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Interaction of oxygen and ethylene with defected Ag surfaces

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# Index

1 Introduction 1

References 3

2 Overview on $O_2$ and $C_2H_4$ interaction with Ag surfaces 5

2.1 Introduction 5

2.2 Oxygen interaction with Ag surfaces 5

2.2.1 Ag(100) 5

2.2.2 Ag(110) 9

2.2.3 Ag(111) 10

2.3 Ethylene adsorption on Ag(100) and Ag(110) 10

2.3.1 $C_2H_4$/Ag(100) 10

2.3.2 $C_2H_4$/Ag(110) 12

References 13

3 Experimental apparatus and measuring techniques 15

3.1 Experimental apparatus 15

3.1.1 The main chamber 15

3.1.2 The molecular beam chamber 16

3.1.3 The detection chamber 17

3.1.4 The HREEL Spectrometer 17

3.2 Supersonic molecular beam technique 18

3.2.1 Calibration of energy 19

3.2.2 Determination of flux and exposure 20

3.2.3 Measurement of $S_0$ 22

3.3 Determination of coverage 23

3.4 Preparation of the sample 26

References 26

4 Oxygen interaction with disordered and nanostructured Ag(100) and with Ag(n10) surfaces 27

4.1 Introduction 27

4.2 Experimental 28

4.3 Surface geometry 29

4.3.1 Sputtered Ag(100) surfaces 29

4.3.2 Stepped surfaces: Ag(410) and Ag(210) 30
4.4 Oxygen adsorption on disordered and nanostructured Ag(100) 31
  4.4.1 Data presentation 31
  4.4.2 Discussion 39
    4.4.2a Identification of the active site 39
    4.4.2b Vibrational frequencies 40
4.5 Oxygen adsorption on Ag(410) 42
  4.5.1 KW experiments 42
  4.5.2 HERRLS experiments 49
4.6 Preliminary results for oxygen adsorption on Ag(210) 53
4.7 Discussion on oxygen adsorption on Ag(n10) surfaces 53
  4.7.1 Energy barriers and final adsorption states 53
  4.7.2 Surface disorder and concentration of minority defects 54
4.8 Conclusions 56
  References 56

5 Ethylene interaction with Ag(410) and Ag(210) 59
  5.1 Introduction 59
  5.2 Experimental 60
  5.3 Data presentation 61
    5.3.1 C₂H₄/Ag(410): analysis of the KW traces 61
    5.3.2 C₂H₄/Ag(410): sticking probability 65
    5.3.3 HREELS experiments 69
  5.4 Discussion 72
    5.4.1 Characteristic desorption time and physisorption energy 72
    5.4.2 Sticking probability and adsorbate-assisted adsorption 73
    5.4.3 Effect of rotations on sticking probability 75
  5.5 Conclusions 75
  References 76

6 Conclusions 77

7 Acknowledgements 78

A Publication list A
1 Introduction

Most industrial catalysts and gas sensors used in everyday life were developed empirically by chemists and chemical engineers. In spite of the high level of efficiency and selectivity obtained, a further improvement of the control on catalytic reactions is highly desirable, and in several cases absolutely necessary, in order to reduce production costs and to limit the environmental impact.

The surface science approach to heterogeneous catalysis consists in the analysis of the elementary steps, which constitute the reaction (like adsorption, surface diffusion, chemical transformation and desorption of the adsorbed species), and in the identification and characterisation of the active sites and of the mechanisms operating at the atomic level. Physicists and chemical physicists have contributed to the advancement of this knowledge by working under controlled conditions, e.g. investigating single crystal surfaces in ultra high vacuum (UHV), performing state resolved experiments and comparing the results with those obtained by numerical simulations based on ab-initio calculations. It is evident that this kind of studies is quite far from the industrial conditions, making the comparison between scientific results and products of industrial reactions problematic.

Reactors usually work at high temperature and at, or above, atmospheric pressure, i.e. at least 10 orders of magnitude higher than typical UHV values. This implies that the number of molecules in the high energy tail of Boltzmann distribution is large enough to dominate the whole process if adsorption of one of the reactants is activated. Such shortcoming between catalytic and UHV conditions, known as pressure gap, can be overcome by the use of supersonic molecular beams, which simulate the high energy tail of the Boltzmann distribution and allow to investigate activated systems.

Moreover, real catalysts consist of a highly dispersed state of small particles on an inert substrate, and are therefore quite unlike the nearly perfect low Miller index surfaces investigated in surface science laboratories. This second shortcoming, addressed as structure gap, turns out to be extremely important if the active site for one of the elementary steps of the reaction is a minority site associated to surface defects, and evidences the essential role played by the latter ones in catalytic reactions.

Although the importance of defects in heterogeneous processes has been demonstrated since a long time [1,2], their role was investigated thoroughly only recently. For instance it was shown, both by theory and experiment, that for Ru(0001) atomic steps are the only active sites for NO and N₂ bond dissociation [3,4,5]. For N₂ steps were found to be $10^9$ times more reactive than terraces [5]. Similarly, it was shown by scanning tunnelling microscopy that oxygen dissociation on Pt(111) occurs at closed packed steps [6]; as adatoms are found only close to the upper side of the steps, this was concluded to be the active site.

The structure gap can be attacked at different levels. The simplest way is artificially introducing defects in low Miller index surfaces, e.g. by ion bombardment. This technique was successfully applied to the study of the NH₃ formation rate on Ru(0001), that was found to increase for the sputtered surface [7]. An increase in the product formation rates caused by the defectiveness of the catalyst, induced in this
case by a pulsed laser, was observed also for CO oxidation on Pt(111) [8] and ascribed to the enhanced sticking probability of oxygen. In these experiments all kinds of defects are present on the surface; they are therefore useful to understand if a particular catalytic reaction is generally influenced by the concentration of defects, but they do not allow telling which one acts as active site. If some indication in this sense is given, the simplest approach for the identification of the active site for a specific reaction is to investigate single crystals cut along high Miller index planes, i.e. surfaces with a high density of a selected defect. Studies in this direction have been performed, e.g., for O₂/Pt(533), showing that (100) closed-packed steps are the active site for the conversion from the physisorbed into the chemisorbed precursor on the, otherwise inert, Pt(111) planes [9]. In another experiment it was shown by microcalorimetric measurements that, on Pt(211), C₂H₄ adsorbs initially as quad-σ-acetylene and, at higher coverage, as ethylidyne (C-CH₃), while on the more corrugated Pt(311) only ethylidyne (C-CH₂) forms [10]. For CO oxidation on Pt(112), on the contrary, defects have a poisoning effect, since a reduced reactivity is reported for step sites as compared to terrace sites [11,2].

Silver surfaces have attracted much attention from the surface science point of view because of their role as a model system in the study of gas-metal interaction, and because silver powders are an extremely selective catalyst for the ethylene epoxidation reaction, which is at the basis of a rich industry. In spite of a several decades long investigation, this process could not be reproduced in controlled, ultra high vacuum conditions and the active site has never been identified [12]. These studies lead, however, to a complete characterisation of the oxygen and ethylene interaction with flat Ag surfaces, showing, e.g., that O₂ adsorption is structure sensitive [13,14] and that different dissociation mechanisms, possibly related to defects, are present for the low Miller index planes [15,16]. Moreover, activated ethylene adsorption in the π-bonded state was observed on Ag(100) [17], contrary to the predictions of theory [18], thus suggesting the possible existence of a defect-related mechanism.

On the basis of this theoretical and experimental background I decided to investigate the interaction of O₂ and C₂H₄ with defected Ag surfaces. In order to understand if defects really play a key role in adsorption processes, I initially performed O₂ adsorption experiments on an Ag(100) substrate damaged and nanostructured by ion bombardment. Once confirmed the active role of defects in the O₂ dissociation process, the natural prosecution of my study was the research of the active site. Since some recent literature [16] indicated the kink site as the most probable candidate, I focussed my attention to Ag(410) and Ag(210), high Miller index surfaces characterised by a high concentration of open steps (25% and 50%, respectively), which consist in a sequence of kinks. Moreover, Ag(410) forms naturally upon massive O₂ exposures on Ag(100) [19]. Ag(n10) surfaces are interesting also from the point of view of ethylene adsorption, as they can help in filling the gap between experimental and theoretical results obtained for C₂H₄ chemisorption on Ag(100).

In this thesis I report therefore a complete characterisation of the oxygen and ethylene interaction with defected silver surfaces. Information about the dynamics of the gas-surface interaction is gained by measuring the sticking coefficient as a function of energy and angle of incidence of the impinging molecules as well as of crystal temperature. The adsorption products are monitored by vibrational spectroscopy,
which allows drawing information about the final chemisorption state and dissociation probability. For O\textsubscript{2} adsorption on a defected Ag substrate, a dissociative adsorption channel opens already at crystal temperatures of 105 K, at which only molecular adsorption was detected on flat Ag(100). The study of Ag(n10) surfaces allows to identify for the first time open steps with the active sites for O\textsubscript{2} dissociation on Ag surfaces, which occurs through a non activated adsorption channel. It shows, moreover, that new adsorption pathways with a reduced activation barrier with respect to the flat surface open for molecular adsorption at steps. Interestingly, the O\textsubscript{2} sticking probability at terrace sites decreases for narrow terraces. For C\textsubscript{2}H\textsubscript{4}/Ag(n10) defects are found to remove the translational barrier into the chemisorbed state and to induce an adsorbate-assisted adsorption mechanism for the physisorbed species.

My results confirm therefore the important role played by defects in catalytic processes and their interest for attacking the structure gap, which separates industrial from controlled working conditions. Introducing defects might therefore be a useful step in the understanding of more complicated processes as, e.g., the so far unexplained ethylene epoxidation reaction.

References

2 Overview on O$_2$ and C$_2$H$_4$ interaction with Ag surfaces

2.1 Introduction

Silver surfaces have always interested the surface science community because of the role played by this metal as a model system for the understanding of the gas-metal interaction. Moreover, Ag powders are an extremely selective catalyst for the ethylene epoxidation reaction. Such process is at the basis of a rich industry but it could not be reproduced under controlled, ultra high vacuum conditions, so far; in spite of many years of research efforts in several laboratories [1,2], in fact, the active site and the active oxygen species for this reaction escaped identification.

For these reasons low Miller index Ag surfaces are nowadays very well characterised both from the electronic and from the chemical point of view [3].

In the following I will give a brief overview of the interaction of oxygen and ethylene with low Miller index Ag surfaces. Ag(100) and Ag(110) correspond to the geometry of terraces and step heights, respectively, on stepped Ag(n10) crystals and constitute therefore an essential starting point for the understanding of the results obtained on those surfaces.

2.2 Oxygen interaction with Ag surfaces

2.2.1 Ag(100)

Oxygen adsorption occurs on Ag(100) both in the molecular and dissociative phase, depending on crystal temperature, T, and subsequent surface treatment. Moreover, several oxygen and di-oxygen moieties and the corresponding adsorption sites have been identified. O$_2$ chemisorption is activated, with an average energy barrier of 0.37 eV, and the adsorption process is not mediated by physisorbed precursors. The initial sticking coefficient scales with normal energy if the translational energy of the impinging molecules is $E_i<0.7$ eV (for which it reads $S_0\approx0.7$) and decreases thereafter [4,5]. High Resolution Electron Energy Loss Spectroscopy (HREELS) investigations showed that below 110 K only molecular adsorption occurs. At low coverage two different O$_2$ species, characterised by loss peaks at 79 meV and 84 meV, were identified and assigned to the internal vibration of O atoms for molecules in four-fold hollow and bridge sites, respectively [6]. At large coverage the higher frequency species becomes dominant. This behaviour is evident in the bottom spectrum of Fig. 2.1A, where, after prolonged O$_2$ exposure by supersonic molecular beam at a crystal temperature $T=105$ K, the loss has moved to 84 meV. The minor peak at 64 meV was ascribed to molecules at defects sites [7] while the one around 32 meV, due to the molecule vibration against the surface, was proved to scale with the O$_2$ stretch intensity [8]. When dosing at $T=130$ K the spectrum is radically different (see upper trace in Fig. 2.1A). The loss peak at 80 meV, corresponding to the internal O$_2$ vibration, is indicative of non-dissociative adsorption. The two oxygen moieties
identified in ref. [6] cannot be resolved in the present experiment and the observed frequency is therefore the result of the convolution between the peaks at 79 meV and 84 meV. The loss at 30 meV is now much more pronounced and not proportional to the O$_2$ stretch intensity. It must therefore be due to oxygen adatoms vibrating against the surface, indicating that a thermal dissociation channel is operative at T=130 K. Comparison of the frequencies of the O-O internal vibration in the two spectra suggests that, at 130 K, the molecules at bridge sites are more prone to dissociate than the ones in the four-fold hollows.

