ as shown in Fig. 6. Such anomalous dependence is indicative that dissociation on Ag(110) is induced by thermally activated defects, while on Ag(110) it takes place mainly on the atomically flat terraces. Indeed it was recently proven by STM by Pai and Reutt-Robey 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. For Ag(001) an Arrhenius like plot of the initial oxygen uptake at low exposures allows to estimate the defect creation energy, $E_{\text{cre}} \approx 76$ meV, as shown in Fig. 6. The defect creation energy in turn determines via the Boltzmann factor the defect population under equilibrium conditions.

On Ag(001) we find that O$_2$ molecules sitting at terrace sites preferentially desorb instead of dissociating ($P_{\text{dis}} < 4.4 \times 10^{-7}$). From Temperature Programmed Desorption (TPD) and isothermal desorption measurements $^{11,12}$ we learn that the desorption parameters of O$_2$–Ag(001) are comparable to those of O$_2$–Ag(110) therefore concluding that the different branching ratio between desorption and dissociation observed on the two Ag faces is due to different dissociation paths. On Ag(001) only the O$_2$ molecules adsorbed at special sites can dissociate while those sitting at terrace sites desorb. On the basis of the defect creation energy shown in Fig. 6 the active sites for O$_2$ dissociation on Ag(001) could be identified with kinks. $^{12}$

4. Collision induced desorption and dissociation

In a sticking experiment, the energetic dependence of the sticking probability is dominated by the magnitude of the adsorption barrier and by surface corrugation. The eventual energy transfer between the molecule and the surface is hidden by the complexity of the multidimensional barrier. Thermal desorption experiments, on the other hand, provide energy to the chemisorbed molecule in an indirect way and sample only the lowest energy path to desorption and dissociation. The possibility to supply energy and momentum to the molecule in a well defined direction by collision with a chemically unreactive inert gas atom like Xe may help in obtaining more detailed information. We have thus performed recently collision induced experiments where the sample is exposed to O$_2$ at 100 K and then exposed to a hyperthermal Xe beam. We have demonstrated both desorption and dissociation to occur on Ag(001) $^{22}$ and on Ag(110). $^{23}$ Figure 7 shows the cross section for removal of molecular oxygen $\Sigma_{\text{m}}$, i.e. desorption plus dissociation, as a function of Xe total energy for normal and grazing incidence. After collision with the inert gas atom, the oxygen molecule is compressed against the metal surface and is thereafter reflected. Desorption or dissociation may occur provided O$_2$ has acquired an energy larger than the desorption or dissociation barrier. The value of the cross section at normal incidence is small even at energies sensibly larger than the binding energy. As after collision with Xe, oxygen acquires an energy...
and then collides with O1. This second mechanism may play a role in the cross section at grazing incidence. When Xe is first reflected by the surface and then collides with O2, the cross section is larger than at normal incidence. The data correspond to an initial molecular coverage of O2 of about 0.19 ML.

The high energy threshold and the relatively low values of the cross section are reproduced by a classical MD simulation of the collision process between Xe and chemisorbed oxygen. The simulation is based on a hard sphere model thus allowing direct integration of the trajectories. The surface is modelled as an array of balls in fixed position of effective mass \( m_{\text{eff}} \). The model thus includes surface corrugation and energy loss to phonons, even in an oversimplified and not quantitative way.

Dissociation is not included in the simulation as a multidimensional oxygen–silver potential is needed to describe both dissociation and desorption. The cross section is lowered and the energy threshold is increased due to substantial energy losses to the surface. The anomalously large increase in the cross section with the impact angle is due to the lower amount of energy transferred to the surface at grazing incidence and to the role of surface corrugation. Such a strong angular enhancement, was not observed on other systems, characterized by a more limited energy loss to phonons or by a lower surface corrugation.

Inspection of the impact parameters leading to desorption demonstrates that removal of molecular oxygen is not due to local heating of the surface, as a collision between oxygen molecule and Xe is needed to make O2 desorb. If Xe hits the lattice close to the molecule site but not the molecule itself no desorption can occur in the energy range accessible to a molecular beam (some eV for Xe).

5. Conclusions

In conclusion, we have shown that the combination of supersonic molecular beams, vibrational spectroscopy, thermal desorption spectroscopy and King and Wells method allows a complete characterization of the dynamics of the interaction of a gas molecule with the surface. Most of our efforts were so far dedicated to the case of O2 on Ag, a system simple enough to be understood in detail and yet sufficiently complicated to give rise to an interesting variety of new phenomena.

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