The HREELS experiment reported in Fig. 2.1B shows an example of oxygen adatoms production induced by thermal dissociation [9]. The starting condition is the one described in the upper spectrum of panel A. After dosing O$_2$ at T=130 K, the crystal was flashed to different temperatures and the spectra were then recorded after cooling the sample to T<110 K. When annealing to 150 K thermal dissociation is completed and the O-Ag vibration reads 30 meV; at 190 K it shifts to 36 meV, value previously reported by C.A. Fang for the same system [10]. Above room temperature the vibrational frequency moves back to 28-31 meV, the shift being larger when the initial atomic oxygen coverage is greater. The different frequencies for the O-Ag stretch indicate the formation of two atomic oxygen species, which are selectively populated depending on the annealing temperature.
Moreover, collision induced dissociation of O$_2$/Ag(001) by hyperthermal Xe atoms generates adatoms with stretching frequencies in the range from 28 to 36 meV, depending on impact energy and angle [11,12]. A further O-adatom moiety vibrating at 35 meV is produced at low T by CO oxidation of O$_2$/Ag(001) [13]. In this latter case the production of dissociated oxygen and the consumption of O$_2$ molecules are indicative that CO oxidation, leading to CO$_2$ formation, occurs, although with a very low reaction rate (P$_r$~5 10$^{-4}$).

![Scheme of the 2\sqrt{2}x\sqrt{2} geometry of the Ag(100) surface in presence of the missing row reconstruction. The O530 adatoms sit in the previous four-fold hollow sites, slightly displaced towards the missing rows. This configuration is stable below RT.](image)

A recent investigation of the O/Ag(001) system by X-rays photoelectron spectroscopy (XPS) and photoelectron diffraction (XPD) demonstrated that O-adatoms produced by thermal dissociation adsorb on Ag(100) in two different phases [9], linked by a reversible phase transition just above room temperature (RT). Below RT the system shows a local 2\sqrt{2}x\sqrt{2} geometry associated to a missing row reconstruction of the substrate (see Fig.2.2), similar to the one observed for O/Cu(100) [14]. Oxygen adatoms with a binding energy of the O1s electrons E$_{B}$(O1s)=530.3 eV (O530 in the
following) sit in the previous four-fold hollow sites, slightly displaced towards the missing rows. Above RT the surface de-reconstructs and the oxygen atoms, now characterised by $E_B(\text{O}1s)=528.3$ eV (O528 in the following), move to the four-fold hollow sites. The conversion process of O530 into O528 and the back-conversion are shown in Fig. 2.3, panel A and B respectively [9]. O530 was produced by dosing O$_2$ at $T=150$ K and by annealing the adlayer to 247 K. The estimated atomic oxygen coverage is $\Theta_\text{O}=0.22$ ML. When heating the crystal above RT, the O530 peak decreases and the O528 one appears. The conversion process is complete at 350 K. From comparison of the starting with the final spectrum it is evident that only part of the low-temperature-phase atoms convert, while the others diffuse into the bulk. This behaviour is confirmed by the existence of a critical coverage of O530 below which no O528 formation is observed. The residual intensity at $E_B=530.9$ eV in the upper spectrum is assigned to atomic oxygen in subsurface sites. The back-conversion process from the high temperature to the low temperature phase occurs with characteristic times between $2 \times 10^3$ sec and $2 \times 10^4$ sec, depending on the subsurface oxygen content of the crystal.

From comparison of the XPS data with the thermal dissociation experiment reported in Fig. 2.1B, the oxygen adatom moiety vibrating around 36 meV was identified with the O530 species and the one characterised by frequencies in the 28-31 meV range was ascribed to O528.

![Fig. 2. 3: Panel A: Evolution of the XPS spectra vs. annealing temperature for a starting coverage of O530 of 0.22 ML. At T=300 K the oxygen starts converting from the phase with $E_B(\text{O}1s)=530.3$ eV to the one with $E_B(\text{O}1s)=528.3$ eV. Panel B: Sequence of XPS spectra showing the back-conversion process of O528 into O530 after cooling the crystal to 246 K.](image-url)
The reactivity of the two oxygen adatom species towards CO was investigated both by vibrational and by photoelectron spectroscopy, finding out that O530 is almost inert towards CO oxidation (P r < 1 10^-4) [9]. The O528 moiety, on the contrary, can be removed by CO either above or below RT, but the reaction rate was very different in different experimental runs at Elettra, probably depending on the concentration of oxygen atoms in the subsurface region.

A complete electronic characterisation of the clean and oxygen covered Ag(100) surface was also gained both by theory [15] and experiment [16,17,18]. However, since these results are less related to the chemical reactivity of Ag surfaces, they are not included in the present overview.

2.2.2 Ag(110)

HREELS and thermal desorption experiments demonstrated that, at low temperature, molecular oxygen chemisorbs in two different states also on Ag(110) [19]: α-O2 co-exists with the physisorbed precursor already at T=15 K and forms upon annealing of the physisorbed layer. It is characterised by an O-O stretch vibrating at 85 meV and by a desorption temperature of 100 K, β-O2, the more stable species, is produced by dosing around 100 K and its internal stretch mode vibrates at 79.5 meV. The two moieties do not convert into each other and only the latter one undergoes thermal dissociation when annealed above 150 K.

As it was the case for O/Ag(100), the presence of oxygen adatoms is revealed in the HREEL spectra by the O-Ag stretch mode at ~40 meV. Such frequency is actually slightly dependent on coverage and this effect can be easily explained in terms of dipolar shift [20,21].

For T<200 K thermal dissociation gives rise to a disordered O-adatoms layer, while an ordered nx1 overlayer forms above this temperature [22]. n ranges from 2 to 8, implying that the reconstruction occurs already at low coverage. The saturation coverage, Θ=0.5, corresponds then to the 2x1 superstructure. As it will be reported in chapter 3, the presence of an nx1 overlayer, easily observable by Low Energy Electron Diffraction (LEED), was employed for a direct calibration of the HREELS intensities with the atomic oxygen coverage. The normal component of the dynamical dipole moment relative to the O-Ag(110) stretch was the estimated to be 0.075 D [23].

The annealing process is not the only way to produce oxygen adatoms on the surface, since dissociation induced by collision with hyperthermal Xe atoms was reported in literature [24].

Measurements of the initial sticking coefficient, S0, as a function of translational energy, Ei, demonstrated a substantial anisotropy of the Ag(110) surface [4]. At T=100 K, in fact, S0(Ei) shows a different behaviour for O2 molecules impinging along the flat <110> and along the corrugated <001> directions. In both cases the adsorption process is activated and the calculated energy barrier is 0.37 eV, as for the Ag(001) surface. Only when the beam is aligned with the atomic channels normal energy scaling is however respected. When dosing along the corrugated direction, S0 scales with Eicosθ, with n~1 at low Ei, and produces a greater spread of the data when plotting them vs. normal energy. As demonstrated by Darling and Holloway [25] a geometric corrugation could cause this 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 potential energy barrier to adsorption when molecules impinge along the local normal to the surface and such effect dominates indeed at low impact energies, where the steering is most effective.

CO oxidation experiments performed with HREELS demonstrated that both the molecular and the atomic oxygen species adsorbed on Ag(110) are reactive towards CO. The estimated reaction probability is ~2 orders of magnitude higher than in the case of Ag(100) [26], clearly indicating that this reaction is structure sensitive.

2.2.3 Ag(111)

Four different oxygen moieties were identified on Ag(111), as summarised in ref. [27]. The most weakly bound is physisorbed O$_2$, which shows a trapping probability close to unity and a desorption temperature of 50 K. Molecular chemisorbed O$_2$ was reported to desorb at 217 K, i.e. considerably higher than for Ag(100) and Ag(110). XPS investigations suggested moreover that such molecules have a superoxo-like nature (O$_2^-$), rather than the peroxy-like nature (O$_2^{2-}$) previously observed on Ag(110) [28].

Dissociatively adsorbed oxygen was detected upon exposure at high temperature. Such moiety associatively desorbs at ~580 K, while O-atoms in subsurface sites are stable up to T>700 K. The sticking coefficient for chemisorption both in the undissociated and in the atomic phase is ~5 10$^{-6}$, i.e. much lower than for the other low Miller index Ag planes [29].

A more recent investigation demonstrated that a transient trapping desorption mechanism is active for molecular oxygen chemisorption [30]. During such process O$_2$ molecules are trapped at the surface in a shallow well and are therefore prone to return into the gas-phase already at 140 K.

2.3 Ethylene adsorption on Ag(100) and Ag(110)

2.3.1 C$_2$H$_4$/Ag(100)

Below T=85 K ethylene physisorbs in multilayers [31]. At T=100 K, on the contrary, different adsorption states are populated depending on translational and internal energy of the impinging molecules: a physisorbed state [32], a weakly chemisorbed state, with molecules in the non re-hybridised $\pi^-$-bonded state, and a more strongly bound, undissociated state coupled with radical formation [33].

Physisorption is unstable at 100 K. As demonstrated by Vattuone e al. [32], at this temperature C$_2$H$_4$ molecules have a lifetime of ~0.7 sec at the surface and a physisorption energy $E_{\text{phys}}$=0.25 eV, in accord with theory [34]. The physisorption probability was investigated as a function of translational and internal energy of the ethylene molecules ($E_i$, and $E_{\text{int}}$, respectively) and the sticking probability was found to decrease with increasing $E_i$, as expected for non-activated systems. Little dependence of the sticking probability on translational energy is present at large $E_{\text{int}}$ values. This behaviour is connected to the opening of an activated chemisorption channel by internal energy. Moreover, the physisorption probability of ethylene
molecules with the same $E_i$ but different internal energies is much smaller for vibrationally excited molecules. The effect is ascribed to the cartwheel rotational motion, which decreases the time that molecules spend with the C-C bond parallel to the surface, presumably the only orientation allowing molecules to arrive close enough to the surface to get physisorbed.

Fig. 2.4: HREEL spectra recorded after dosing 40 ML of pure C$_2$H$_4$ at different $T_N$ on clean Ag(100) at $T=105$ K.

HREEL investigations performed upon exposing Ag(100) at $T=105$ K to a C$_2$H$_4$ beam with different translational and internal energies indicate that stable adsorption is an activated process and that two chemisorption states are populated [33]. The experimental results are summarised in Fig. 2.4: 40 ML of pure C$_2$H$_4$ are dosed on Ag(100) at $T=105$ K by the supersonic molecular beam with increasing nozzle temperatures, $T_N$, i.e. with increasing $E_i$ and $E_{\text{int}}$. The absence of loss peaks when dosing at $T_N<850$ K indicates that only physisorption occurs. For $T_N=850$ K (corresponding to $E_i=0.35$ eV), on the contrary, ethylene adsorbs non-dissociatively, as witnesses by the loss features at 32 meV, 117 meV and 367 meV. These modes are assigned respectively to the molecule-surface stretch, to the wagging and to the CH stretch motion of $\pi$-bonded ethylene from comparison with the frequencies measured in the parallel experiments with deuterated ethylene and with those reported for C$_2$H$_4$/Ag(110) [35] and for gas phase molecules [36]. The desorption temperature of 140 K confirms that molecules are in the $\pi$-bonded state, which is also the only stable
state detected for ethylene adsorption on Ag(110) and Ag(111) [35]. The latter surfaces show, however, a reduced sticking coefficient with respect to Ag(100). Moreover I mention that a similar spectrum was obtained upon dosing C$_2$H$_4$ seeded in He with the same E$_i$ and T$_N$=RT (not vibrationally excited) and that recent, time-resolved XPS experiments confirmed these results [37]. The adsorption process is therefore activated, with an early translational barrier to access the π-bonded state. As for a π-bonded molecule little distortion occurs, the activation energy might be due to displacement of substrate atoms or to non-adiabatic effects.

When dosing ethylene with T$_N$=870 K (E$_i$=0.36 eV) the loss energy spectrum becomes qualitatively different. The doublet at 112 meV and 124 meV, due to a Fermi resonance, indicates the presence of undissociated ethylene in a state different from π-bonded, while the peak at 85 meV is ascribed to fragments. Since the ethylene desorption temperature reads ~200 K, this species is a more stable one, possibly di-σ-bonded ethylene. The more strongly bound state is not accessed by an ethylene beam with the same E$_i$ but lower internal energy, indicating that only vibrationally excited molecules can overcome the barrier to adsorption. The translational energy threshold for adsorption of vibrationally hot molecules in the di-σ-bonded state is ~0.35 eV, i.e. very close to the one for non-vibrationally excited, π-bonded molecules. At even higher T$_N$ the dissociative fraction increases and significant radical formation is observed, as witnessed by the enhanced intensity of the CH stretch at 381 meV. By changing the internal energy of ethylene molecules it is therefore possible to select their final adsorption state at a given crystal temperature. This result might be important under catalytic conditions because of the vibrationally hot molecules present in the tail of the Boltzmann distribution.

When dosing ethylene on oxygen precovered Ag(100), adsorption in the π-bonded state is detected also at the lowest E$_i$ [33]. This effect is in accord with what observed on Ag(110) [35] and was tentatively explained with a reduction of the translational barrier by O-adatoms.

It is worth to mention that, contrary to experimental observation, no stable C$_2$H$_4$ adsorption state was found on Ag(100) by recent Local Density Approximation (LDA) calculations [38]. Theory suggests therefore that the observed admolecules sit at defect sites, as in the case of C$_2$H$_4$ on aluminium [39]. The unexpected barrier to adsorption of ethylene into the π-bonded state would then be linked to the energy required for creation of an adatom at which the molecule can stick with high enough binding energy to be stable at 100 K.

### 2.3.2 C$_2$H$_4$/Ag(110)

Ethylene adsorption on Ag(110) was investigated by Backs et al. [35]. At T=110 K they found a low sticking probability on the clean surface and a strong increase of the reactivity in presence of atomic oxygen. Moreover the activation energy for C$_2$H$_4$ desorption on clean silver is approximately 9 kcal/mol, whereas on the oxygen-precovered surface two states are found with activation energies of 8.5 and 12.5 kcal/mol. The reported vibrational frequency of 120 meV for the wagging mode and the desorption temperature of 140 K allow to identify this chemisorbed species with π-bonded ethylene.
References

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3 Experimental apparatus and measuring techniques

3.1 Experimental apparatus

The experimental apparatus consists in a complex ultra high vacuum (UHV) system equipped with a high resolution energy loss spectrometer (HREELS) and a supersonic molecular beam. The latter, combined with a mass spectrometer for residual gas analysis, allows to perform adsorption experiments for the determination of sticking coefficients using the retarded reflector method of King and Wells [1]. HREELS is employed, on the contrary, to investigate the final chemical state of the adsorbates. The apparatus [2] is schematically shown in Fig. 3.1 for a more detailed description. It consists of three parts, separated by all metal valves: 1) the main chamber, containing the crystal and the instrumentation for surface analysis, 2) the supersonic molecular beam chamber, and 3) the detection chamber of the supersonic beam.

![Schematic picture of the experimental apparatus](image)

**Fig. 3.0:** Schematic picture of the experimental apparatus. S1, S2, S3 and S4 are the skimmers and collimators placed along the beam axis, CH is the chopper in the second stage of the molecular beam chamber, SH1 and SH2 are flags intercepting the beam.

3.1.1 The main chamber

The main UHV chamber is a vertical Inox 316 cylinder, 90 cm high and 48 cm in diameter. It contains the sample and all the instrumentation necessary for surface analysis. The crystal is mounted on a manipulator allowing translations in the x-y-z directions and rotations around the main axis of the chamber. It can be annealed up to ~ 1000 K by electron bombardment, using a tungsten filament placed at its back, and cooled down to 100 K by a liquid nitrogen flux. The temperature is measured through a
chromel-alumel thermocouple (type K) placed on the sample holder, at the side of the sample. A systematic error up to 5 K in the temperature reading is therefore possible. The instrumentation is distributed on two levels. In the upper one we find:

- an ion gun for \textit{in situ} preparation of the surface by ion bombardment,
- a retarding field analyser (RFA) for inspection of surface order and orientation by low energy electron diffraction (LEED),
- a cylindrical mirror analyser (CMA) to record Auger spectra of the surface and check its cleanliness.

The lower level contains:

- the high resolution electron energy loss spectrometer,
- the entrance of the supersonic molecular beam.

Moreover inlets for four different gases and a quadrupole mass spectrometer (QMS) not in line of sight with the molecular beam are present. The former ones allow to introduce the sputtering gases and to perform adsorption experiments by backfilling the chamber; the QMS is used for residual gas analysis and King and Wells experiments.

The pumping system consists of: a turbo-molecular pump (450 l/sec) and a rotative pump (16 m$^3$/h) in cascade, an ion pump (400 l/sec) combined with a titanium sublimation pump (~5000 l/sec), and a liquid nitrogen cold trap. The different pumping systems are necessary to pump efficiently the different gases. The basic pressure after baking the chamber at a temperature of 200 °C is $1 \times 10^{-10}$ mbar.

The chamber has a double $\mu$-metal shield in order to reduce the earth magnetic field inside it below 10 mgauss and allow for HREELS measurements.

### 3.1.2 The molecular beam chamber

The supersonic molecular beam (MB) is produced in an UHV chamber divided into three differentially pumped stages (see Fig. 3.1). The latter ones are connected by the copper skimmers S1 (470 $\mu$m diameter) and S2 (1 mm diameter).

The gas flows into the first stage through a 100 $\mu$m diameter nozzle and passes from a region at a pressure of ~1 bar to one at $5 \times 10^{-4}$ mbar, undergoing a supersonic expansion. The first stage is pumped through a turbo-molecular pump (pumping speed: 1000 l/sec) followed by a molecular pump (40 l/sec) and a rotative pump (16 m$^3$/h). The ceramic nozzle is aligned by construction with the skimmer S1 and can be moved in the x-y and in the z directions. The former movement allows to align the beam with the collimators present in the subsequent stages, while the latter is necessary to optimise the nozzle-skimmer distance (~1 cm). The nozzle can be resistively heated up to ~1000 K and its ceramic walls are non-reactive even at the highest working temperatures.

The second stage is pumped by a turbo-molecular pump with a pumping speed of 450 l/sec and characterised by a typical pressure of $\sim 1 \times 10^{-6}$ mbar in working conditions (beam on). It contains a shutter (SH1), controlling the entrance of the beam into the main chamber, and a chopper (CH), employed for time of flight (TOF) measurements of the velocity distribution of the beam molecules. The third stage is pumped by a turbo-molecular pump (450 l/sec) and has a pressure of $\sim 1 \times 10^{-8}$ mbar with the beam on. A rotative pump provides the fore vacuum both for the second and the third stage. A further collimator (S3) is placed immediately before the slit valve connecting the molecular beam chamber to the main chamber. It is aligned with the collimator S4 (7.5 mm diameter), placed behind the sample, at the entrance of the detection
chamber. The diameter of S3 determines the dimension of the spot at the position of the crystal. It is chosen depending on the kind of experiment performed: for HREELS experiments the whole surface must be uniformly illuminated and the spot needs therefore to be larger than the sample. In adsorption experiments employing the retarded reflector method of King and Wells [1] (KW in the following), on the contrary, all the molecules must strike against the surface even for grazing incidence conditions, so the beam diameter has to be smaller than the one of the sample. For experiments on the Ag(100) sample, which is a disk of 10 mm diameter, I worked with a collimator of 3.1 mm in both kinds of experiments. For the Ag(410) and Ag(210) crystals, which have a diameter of 7 mm, S3 was chosen of 3.1 mm diameter for HREELS and of 1.0 mm for KW measurements. In both cases the collimators S1, S2 and S3 strongly limit the angular divergence of the beam. At the sample position it reads \( \sim 0.4^\circ \) and \( \sim 0.1^\circ \) for the S3 collimators with 3.1 mm and 1.0 mm diameter, respectively.

### 3.1.3 The detection chamber

The detection stage of the supersonic beam is connected to the main chamber by a straight through all-metal valve and contains a quadrupole mass spectrometer (Extranuclear) in line of sight with the molecular beam source. It allows: 1) to evaluate the translational energy and the velocity distribution of the beam molecules by time of flight measurements; 2) to easily investigate the presence of possible contaminants in the molecular beam.

The beam flux is measured by a Spinning rotor gauge (VISCOVAC, Leybold). This instrument is mounted in a small chamber with known pumping speed, which can be filled by the beam gas. It reads absolute values of pressure, which are converted in absolute values of flux (mol/cm\(^2\) sec), and is employed as international standard for pressure measurements.

### 3.1.4 The HREEL Spectrometer

Electron energy loss spectra were recorded by a self-constructed, high resolution spectrometer [3], built following the model of ref. [4] and shown in Fig. 3.2.

The electrons are produced by a LaB\(_6\) filament (cathode) by thermoionic effect and are focused on the slit FEND1 through a system of electrostatic lenses (lenses A). FEND1 is the entrance slit to the premonochromator – monochromator system, where the width of the energy distribution is reduced from \( \Delta E=400 \) meV, the natural width of thermoionic emission at a filament temperature of 1800 K, to \( \Delta E=6 \) meV. A second system of electrostatic lenses (lenses B) accelerates the electrons and focuses the beam on the sample. Then it decelerates the reflected beam to the pass energy of the analyser and focuses it onto the entrance slit of the analysing system (FEND4).

In the present configuration of the spectrometer the electron energy, \( E_e \), is therefore determined by the sum of the pass energy of the monochromator and the accelerating voltage given by the potential energy difference between the scattering chamber and the monochromator exit slit. It is possible to correct for the work function difference between the sample and the spectrometer walls by applying a voltage to the sample. The double-pass analysing system is formed by an analyser and a post-analyser. The voltage difference with respect to the monochromator system is varied during the
measurement in order to record the energy loss spectrum. Peaks are then observed at the electron energy losses corresponding to surface or adsorbate excitations. The B5 lens, located just before the detector, focuses the beam into it. The detector is a channeltron of the Galileo Company, with a dark counts level of 0.7 count/sec. Both the lens setting and the data acquisition are remote controlled by a digital electronics via an IEEE488 interface.

The angle of incidence of the electrons on the sample can be varied from 0° to 90° by rotating the monochromator and the sample. Typical working conditions for our experiments are a resolution $\Delta E \sim 7$ meV and primary electron energy $E_e = 1.7$ eV (the low $E_e$ value is chosen to maximise the cross section for dipolar scattering). With these parameters the instrument shows a direct beam intensity of $\sim 8 \times 10^{-11}$ A and an angular acceptance of $\sim 6^\circ$.

![Scheme of the HREEL spectrometer. The slits FEND1,...,FEND6, the A and B lenses, the monochromator (PREMONO and MONO) and the analyzing (ANA and POST-ANA) systems are shown.](image)

### 3.2 Supersonic molecular beam technique

The supersonic molecular beam technique allows to produce intense and well-collimated beams of molecules with a narrow energy distribution and to select easily both the translational and the internal energy of the molecules in a rather large range. Possibly more important for the present thesis, also the angle of incidence on the surface can be accurately defined. Such technique has been widely used in the study of activated systems and to understand the effects of molecules in the high-energy tail of the Boltzmann distribution.
A gas undergoes a supersonic expansion when it flows from a high pressure (1-100 bar) to a low pressure region through a small orifice (nozzle). In this process the gas cools down because its degrees of freedom corresponding to rotational and translational motion are frozen, and the energy is converted into translational energy in the direction on the beam [5].

### 3.2.1 Calibration of energy

The kinetic energy of the molecules, $E_i$, can be varied by resistively heating the nozzle source, in order to increase the internal energy of the molecules before the adiabatic expansion. As a function of the nozzle temperature, $T_N$, $E_i$ is given by

$$E_i = \frac{\gamma}{\gamma - 1} kT_N$$

with $\gamma=c_p/c_v$ ($c_p, c_v$ specific heat at constant pressure and volume respectively). $T_N$ is calibrated by TOF measurements, as explained hereafter.

It is also possible to vary $E_i$ by seeding the gas of interest in an inert carrier with a different mass and a much higher concentration, $X$. The scattering between particles causes the velocities to become uniform (thermalisation process), so that, if the seeded species is heavier than the carrier, it gains in energy following the law [5]:

$$E_i = \frac{M_j}{<M>} \frac{\gamma}{\gamma - 1} kT_N$$

where

$$<M> = \sum_i X_i M_i$$

and

$$\frac{\gamma}{\gamma - 1} = \sum_i X_i \frac{\gamma_i}{\gamma_i - 1}$$

Since the thermalisation process might be not perfect, for an accurate calibration of the translational energy it is always necessary to verify the value of $E_i$ predicted by formula (3.2) by TOF measurements. To this purpose the beam is chopped in the second stage of the MB chamber and it is revealed in the detection chamber by the quadrupole mass spectrometer in line of sight with the beam and located at distance $L=(135.0 \pm 0.5)$ cm from the chopper. The quadrupole signal is displayed by a digital oscilloscope and gives information about the time $t_0$ necessary for the molecules to reach the detector. $L$ is calibrated by comparing the experimental value of $E_i$ with the one calculated from formula (3.2) for a pure Ne beam, for which there are no complications due to internal modes, $\gamma=5/3$ and equation (3.2) reduces therefore to $E_i=5/2kT_N$. This method allows a more precise determination of the position of the detector with respect to a direct measurement. Once $L$ and $t_0$ are known, the velocity and kinetic energy of the molecules can be easily deduced.

The TOF method is also employed to calibrate the translational energy of pure and seeded gases and the nozzle temperature vs. the heating power applied to the nozzle. A pure noble gas beam (Ne in the present case) was used for the measurement of $T_N$, because it has no internal degrees of freedom and therefore undergoes always a complete supersonic expansion. The results for $T_N$ and for the gases employed in my experiments ($O_2$ and $C_2H_4$, pure and seeded in helium with concentration $X_{O_2}=3\%$ and $X_{C_2H_4}=3\%$) are reported in table 3.1. It is evident that, by combining the use of seeded gases with the possibility of heating the nozzle source, it is easy to vary the
translational energy of the molecules over a wide range. Moreover translational and vibrational energy can be selected quite independently.

The energy distribution of the supersonic beam has approximately a gaussian shape [5] and a width of ±10% $E_i$, determined by TOF measurements.

<table>
<thead>
<tr>
<th>$W_{\text{NOZZLE}}$ (watts)</th>
<th>$T_N$ (K)</th>
<th>$E_i$ (eV)</th>
<th>$E_i$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Pure $O_2$</td>
<td>$O_2$ seeded in He ($X_{O_2}=3%$)</td>
</tr>
<tr>
<td>0.0</td>
<td>294</td>
<td>0.09</td>
<td>0.39</td>
</tr>
<tr>
<td>3.6</td>
<td>506</td>
<td>0.21</td>
<td>0.67</td>
</tr>
<tr>
<td>9.3</td>
<td>732</td>
<td>0.25</td>
<td>0.81</td>
</tr>
<tr>
<td>14.6</td>
<td>850</td>
<td>0.29</td>
<td>0.96</td>
</tr>
<tr>
<td>22.33</td>
<td>940</td>
<td>0.31</td>
<td>1.01</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$W_{\text{NOZZLE}}$ (watts)</th>
<th>$T_N$ (K)</th>
<th>$E_i$ (eV)</th>
<th>$E_i$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Pure $C_2H_4$</td>
<td>$C_2H_4$ seeded in He ($X_{O_2}=3%$)</td>
</tr>
<tr>
<td>0.0</td>
<td>294</td>
<td>0.10</td>
<td>0.36</td>
</tr>
<tr>
<td>3.1</td>
<td>487</td>
<td>0.21</td>
<td>0.57</td>
</tr>
<tr>
<td>5.1</td>
<td>552</td>
<td>0.24</td>
<td></td>
</tr>
<tr>
<td>9.3</td>
<td>732</td>
<td>0.27</td>
<td>0.70</td>
</tr>
<tr>
<td>14.6</td>
<td>850</td>
<td>0.32</td>
<td></td>
</tr>
<tr>
<td>22.33</td>
<td>940</td>
<td>0.35</td>
<td>0.86</td>
</tr>
</tbody>
</table>

Table 3.1: Calibration of $T_N$ and $E_i$, estimated by TOF measurements, vs. the heating power applied to the nozzle. For evaluating the nozzle temperature, a pure Ne beam was employed. The upper table reports the data for a pure and a seeded (3% in He) oxygen beam, the lower one for pure and seeded (3% in Helium) ethylene.

### 3.2.2 Determination of flux and exposure

The total exposure, $\chi$, of a gas on a surface is given by the general expression:

$$\chi = \frac{n_i}{n_0}$$  \hspace{1cm} (3.5)

where $n_i$ is the number of impinging molecules per unit of surface and $n_0$ is the density of surface atoms of the substrate. $n_0$ reads $1.18 \times 10^{15}$ atoms/cm$^2$ for Ag(100), $1.14 \times 10^{15}$ atoms/cm$^2$ for Ag(410) and $1.07 \times 10^{15}$ atoms/cm$^2$ for Ag(210).

When dosing the gas by a supersonic molecular beam, $\chi$ can be written as:

$$\chi = \frac{\Phi t \cos \theta}{n_0} X$$  \hspace{1cm} (3.6)

$\Phi$ being the flux, $t$ the exposure time (controlled by the shutter SH1), $\theta$ the angle of incidence of the beam on the crystal surface and $X$ the concentration of the relevant component of the gas.

For pure gases, $\Phi_{\text{pure}}$ is measured by a spinning rotor gauge. This method, which allows an absolute measurement of the pressure in the range $10^{-3}$-$10^{-6}$ mbar, is based
on the deceleration of the rotation of a magnetically suspended sphere, because of the viscous friction of the gas particles. The flux is estimated from the average value of a series of data recorded with the beam on, subtracting the average background value due to other sources of friction. The so-determined flux is then weighted with respect to the Ag surface atom density and expressed in monolayers of Ag per second (ML/sec). The conversion factor is slightly different for Ag(100), Ag(410) and Ag(210) because of the different atom density of the three crystallographic planes.

For seeded beams, on the other hand, the pressure measurement is often complicated by the different pumping speed for the carrier and for the gas of interest. In this case the flux ($\Phi_{\text{seed}}$) is estimated by comparing the increment of the partial pressure in the main chamber ($I_{\text{seed}}$) with the one recorded as reference during the direct measurement of the pure beam flux ($I_{\text{pure}}$). $I_{\text{pure}}$ and $I_{\text{seed}}$ are determined from QMS traces taken with identical settings and identical pumping conditions. The flux of the seeded beam is then deduced from the law:

$$\frac{\Phi_{\text{pure}}}{\Phi_{\text{seed}}} = \frac{I_{\text{pure}}}{I_{\text{seed}}}$$

I note that variations up to 15% in the flux are observed for different experiments performed with the same gas because of differences in the nozzle pressure, the absolute value of which is controlled within $\pm15\%$ in typical working conditions. The stability of the beam, however, is better than 1% once the beam is on. For a careful calibration of the flux the increase in the partial pressure due to the beam has therefore to be compared with the one of reference for each experiment.

The flux values measured for O$_2$ and C$_2$H$_4$ during my experiments are reported in table 3.2; they are expressed in ML/sec, taking into account the surface atom density of the different Ag faces. For pure gases, the experimental error is deduced from the standard deviation of repeated direct measurements. For fluxes determined through relation (3.7), the percentage error must be increased by a further $\sim2\%$, due to the errors on $I_{\text{pure}}$ and $I_{\text{seed}}$ ($\sim1\%$).

<table>
<thead>
<tr>
<th>P$_{\text{1st stage}}$ (mbar)</th>
<th>Flux (ML/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ag(100)</td>
</tr>
<tr>
<td>O$_2$ pure</td>
<td>3.3 $10^{-4}$</td>
</tr>
<tr>
<td>O$_2$ seeded (3 % in He)</td>
<td>3.3 $10^{-4}$</td>
</tr>
<tr>
<td>C$_2$H$_4$ pure</td>
<td>8.3 $10^{-4}$</td>
</tr>
<tr>
<td>C$_2$H$_4$ seeded (3% in He)</td>
<td>8.3 $10^{-4}$</td>
</tr>
</tbody>
</table>

Table 3.2: Calibration of the flux for oxygen and ethylene beams with the nozzle at 300 K. The pressure in the 1st stage is not reported for the seeded beams since their flux is calibrated through formula (3.7), as explained in the text.
3.2.3 Measurement of $S_0$

The sticking coefficient, $S$, is a function of coverage, $\Theta$, which quantifies the rate of adsorption of a gas on the substrate. It is defined as:

$$S(\Theta) = \frac{d\Theta}{d\chi} \quad (3.8)$$

where $\chi$ is the exposure.

Its initial value, $S_0 = \left. \frac{d\Theta}{d\chi} \right|_{\Theta=0}$, is particularly important because it corresponds to the interaction of the gas with the bare surface.

$S_0$ can be measured with direct and indirect techniques. In the indirect methods $\Theta$ is determined, e.g., from the intensity of the energy loss peaks recorded by HREELS and its increment vs. $\chi$ is calculated by finite differences. The estimate is indirect because it needs a calibration of the dipole moment of the adsorbed species and a direct measurement of the flux.

If $S_0 \geq 0.015$, a direct evaluation is possible by measuring the pressure drop in the main chamber when the surface is exposed to the gas. This method, known as the retarded reflector method of King and Wells (KW in the following [1]), employs the experimental set-up shown in Fig. 3.1. Two shutters are present along the beam path: SH1, in the second stage of the molecular beam chamber, and SH2, just in front of the crystal. A KW trace relative to a pure C$_2$H$_4$ beam impinging on the Ag(410) surface is reported in Fig. 3.3. The translational energy of the beam is $E_i=0.10$ eV, the angle of incidence is $\theta=0^\circ$ and the crystal temperature is $T=105$ K. At the beginning of the experiment both SH1 and SH2 are closed, and the beam cannot reach the main chamber. The QMS installed in the main chamber, not in line of sight with the beam, records only the C$_2$H$_4$ partial pressure of the background gas. At time $t_0$ SH1 is opened and the C$_2$H$_4$ beam enters into the chamber, as indicated by the sudden increase in the QMS signal ($I_{C2H4}$, normalised to unity in the spectrum of Fig. 3.3). The beam cannot, however, strike the surface because it is still intercepted by SH2. Since the background pressure remains very low ($\sim 10^{-9}$ mbar), no significant adsorption occurs in this condition. At time $t_1$ also SH2 is opened: the beam strikes then the Ag(410) surface and part of the C$_2$H$_4$ flux is removed from the gas-phase by adsorption, causing a sudden drop of the partial pressure in the main chamber and, consequently, in the QMS signal ($\Delta I_{C2H4}$). The ratio $\Delta I_{C2H4}/I_{C2H4}$ is a direct measurement of $S_0$. If any metastable species accumulates on the sample, as it is the case for physisorbed ethylene, it desorbs as soon as at time $t_2$ the shutter SH2 intercepts the beam again. The desorption process is evidenced by the increase in the C$_2$H$_4$ partial pressure. Assuming a first order desorption process, a characteristic decay time, $\tau_{des}$, can be determined by fitting the desorption curve with a negative exponential ($f(t)=ke^{-t/\tau_{des}}$).

KW experiments are affected by an error of $\pm 0.015$ in the determination of $S$; the method can therefore be applied only if $S$ is greater than this value. Moreover it measures the total sticking coefficient, without any information on the chemical state of the adsorbed species. In the case of oxygen on Ag(410), e.g., oxygen chemisorbs at low temperature both molecularly and dissociatively, but vibrational spectroscopy is necessary to obtain this information.
1.2 1.0 0.8 0.6 0.4 0.2 0.0
C$_2$H$_4$ part. press. (arb. units)

0 50 100 150 200 200
Time (sec)

E$_i$=0.10 eV
T=105 K
$\theta$=0°

Fig. 3.2: Typical QMS trace recorded during a KW experiment. A pure C$_2$H$_4$ beam with E$_i$=0.10 eV impinges at normal incidence on the Ag(410) surface at T=105 K. Both adsorption, at time $t_1$, and desorption of the metastable species, at time $t_2$, are evident.

3.3 Determination of coverage

From KW traces a lot of information can be gained on the behaviour of S as a function of exposure and on the total coverage on the sample. A typical analysis is reported in Fig. 3.4. Panel A shows the normalised KW trace recorded during an oxygen adsorption experiment performed on Ag(410). The behaviour of the sticking coefficient as a function of exposure time (panel B) is deduced by subtraction of the trace from the level corresponding to the equilibrium partial pressure with the beam on. Once S(t) and the flux, $\Phi$, are known, the total coverage can be calculated from integration of such curve through the formula:

$$\Theta(t) = \Phi \int_0^t S(t') dt'$$  \hspace{1cm} (3.9)

where $\Phi$ is determined by the spinning rotor gauge. $\Theta$ is estimated to be affected by a systematic error of $\sim$20%, which is mainly due to the indetermination on $\Phi$. The result is plotted in panel C vs. exposure time, while panel D displays the dependence of S vs. total coverage. I note that (3.9) gives the total coverage at the time t and takes into account also the contribution of metastable species, if present (see Fig. 3.3). In this case, their desorption would be evident also in the $\Theta(t)$ curve because of a sudden decrease of $\Theta$ as soon as the exposure of the sample to the beam is interrupted.

If the sticking is too small or if information about the partial coverage of different adsorbed species is required, as it is the case in some of my experiments, alternative methods have to be used, e.g. Auger Electron Spectroscopy [6], work function measurements [7] and thermal induced desorption [8].
Letizia Savio

Fig. 3.3: Typical analysis of a KW experiment. Panel A: partial pressure recorded during an O₂ adsorption experiment on Ag(410). In this case Eᵢ=0.97 eV, θ=31° and T=110 K. Panel B: behaviour of S as a function of exposure time. Panel C: total coverage, calculated from formula (3.9) vs. exposure time. Panel D: dependence of the sticking probability on total coverage.

Fig. 3.4: HREEL spectrum recorded after 0.4 ML exposure of O₂ on Ag(410); the beam energy is 0.39 eV, the angle of incidence 29°, the crystal temperature 110 K. Two losses, indicative of the presence of both molecular and dissociated oxygen, are evident. Spectra were recorded with Eₑ=1.7 eV and an θₑ=60°.
I evaluated the partial coverage of molecular and dissociated oxygen from the analysis of the energy loss peak intensities recorded by HREELS. Fig. 3.5 shows a sample spectrum recorded after exposing the Ag(410) crystal at T=110 K to 0.4 monolayers (ML) of O₂, dosed at θ=29° by a supersonic molecular beam with Eᵢ=0.39 eV. The spectrum is recorded in specular, with Eₑ=1.7 eV and an angle of incidence of electrons θₑ=60°. The two losses around 32 meV and 84 meV, assigned to the O-Ag vibration of oxygen adatoms and to the internal stretch of the O₂ admolecules, respectively, clearly show the presence of two different oxygen species. Intensity and position of the loss peaks are determined by fitting the loss spectrum with gaussian curves plus a background. The latter is described by a constant plus a decreasing exponential for energies below 50 meV, where the tail of the elastic peak is non-negligible. At higher energy, on the contrary, a constant background subtraction is sufficient.

Dipolar theory states that, if the coverage is not high enough for depolarisation effects to take place, Θ is proportional to the loss peak intensity through the dynamic dipole moment normal to the surface, μ.

In particular [9]

$$\frac{I_{loss}}{I_0} = \tilde{A} \mu^2 n_s$$

(3.10)

where I₀ and I loss are the elastic and the loss peak intensities and n_s=Θn₀ is the number of molecules/atoms adsorbed on the substrate per surface unit cell. A is a function depending both on the instrumental characteristics of the spectrometer and on the experimental conditions.

The intensity of I loss as a function of coverage must be calibrated by an independent determination of the dynamical dipole moment, which can be done, e.g., from LEED analysis. For O/Ag(110) an ordered (4x1) superstructure forms [7], from which μ can be deduced to be 0.075 D [10]. For O/Ag(100) the same dipole moment as for Ag(110) is assumed, since no ordered LEED structures form and no direct calibration is therefore possible. O₂ on Ag(100), on the contrary, allows an absolute calibration of the intensity of the O-O stretch from KW experiments, because only admolecules are present [11]. Following these calibrations, the relation between the coverage of the X-species and the intensity of the corresponding loss peak reads:

$$\Theta_X = c_X \frac{I_{loss}}{I_0}$$

(3.11)

with C₀₂=15.4 and C₀=11.1 for molecular and atomic oxygen on flat Ag(100), respectively.

For oxygen adsorption on Ag(n10) surfaces and on sputtered Ag(100) the effects of the different surface morphology have to be considered in the calibration of the partial coverage of O₂ and O, Θ₀₂ and Θ₀ respectively. For O₂ admolecules it is reasonable to assume that the O-O intermolecular stretch is only slightly perturbed by the substrate geometry and that the proportionality factor C₀₂ is the same as for flat Ag(001). Θ₀₂, is therefore calculated from formula (3.11). For atomic oxygen the situation is different, since the dynamic dipole moment associated to the O-Ag vibration can be heavily affected by the morphology of the substrate. If the dissociated and undissociate species co-exist on the surface, Θ₀ is determined from
the difference between the total oxygen uptake, evaluated from KW traces, and $\Theta_{O_2}$. Once $\Theta_{O_2}$ is known, it allows to deduce the dynamic dipole moment for these surfaces, which comes out to be approximately $\sqrt{3}$ times larger for Ag(410) than for flat Ag(100) and Ag(110). When only atomic oxygen is present, on the contrary, its coverage can be directly estimated from the KW traces. For instance, this is the case for oxygen adsorption on Ag(210) and on Ag(410) at low energy.

### 3.4 Preparation of the sample

In my experiments I employed Ag single crystals cut along the (100), (410) and (210) surface planes. The first sample is a disk of 10 mm diameter oriented within 0.1° with the (100) plane, the other ones have a diameter of 7 mm and are oriented within 1° with the (410) and 0.25° with the (210) crystallographic planes, respectively. Their surface geometries will be described in details in Chapter 4. Surfaces are prepared before each experiment by sputtering with Ne$^+$ ions ($I_{Ne^+}$=1.0 µA, $E_{Ne^+}$=1 keV, $\chi_{Ne^+}$~10 ML) and annealing to 700 K for 60 sec. Ion bombardment removes the first surface layers, where the higher concentration of contaminants is present, while the heating procedure restores surface order. Several sputtering and annealing cycles are performed, until no more contaminants are detected in the HREEL spectra and a sharp LEED pattern is present.

### References

4 Oxygen interaction with disordered and nanostructured Ag(100) and with Ag(n10) surfaces

4.1 Introduction

Defected surfaces have attracted increasing attention in the last few years because of the role they play in attacking the, so called, structure gap between controlled UHV and industrial conditions of catalytic processes. Atomic steps have been demonstrated by low temperature Scanning Tunnelling Microscopy (STM) and by density functional theory calculations to be the only active sites for NO dissociation on Ru(0001) [1,2]. N\textsubscript{2} on the same surface was also shown to dissociate only at steps both by thermal desorption experiments and by theory [3]. In order to clarify the role of defects a number of different and sometimes complex approaches have been employed, as e.g. atomic-scale fabrication of novel surfaces [4] by the tip of a scanning tunnelling microscope. A simpler way to contribute to this research topic is to modify the structure of single crystal surfaces by ion bombardment, and to investigate firstly the adsorption of molecules, which might dissociate preferentially at defect sites [5], and subsequently bimolecular reactions. This technique was successfully applied to the NH\textsubscript{3}/Ru(0001) system, finding an increased reactivity of NH\textsubscript{3} molecules on the sputtered surface [6]. Alternatively, if some indication about the nature of the active defect is available, one can study monocrystals cut along high Miller index surface planes, i.e. surfaces characterised by a large density of a selected defect. A recent investigation on O\textsubscript{2}/Pt(533) demonstrated indeed the active role of (100)-oriented steps for O\textsubscript{2} conversion from the physisorbed into the chemisorbed precursor; this defect was therefore suggested to determine the reactivity of the, otherwise inert, Pt(111) planes [7].

In a recent publication it was demonstrated by STM [8] that the morphology of Ag surfaces can be changed in situ by Ar bombardment because of the interplay between the sputtering action of Ar\textsuperscript{+} ions and the surface mobility. This process leads to the formation of tiny (10 Å diameter) holes when sputtering is performed at crystal temperatures T<180 K and to large corrugations when it takes place near room temperature. When sputtering the surface at normal incidence the nanostructuring takes the form of ripples for Ag(110) [8] and of a checkerboard structure of pits for Ag(100) [9,10]. The latter crystal face is particularly interesting with respect to chemical reactivity as, on flat Ag(100), O\textsubscript{2} adsorption takes place only molecularly at T=105 K [5,11].

In my study on the role of defects in the O-Ag interaction, which I report in this chapter, I started therefore investigating the chemisorption of oxygen on sputtered and nanostructured Ag(100). I found that defects are an important element in the O\textsubscript{2} dissociation process since, in presence of the checkerboard structure, dissociation occurs already at 105 K. The dissociation probability, P\textsubscript{diss}, correlates well with the density of kink sites [12,13]. In spite of that, the assignment of kinks as the active sites for O\textsubscript{2} dissociation is not straightforward because the sputtering process generates many kinds of defects.
To determine the nature of the active site unambiguously I switched thus to the investigation of Ag(410) and Ag(210) surfaces, which are characterised by a high density of open steps (25% and 50%, respectively). Moreover Ag(410) forms naturally when exposing Ag(100) to massive oxygen doses [14]. Information about the dynamics of the gas-surface interaction is gained by measuring the sticking coefficient as a function of the translational energy and of the angle of incidence of the impinging molecules, as well as of the crystal temperature. The final adsorption products are then monitored by vibrational spectroscopy.

My results finally demonstrate the role of open steps as active sites for O\textsubscript{2} dissociation and show the existence of defects-related adsorption paths with reduced or vanishing activation barriers with respect to flat Ag(100).

### 4.2 Experimental

All adsorption experiments were performed in the combined HREELS and supersonic molecular beam apparatus described in Chapter 3, while the surface morphology of the sputtered Ag(100) crystal was investigated in a different UHV apparatus equipped with Scanning Tunnelling Microscopy (STM).

In experiments on Ag(100) the clean surface is bombarded with 1 keV Ne\textsuperscript{+} ions and a current on the sample of 1.2 \(\mu\text{A}\), at different sputtering temperatures, \(T_{\text{spat}}\), and with different Ne\textsuperscript{+} doses, in order to obtain the nanostructuring. Experiments are performed both at normal and at grazing sputtering angle (\(\theta_{\text{spat}}=70^\circ\)), with the Ne\textsuperscript{+} beam impinging along the <001> direction. Such a direction is chosen because the ripples forming after sputtering at the appropriate temperature exhibit steps with a high kink density.

The Ne pressure is adjusted to keep constant the Ne\textsuperscript{+} current at the sample. The choice of Ne\textsuperscript{2} as sputtering gas instead of Ar\textsuperscript{+} is determined by the lower contamination level achieved, as a liquid N\textsubscript{2} trap can be operated while sputtering. The morphology obtained by Ne\textsuperscript{+} bombardment is, in any case, the same as with Ar\textsuperscript{+}. The adsorption experiments were performed for Ne\textsuperscript{+} doses, \(\chi_{\text{Ne+}}\), up to 13.5 ML, which correspond to the conditions investigated thoroughly by STM [9]. After each sputtering treatment at a given \(T_{\text{spat}}\), the sample is cooled down to below 130 K, thus freezing in the non-equilibrium surface shape. O\textsubscript{2} seeded in He is then dosed with the supersonic molecular beam impinging on the surface at normal incidence, in order to achieve a large sticking coefficient [15]. Two different values of the translational energy are employed: \(E_i=0.39\) eV and \(E_i=0.80\) eV, the latter corresponding to the maximum of \(S(E_i)\) on flat Ag(100) (\(S(E_i=0.80\) eV)=0.7 [15]). The sticking coefficient is evaluated by the KW method and the uptake is determined by integration of the KW traces with respect to the O\textsubscript{2} beam flux, which reads (0.20\(\pm\)0.01) ML/sec with the nozzle at room temperature in this series of experiments.

The HREEL spectra are recorded in specular, at an angle of incidence of 63\(^\circ\) and with \(E_e=1.7\) eV. The elastic count rate of the specular beam decreases with increasing Ne\textsuperscript{+} exposure from \(~10^5\) cps (flat surface limit) to \(~10^3\) cps at \(\chi_{\text{Ne+}}\sim1\) ML, thereby indicating that a substantial defect concentration builds up already at a moderate sputtering dose and remains then approximately constant for higher exposures. This result is consistent with the large sputtering yield reported for silver [16]. In order to obtain a sufficient count rate the energy resolution was reduced to about 7-9 meV.
When investigating the stepped Ag(n10) crystals, O\(_2\) is dosed by the supersonic molecular beam on the surface previously cleaned by sputtering and annealing cycles. Due to the smaller dimension of the samples (7 mm diameter), the beam is collimated to a spot diameter of 2 mm at the crystal for KW measurements and to 8 mm for HREELS experiments. The translational energy, E\(_i\), of the impinging molecules is varied from 0.09 eV to 0.97 eV both by heating the ceramic nozzle and by seeding the gas in He (X\(_{O2}\)=3\%). To reach E\(_i\) values between 0.30 eV and 0.39 eV, seeded mixtures with X\(_{O2}\)>3\% are however employed. HREEL spectra are recorded in specular at 60° of incidence and primary electron energy E\(_e\)=1.7 eV.

### 4.3 Surface geometry

#### 4.3.1 Sputtered Ag(100) surfaces

The STM images reported in Fig. 4.1 show the different nanopatterning of the Ag(100) surface achieved after sputtering at normal incidence and for increasing sputtering temperatures. Below T\(_{sput}\)=180 K (Fig. 4.1a) the surface is quite rough and the atomic structure cannot be resolved by STM. The local morphology consists of randomly oriented steps, Ag adatoms and vacancies. With increasing T\(_{sput}\) surface mobility sets in and the checkerboard structure develops, consisting of pyramidal pits with ordered (100) terraces and straight \(<011>\) steps (see Fig. 4.1b). Above 400 K (Fig. 4.1c) the surface becomes smoother, though still not perfectly flat. On the contrary, if the surface is sputtered at grazing angle of incidence of the Ne\(^+\) beam and in the temperature range between 180 K and 350 K [8], ripples form with hills and valleys parallel to the beam direction. If the latter is aligned along the \(<001>\) direction, the density of kink sites is maximum.

![STM images recorded after sputtering the Ag(001) surface at normal incidence and different T\(_{sput}\). \(\chi_{Ne^+}\) was 13.5 ML (calculated with respect to the Ag(100) surface atoms density) and the ion energy 1 KeV. (a) T\(_{sput}\)=180 K, image size 85x85 nm\(^2\); (b) T\(_{sput}\)=380 K, image size 340x340 nm\(^2\); (c) T\(_{sput}\)=450 K, image size 700x700 nm\(^2\). Immediately after sputtering, the surface is cooled down to below 130 K to freeze in the non-equilibrium morphology and an STM image is then acquired. The images are taken from ref. [13].](image-url)
4.3.2 Stepped surfaces: Ag(410) and Ag(210)

A sketch of the Ag(410) and Ag(210) surface geometries is shown in Fig.4.2.

The Ag(410) surface (panel A) is formed by three-atom-row wide (100)-like terraces and (110)-like steps. The step edge consists therefore in a sequence of open steps. The angle of incidence of the impinging molecules with respect to the normal to the surface is designated by $\theta$. In all experiments the scattering plane is defined by the normal to the surface and the $<\bar{1},4,0>$ direction (xy plane, across the steps). Since the surface forms an angle of 14° with the (100) terraces, $\theta_{t}=-14^\circ$ and $\theta_{s}=+31^\circ$ correspond to molecules impinging normally to the (100) terraces and to the step heights, respectively.

Also the Ag(210) surface (panel B) is formed by a sequence of (100)-like terraces and (110)-like steps. The terrace width is further reduced with respect to Ag(410) and all terrace atoms are also adjacent to a step. The surface forms an angle of 26.5° with the (100) terraces, so that $\theta_{t}=-26.5^\circ$ and $\theta_{s}=+18.5^\circ$ correspond to molecules impinging normally to the (100) terraces and to the step heights, respectively. In the HREELS experiments shown in this chapter, however, the scattering plane is defined by the normal to the surface and the $<001>$ direction (xy plane, along the steps) and only exposures normal to the surface plane are performed.

![Fig. 4.2: Panel A: geometry of the Ag(410) surface. The scattering plane is aligned along the $<\bar{1},4,0>$ direction (across the monoatomic steps). Panel B: geometry of the Ag(210) surface. In both cases positive $\theta$ values correspond to molecules impinging against the step heights. The primitive unit cells are also drawn.](image-url)
These pictures are of course a representation of the ideal surfaces and can be quite far from the true Ag(n10) face morphology. In fact a stepped surface is more defective than a low Miller index one and the open steps of (n10) faces could be prone to disorder. In particular, they are expected to roughen at relatively low temperature, forming (111) facets along steps oriented in the <110> directions.

Indeed a good morphological characterisation of stepped surfaces is difficult to achieve. No atomic resolution could be obtained by STM on Cu(410) at room temperature [17], indicating that this surface is disordered at 300 K, and, to my best knowledge, no STM or SPA LEED investigation was performed at low temperature. Investigation on stepped Ag was done for the (115) face, consisting however of (100) terraces and closed steps, and the lower limit for the roughening temperature was established at 450 K by STM [18]. A lower roughening temperature is expected for open steps, but it is very improbable that it is as low as 110 K, the temperature at which my adsorption experiments are performed. This hypothesis is confirmed \textit{a posteriori} by my results; however, since the demonstration is based on the data presented in this chapter, I postpone the discussion to the discussion session.

4.4 Oxygen adsorption on disordered and nanostructured Ag(100)

4.4.1 Data presentation

KW measurements were recorded for the Ag(100) surface sputtered with $\chi_{\text{Ne}^+}=13.5$ ML for different $T_{\text{sput}}$ and $E_i$. Fig. 4.3 (left panels) shows the total sticking probability, $S$, plotted vs. the total (molecular plus atomic) oxygen coverage, $\Theta$ (in ML of molecules, calculated with respect to the Ag(001) surface). As I will demonstrate later, partial dissociation takes place here also when dosing $O_2$ at $T=105$ K, contrary to the flat surface case. The total $O_2$ uptake as a function of $O_2$ exposure ($\chi_{O_2}$) is reported in the right panels. Fig. 4.4 shows the corresponding curves for $T_{\text{sput}}=105$ K and parametric in $\chi_{\text{Ne}^+}$.

It is evident that both the total sticking probability and the total uptake diminish with decreasing $T_{\text{sput}}$ for both $E_i$ values. The decrease of $S$ is about 30% at $T_{\text{sput}}=105$ K. Moreover Figs. 4.3 and 4.4 show that:

a) for all $T_{\text{sput}}$, $S$ increases with $E_i$ as it does for the flat surface;

b) the slope of $S$ vs. $\Theta$ is the same as for the flat surface, indicating that the coverage dependence for the oxygen admolecules is not significantly affected by sputtering;

c) the sticking probability and the total uptake are reduced with respect to the flat surface already in the limit of the smallest Ne$^+$ dose (0.06 ML);

d) both the total sticking probability and the total uptake decrease monotonously with increasing $\chi_{\text{Ne}^+}$.

The information about the fractional coverage of atoms and molecules is determined by vibrational HREELS. The spectra, shown in Fig. 4.5 parametric in $T_{\text{sput}}$, are recorded for $\chi_{\text{Ne}^+}=13.5$ ML and after dosing 0.1 ML of $O_2$ with $E_i=0.39$ eV at $T=105$ K. The result for the flat surface is shown for comparison, too. Two main losses are present for the damaged surfaces: at 34-37 meV and at 81 meV. At the same $T$, only the 81 meV loss is present on the flat surface and it dominates for high $T_{\text{sput}}$, when the checkerboard structure has washed out.
Fig. 4.3: Dependence of sticking vs. total coverage (left panels) and coverage vs. O₂ exposure (right panels) for $\chi_{Ne^+}=13.5$ ML, $\theta=0^\circ$ and different $T_{sput}$. Data are presented for the translational energies $E_i=0.39$ eV (upper panels) and 0.80 eV (lower panels).

Fig. 4.4: Dependence of sticking vs. coverage (left panels) and coverage vs. exposure (right panels) for $T_{sput}=105$ K and different $\chi_{Ne^+}$. O₂ was dosed at $T=105$ K, $\theta=0^\circ$ and $E_i=0.39$ (upper panels) and 0.80 eV (lower panels).
The latter mode corresponds to the internal vibration of oxygen admolecules [11,19], which are therefore stable also on such a heavily damaged surface. The intensity of the loss is, however, reduced compared to the flat surface case, indicating a smaller molecular oxygen coverage in accord with KW measurements.

The losses at 34-37 meV are due to oxygen adatoms, characterised by vibrational energy in the range from 28 to 37 meV also for flat Ag(001), the exact value depending on oxygen coverage and surface reconstruction [20]. They are therefore indicative that dissociation has taken place. A significant contribution of the molecule surface vibration to the energy loss spectra can be excluded, as it would be expected at 30-32 meV and with a much smaller intensity than the mode at 80 meV [11].

Inspection of the HREELS data shows moreover that the Ag-O vibrational energy, $\hbar \omega(\text{Ag-O})$, decreases with increasing sputtering temperature from 37 meV for $T_{\text{sput}}=105$ K to 34 meV for $T_{\text{sput}}=300$ K, when the checkerboard structure forms. This shift cannot be due to the contribution of the Ag-O$_2$ stretch, as such mode has a negligible intensity at low coverage. A possible objection is that, on a nanostructured surface, its dynamical dipole moment might be larger and the loss could be visible already at low coverage. This explanation is however unlikely, since the intensity of the loss at 34-37 meV is unaffected by annealing the surface above 150 K, when O$_2$
Letizia Savio Chapter 4

Fig. 4.6: Coverage of atomic and molecular oxygen (upper panel) and dissociation probability (lower panel) vs. sputtering temperature for a heavily sputtered surface. Data refer to the low coverage limit and to normal and grazing incidence of Ne⁺ ions. The arrow indicates the flat surface limit for ΘO₂. Here and in the following ΘO₂ and ΘO are expressed in ML of molecules/atoms calculated with respect to the Ag(100) surface atoms density.

desorbs. The presence of impurities, especially of H₂O, OH and CO³⁻, is excluded by measuring HREEL spectra up to loss energies of 500 meV (not shown).

Following the procedure described in paragraph 3.3, partial molecular and atomic oxygen coverage was calculated. I can then define the dissociation probability, \( P_{\text{diss}} \), as:

\[
P_{\text{diss}} = \frac{\Theta_O}{\Theta_O + 2\Theta_{O2}} \quad (4.1)
\]

The atomic and molecular oxygen coverage and the, so-determined, dissociation probability were investigated as a function of \( T_{\text{sput}} \) for several Ne⁺ and O₂ exposures. Fig. 4.6 shows the case in which \( \chi_{\text{Ne}⁺} = 13.5 \text{ ML}, \chi_{O₂} = 0.1 \text{ ML and } \Theta_{\text{sput}} = 0° \) and 70° (normal and grazing incidence on the surface); Fig. 4.7 reports the case corresponding to \( \chi_{\text{Ne}⁺} = 2.3 \text{ ML, } \chi_{O₂} = 0.4 \text{ ML and } \Theta_{\text{sput}} = 0° \). Oxygen exposures were always performed at 105 K.

In Fig. 4.8 ΘO₂, ΘO, the total coverage and \( P_{\text{diss}} \) are plotted vs. \( \chi_{\text{Ne}⁺} \) for an experiment in which the sample is sputtered at normal incidence with \( T_{\text{sput}} = 105 \text{ K and } 0.1 \text{ ML of} \)
Fig. 4. 7: Coverage of atomic and molecular oxygen (left panel) and dissociation probability (right panel) vs. $T_{\text{sput}}$ for $\chi_{\text{Ne}^+} = 2.3$ ML, $\theta_{\text{sput}} = 0^\circ$ and $\chi_{\text{O}_2} = 0.4$ ML.

Fig. 4. 8: Atomic and molecular oxygen coverage (upper panel) and dissociation probability (lower panel) vs. Ne$^+$ dose for $T_{\text{sput}} = 105$ K, $\chi_{\text{O}_2} = 0.1$ ML and normal incidence. The arrows indicate the flat surface limit for $\Theta_{\text{O}_2}$ and $P_{\text{diss}}$. Diamonds in the upper panel refer to the total coverage deduced from KW experiments; the dashed line in the lower panel is the logarithmic best fit to the $P_{\text{diss}}$ data points.
O₂ is then dosed at T=105 K. Fig. 4.9 reports, on the contrary, Θ vs. χ_{Ne⁺} for low and intermediate O₂ exposure, for sputtering and dosing at T=105 K.

The analysis shows that:

a) Θ_{O₂} is smaller for the sputtered than for the flat surface (especially at T_{sput}=105 K) and recovers with increasing T_{sput} (Fig. 4.6 upper panel, the arrow indicates the value for flat Ag(100)).

b) In the T_{sput} range between 180 and 350 K, P_{diss} is more than twice as large when sputtering is performed at grazing incidence rather than at normal incidence (see lower panel in Fig. 4.6). This experimental condition corresponds to the formation of ripples aligned along the <001> direction, i.e. to a high density of kinked steps. The difference in P_{diss} between grazing and normal sputtering conditions is small when T_{sput} <180 K or T_{sput} >350 K.

c) P_{diss} is largest for T_{sput}=105 K and decreases up to T_{sput}=180 K. It remains then constant for 180 K<T_{sput}<330 K, i.e. in the temperature range in which ordered nanostructures are present, becoming eventually negligible for still larger sputtering temperatures (Fig. 4.6, lower panel).

d) The dependence of P_{diss} on T_{sput} for larger oxygen doses and smaller χ_{Ne⁺} (Fig. 4.7) is similar to that observed at low oxygen dose and large χ_{Ne⁺}. Also in this case P_{diss} drops between T_{sput}=100 K and 240 K and stays then constant up to 330 K. The total oxygen coverage is reduced with respect to the flat surface limit and recovers for higher T_{sput}. The values of P_{diss} are substantially smaller than the ones reported in Fig. 4.6, indicating that after saturation of the defects active for dissociation, occurring in the very early stages of the oxygen exposure, the dynamics of the system is dominated by molecular chemisorption.

e) P_{diss} increases logarithmically with χ_{Ne⁺} (see Fig. 4.8). Above χ_{Ne⁺}=7 ML, the dissociation probability is, however, larger than expected, although the effect
is at the limit of experimental resolution. Fitting the data with the function
\[ P_{\text{diss}}(\chi) = a \ln(b\chi + 1) \]
which takes into account the condition \( P_{\text{diss}}(\chi_{\text{Ne}^+} = 0) = 0 \), I
obtain the best fit parameters: \( a = 0.007 \) and \( b = 326 \). Their product, \( ab \approx 2.3 \),
gives information about the behaviour of \( P_{\text{diss}} \) at low \( \chi_{\text{Ne}^+} \). Considering the
sputtering yield for Ne\(^+\)/Ag [16], the estimated value is indicative of a nearly
unitary efficiency of the dissociation process.

f) In the low exposure limit the total coverage is affected only for large \( \chi_{\text{Ne}^+} \),
while for \( \chi_{\text{O}_2} = 1.2 \text{ ML} \) \( \Theta \) decreases appreciably with respect to flat Ag(100)
already at small Ne\(^+\) doses (see Fig. 4.9).

Fig. 4.10 shows other sets of HREELS data recorded for different \( \chi_{\text{Ne}^+} \), at \( T_{\text{spat}} = 105 \text{ K} \) and dosing 0.1 ML (panel A) and 240 ML (panel B) of O\(_2\) at \( T = 105 \text{ K} \). For the
small O\(_2\) exposure the frequency of the atomic oxygen vibration increases
monotonously with \( \chi_{\text{Ne}^+} \). The frequency of the intermolecular vibration of O\(_2\) has a
more complex behaviour, as it firstly increases abruptly and then decreases slowly. In
the large exposure limit (Fig. 4.10B), on the contrary, the O-O stretch frequency
decreases monotonously, while the atomic oxygen vibration is similar to the case of
\( \chi_{\text{O}_2} = 0.1 \text{ ML} \), except that it is initially at 32.5 meV rather than at 35.5 meV.

The results for the vibrational energies, \( \hbar \omega \), are summarised in Fig. 4.11. As it is
apparent in panel A, the data separate into two families, characterised by Ag-O
stretches \( \hbar \omega = 32-34 \text{ meV} \) and \( \hbar \omega = 35.5-37 \text{ meV} \), respectively. Two distinct atomic
Fig. 4.11: Vibrational frequency of the O-Ag (panel A) and O-O stretch (panel B) modes detected from HREEL spectra and plotted vs. Ne$^+$ exposure. Data refer to two $\chi_{O_2}=0.1$ ML and 240 ML, dosed at $T=T_{sput}=105$ K. The arrows in panel B indicate the flat surface limit for the low (continuous line) and high (dashed line) oxygen exposures.

Oxygen moieties are therefore present: one corresponds to oxygen adatoms at adsorption sites produced only by sputtering at 105 K (loss at 35.5-37 meV), the other to adatoms at sites present also for the checkerboard structure (loss at 34 meV). These sites are populated after saturating the former ones$^*$. Panel B reports the dependence of the internal O-O stretch on $\chi_{Ne^+}$. As mentioned above, the frequency of this mode shifts abruptly to larger energy as soon as some defects are present and recovers eventually the flat surface value for large $\chi_{Ne^+}$. This non-monotonic behaviour will be analysed in the following discussion. However, I anticipate here that it can be explained if one of the two $O_2$ moieties, present on the flat Ag(001) surface and giving rise to a doublet at 79 and 84 meV [19], is destabilised.

$^*$ I note that in the case of large $O_2$ exposure the weight of the contribution of the molecule-surface stretch increases and might therefore cause a shift to lower frequency of the loss attributed to the adatom-surface vibration. The intensity of the former mode is however expected to be of at most 1/5 of the intensity of the $O_2$ stretch and its weight to be negligible with respect to the much larger intensities measured in this frequency range.
In order to check whether the presence of defects enhances the reactivity of oxygen, I also performed CO oxidation experiments. The reaction rate is sensitive to surface geometry, being two orders of magnitude larger for O$_2$/Ag(110) [21,2] than for O$_2$/Ag(100) [22,23]. CO was dosed with the supersonic molecular beam on the O$_2$ precovered surface. A decrease in the intensity of the inter-molecular vibrational loss peak (at ~80 meV) and an increase in the intensity of the oxygen adatom-substrate vibration (at 35 meV) are observed upon CO exposure. This indicates CO$_2$ formation via:

\[ \text{CO(ad)} + \text{O}_2(\text{ad}) \xrightarrow{\text{Ag}} \text{CO}_2(\text{gas}) + \text{O(ad)} \]  

(4.2)

The initial reaction probability:

\[ P_r = \frac{\Delta \Theta_{\text{O}_2}}{\chi_{\text{CO}}} \]  

(4.3)

is, however, approximately equal to the value determined in our prior study for the smooth Ag(001) surface [23], i.e. $P_r \approx 5 \times 10^{-4}$ both for sputtered and non-sputtered surfaces. The increased intensity of the O-Ag vibration with CO exposure suggests that, if removal of atomic oxygen by CO takes place, its rate is smaller than the production through reaction (4.2), as it was the case also for the flat surface. The presence of defects does therefore not affect significantly the reaction probability for CO oxidation of either O(ad) or O$_2$(ad). The small reaction rate observed on the flat surface is thus not due to the low concentration of defects, because otherwise a substantial enhancement of $P_{\text{diss}}$ would be observed for the sputtered surface.

4.4.2 Discussion

4.4.2a Identification of the active site

The interplay between the morphological information provided by STM images and the quantitative data regarding the chemical properties of the nanostructured surface allows to trace a correlation between the density of kinks, $\rho_{\text{kink}}$, on the surface and the dissociation probability. Although highly desirable, an evaluation of $\rho_{\text{kink}}$ obtained by directly counting the kink sites on high resolution STM images turned out to be not feasible, because of the high roughness of the sputtered surface which destroys atomic resolution. It was therefore necessary to extract $\rho_{\text{kink}}$ from a model (described in details in refs. [13,24]) depending on coarser parameters, such as surface roughness, mean nanostructure separation and surface morphology. The so-determined $\rho_{\text{kink}}$ is reported in Fig. 4.12 vs. $T_{\text{sput}}$ and compared with the dissociation probability already shown in Fig. 4.6B. Panel A refers to sputtering at normal incidence, panel B to $\theta_{\text{sput}}=70^\circ$. For $T_{\text{sput}}$ below room temperature, $\rho_{\text{kink}}$ is five times larger for grazing than for normal incidence, as in the former case ripples form, running along the <001> direction. In the same temperature range $P_{\text{diss}}$ is enhanced by a factor of 4 for grazing incidence of the ion beam, as also shown in Fig. 4.6. Both $\rho_{\text{kink}}$ and $P_{\text{diss}}$ decrease, moreover, at $T_{\text{sput}}> 350$ K. The kink density compares with the dissociation probability within a factor 1.5, thus suggesting that $P_{\text{diss}} \sim 1$ at the kink site. The discrepancy in absolute value can be attributed to an underestimate of $\rho_{\text{kink}}$ and/or to the conversion of HREELS intensities into coverage, since in both cases a systematic error of 25% is reasonable. A similar comparison between $P_{\text{diss}}$ and the
density of steps leads to worse results because of different absolute values and of a different dependence on $T_{\text{sput}}$.

Even if very probable, the assignment of kinks with the active sites for $O_2$ dissociation on Ag(100) is however not straightforward since, as explained in the introduction of this chapter, also other defects are produced in large amount during the sputtering process.

Fig. 4.12: Density of kinks and dissociation probability plotted vs. $T_{\text{sput}}$. $\rho_{\text{kink}}$ was obtained by STM through the model described in refs. [13,24]. $P_{\text{diss}}$ is the same reported in Fig. 4.6 and is estimated in the low oxygen coverage limit. Panel A: $\theta_{\text{sput}}=0^\circ$; panel B: $\theta_{\text{sput}}=70^\circ$.

4.4.2b Vibrational frequencies

Adatom-surface vibrations are found at 34 and 37 meV. The lower frequency is observed upon oxygen adsorption at $T=105$ K: i) on the checkerboard structure for all exposures, and ii) on the coldly sputtered surface for large $O_2$ doses. The loss at 37 meV is found, on the contrary, only for surfaces sputtered at low temperature upon oxygen exposures $\chi_{O_2}<0.5$ ML.

As reported in Chapter 2, in our previous studies of oxygen adsorption on flat Ag(001) loss energies between 28 and 37 meV were observed too, whereby the energy loss value depends on the procedure used to dissociate $O_2$. In particular, the highest value was found for the high coverage, $2\sqrt{2} \times \sqrt{2}$ missing row reconstructed surface (see Fig. 2.2 and ref. [20]), in which the oxygen adatoms sit in the former four-fold hollows next to missing <001> Ag rows. By comparison with this surface, I ascribe the higher frequency adatom species found on sputtered Ag(100) to adsorption at vacancies. The assignment suits both to isolated vacancies, present for the coldly sputtered surface, and to the rows of vacancies which build up the $2\sqrt{2} \times \sqrt{2}$ reconstructed Ag(100). This state corresponds therefore presumably to two oxygen adatoms sitting at opposite corners of the same vacancy (site V in Fig. 4.13) and the higher frequency could arise from the stronger dipolar interaction caused by the high local oxygen coverage.

The lower frequency moiety, on the contrary, is ascribed to oxygen dissociation at isolated kink sites (site K in Fig. 4.13), as it is appropriated also for O adsorption on
de-reconstructed Ag(100). The decrease of the oxygen vibration upon large O$_2$ exposures on the coldly sputtered surface is therefore indicative that ion bombardment produces a larger concentration of isolated kinks than of vacancies and that the former ones dominate the dissociation process after saturation of the vacancies. Upon annealing to 190 K the adatom stretch is at 34 meV for all sputtered surfaces, indicating either that the isolated vacancies have disappeared and all adatoms sit now at kinks, or that one of the two oxygen atoms in the vacancy has left it.

Fig. 4.13: Schematic drawing of vacancy (V) and kink (K) sites created on Ag(100) by sputtering at low $T_{\text{sput}}$.

Let's now discuss the influence of defects on molecularly adsorbed oxygen. The dependence of its internal stretch vibration is reported in Fig. 11B vs. $\chi_{\text{Ne}^+}$ and for different O$_2$ doses. I notice firstly that the position of the maximum of the loss peak depends weakly on O$_2$ dose, contrary to the case of flat Ag(100), indicating that the admolecules occupy similar sites at low and large coverage. Indeed, the vibrational frequency at low $\chi_{\text{Ne}^+}$ (82 meV) is significantly up-shifted at low $\chi_{\text{O}_2}$ and downshifted at large $\chi_{\text{O}_2}$ with respect to the flat Ag(100) limits (81 meV and 84 meV respectively, see arrows in Fig. 4.11B). In the flat surface case the loss peak arises from two distinct contributions, at 79 and 84 meV, corresponding to two different O$_2$ moieties [19] which cannot be resolved in the present experiment. The up-shift of the maximum of the loss peak at low $\chi_{\text{Ne}^+}$ and low $\chi_{\text{O}_2}$ is thus probably due to a change in the ratio of the population of the two moieties caused by sputtering. As the O-O stretch frequency is up-shifted for the damaged surface, the destabilisation of the 79 meV-moiety must be stronger than the one of the 84 meV-species. Since the former corresponds to molecules adsorbed at the four-fold hollows [19], its decrease in population reflects the reduced number of non-damaged sites. The 84 meV-moiety, corresponding to adsorption at bridge sites, would be less affected as their concentration is expected to change less with surface damage. Moreover I shall show
later in this chapter that for O$_2$/Ag(410) only a single internal vibration is observed at 85 meV. With increasing $\chi_{Ne^+}$ the O-O stretch related loss broadens and moves back towards 80 meV. A tentative explanation is that at the largest $\chi_{Ne^+}$ also the 84 meV moiety is destabilised, moving the relative coverage of the two species back to the original rate of the flat surface limit. For the large $\chi_{O_2}$ limit, on the contrary, the downshift of the vibrational frequency is also determined by the reduction in surface coverage.

Finally let's address three intriguing observations:

a) The global sticking probability and the total uptake decrease with $\chi_{Ne^+}$.

b) On the sputtered surface it was not possible to detect the minor loss at about 64 meV, assigned to oxygen molecules adsorbed at defect sites on flat Ag(100) [5]. These molecules have thus most probably dissociated in the present case. The explanation is in accord with the pronounced weakening of the intermolecular bond indicated by the low energy loss; such bond might therefore easily be broken by the interaction with the kink sites. Consequently, on flat Ag(001) such molecules must sit at less reactive defects than kinks. The higher density of defects on the sputtered surface could therefore lead to dissociation and suppress this loss feature.

c) The absence of an effect of sputtering on the reactivity of the O$_2$ admolecules towards CO is surprising, as the CO oxidation reaction is known to be sensitive to surface geometry [23,25]. The only possible explanation for this finding is that although sites with (110) geometry are formed with sputtering, the admolecules do not preferentially occupy them.

4.5 Oxygen adsorption on Ag(410)

4.5.1 KW experiments

Fig. 4.14 shows QMS traces of the O$_2$ partial pressure in the main chamber recorded during two KW measurements performed at T=110 K with $E_i=0.97$ eV and different angles of incidence. In both cases the molecules hit the terraces at 45°, but they impinge normal ($\theta=31^\circ$, continuous line) and grazing ($\theta=-59^\circ$, dashed line) to the step heights, respectively. As explained in paragraph 3.2.3, at time $t_0$ the inert flag intercepting the beam just in front of the crystal is removed, and the supersonic O$_2$ beam strikes the sample. The drop in the QMS signal indicates that molecules have been removed from the gas phase and have stuck at the surface. It gives a direct measurement of the sticking coefficient, S, the initial value of which, denoted by $S_0$, is particularly important because it corresponds to the interaction with the bare surface. Since O$_2$ adsorption is stable at T=110 K, no desorption peak is observed immediately after the end of the exposure.

The experiment shows that $S_0$ is much larger when the step heights are illuminated than when they are in the shadow (0.42 against 0.07). Notably, at $E_i=0.97$ eV and $\theta=45^\circ$, $S_0$ reads 0.35 for Ag(100) [15], implying that for Ag(410) the reactivity is
increased at steps and strongly reduced at terraces with respect to flat Ag(100). The former effect is expected because of the smaller coordination of step atoms. The reduced reactivity at terrace sites, on the contrary, is connected to the limited terrace width and may be caused by a modification of the electronic states of terrace atoms or, alternatively, by the poisoning of the Ag-atom rows close to the step edges. In the latter case a reduction of the effective terrace size would, in fact, take place.

In order to calculate the initial sticking coefficient at step sites, I assumed that the total value of \( S_0 \) is given from the sum of step and terrace contributions, weighted with respect to the projected terrace and step areas seen by the beam. For \( \theta = 31^\circ \), assuming \( S_0 = 0.07 \) for the terrace atoms (the beam impinges at 45° on terraces), I obtain \( S_0 \approx 1 \) for molecules dosed normally to the step heights, thus confirming the increased reactivity of the latter ones.

The total \( \text{O}_2 \) coverage, \( \Theta \), on Ag(410) is deduced from formula (3.9) estimating the flux value of 0.020 ML/sec from table 3.2 and equation (3.7). Applying such procedure to the trace of Fig. 4.14 recorded at \( \theta = 31^\circ \), I obtain the \( \Theta(t) \) curve reported in Fig. 4.15 (in ML of molecules, calculated with respect to Ag(410) - panel A) and the behaviour of \( S_0 \) as a function of coverage (panel B). \(^*\)

It is evident that the oxygen coverage increases rapidly in the first 20 seconds, while \( S_0 \) drops correspondingly to zero. I notice that, on the basis of KW experiments, it is not possible to tell the final state of the adsorbed species. From comparison with the results for oxygen on sputtered Ag(100) I expect, however, that both admolecules and dissociated atoms contribute to the total coverage. This information can be obtained by the vibrational spectroscopy experiments shown later on. The value \( \Theta \approx 0.075 \) ML, reported in Fig. 4.15, corresponds to the condition in which the sticking coefficient

\(^*\) Such procedure is not always applicable. In the trace at \( \theta = 59^\circ \) in Fig. 4.14, e.g., the very low \( S \) values do not allow a reliable integration.
Letizia Savio

Chapter 4

Fig. 4.15: Coverage dependence vs. exposure time (panel A) and behaviour of $S_0$ vs. $\Theta$ (panel B) for the adsorption experiment of Fig. 4.14 performed at $\theta=\theta_s$.

drops below the sensitivity of the KW method and should not be confused with the saturation coverage. It gives however an indication for the number of sites, $\Theta_{\text{max}}$, which can be easily accessed from the gas-phase. The saturation coverage, $\Theta_{\text{sat}}$, is higher and much longer exposures are necessary to achieve it. It is however not possible to evaluate it from KW measurements.

$S(\Theta)$ is largest at very low coverage and decreases monotonously to values below the sensitivity of the KW method ($\sim 1.5\%$) for $\Theta>0.075$ ML. This decay is well reproduced by the relation:

$$S(\Theta) = S_0 (1 - \frac{\Theta}{\Theta_{\text{sat}}})^n$$ \hspace{1cm} (4.4)

Assuming $\Theta_{\text{sat}}=\Theta_{\text{max}}=0.075$ ML, I obtain $n=1.5$.

For non-dissociative adsorption $n=1$ is expected if a hit and stick mechanism takes place in absence of an external precursor and if the admolecules do not poison neighbouring sites. $n<1$ indicates that adsorption is mediated by an external precursor, i.e. molecules arriving on an already occupied site get trapped and diffuse on the surface, with a non vanishing probability of reaching a free adsorption site. $n>1$, on the contrary, indicates that a repulsive interaction is present among the admolecules, so that poisoning of adsorption sites close to an occupied one occurs. For dissociative adsorption the hit and stick mechanism is characterised by $n=2$, while the previous considerations remain valid. The values found for $O_2$/Ag(410) is therefore reasonable as adsorption is partly dissociative and partly molecular and physisorbed precursors play no role. Indeed, $\Theta_{\text{max}}=0.075$ ML of $O_2$ corresponds to an effective occupation between 0.075 ML and 0.150 ML, depending on the amount of molecules which dissociate. For non dissociative adsorption on flat Ag(100) and Ag(110) coverages $\Theta_{\text{max}}=0.18$ ML [26] and $\Theta_{\text{max}}=0.12$ ML [27], respectively, were found from KW experiments, with $1<n<1.25$. My result is therefore compatible with the behaviour of the low Miller index surfaces.
The $S_0$ values for O$_2$ dosed at normal incidence and at $T=105$ K are plotted in Fig. 4.16 vs. $E_i$ (circles). The corresponding curves for Ag(100) (continuous line) [15] and Ag(110) (dashed line) [28,29] are reported for comparison. $S_0$ increases with $E_i$, indicating that O$_2$ adsorption is globally activated also in presence of steps, but, at least above $E_i=0.30$ eV, it is ~30% lower than for the low index surfaces. These results are in accord with the values measured for sputtered Ag(100) and shown by squares and crosses in Fig. 4.16. The two symbols refer to different sputtering temperatures, $T_{\text{sput}}$, corresponding to a strongly disordered surface ($T_{\text{sput}}=105$ K) and to the formation of a nanostructure of square pits ($T_{\text{sput}}=325$ K), respectively (see Fig. 4.1 and ref. [13]). At variance with the low Miller index surfaces, $S_0$ reads ~0.05 at low $E_i$. This detail is evidenced in the inset, where the data are plotted on a logarithmic scale. The non-vanishing sticking coefficient is indicative of the existence of a non-activated adsorption channel related to defects.

The energy dependence of $S_0$ for an activated system is usually described by the error function:

$$S_0(E_i) = \eta \int_0^E e^{-\frac{E-E_B}{W}} dE$$  \hspace{1cm} (4.5)$$

where $E_B$ is the average barrier height, $W$ is the width of the barrier distribution and $\eta$ a normalisation factor. For the Ag(410) data reported in Fig. 4.16 the fit with a single error function yields $E_B$~0.37 eV and $W$~0.25 eV. $E_B$ compares well with the value of 0.37 eV reported for O$_2$/Ag(110) [29,30] and O$_2$/Ag(100) [15,30] while $W$ is larger (it reads 0.17 eV for the flat Ag surfaces), giving a further indication that less activated channels are present.

![Fig. 4.16: $S_0$ vs. $E_i$ at $T=105$ K and $\theta=0^\circ$ for O$_2$ on Ag(410) (⊕: pure beam, ⊗: seeded beam, 3% O$_2$ in He). The data are compared with the corresponding curves for Ag(110) [28,29] (dashed line) and Ag(100) [15] (continuous line). Squares and crosses represent data points recorded for O$_2$ adsorption at $T=105$ K on Ag(100) sputtered at $T_{\text{sput}}=325$ K and $T_{\text{sput}}=105$ K, respectively. Inset: comparison of the data points at low $E_i$ for Ag(100) (*) and Ag(410) (⊗). The lowest point for Ag(100) is below the KW sensitivity and was measured by evaluating the HREELS intensities.](image-url)
Fig. 4.17: $S_0$ vs. $E_i$ at $T=105$ K for an O$_2$ beam impinging at 16° off normal to the terraces ($\theta=-30^\circ$, filled diamonds) and normal to the step edges ($\theta=+31^\circ$, open circles, different symbols indicate pure beam, $\otimes$, and different O$_2$ concentrations in the seeded beams). Notice the anomaly for $\theta=+31^\circ$ around $E_i=0.3$ eV. The fitting curve was obtained by assuming two barrier distributions corresponding to the interaction with terraces and step edges, as explained in the text.

Fig. 4.17 shows $S_0(E_i)$ curves recorded for $\theta=-30^\circ$ and $\theta=+31^\circ$, i.e. close to normal incidence on the terraces and normal to the step heights, respectively. The former curve is similar to the one of Fig. 4.16 and could, in principle, be fitted with a single error function. The latter, on the contrary, shows evidently an anomalous behaviour near 0.3 eV, since two thresholds are present. Assuming that both step heights and terraces contribute to the measured $S_0$ values, the best fit curve in Fig. 4.17 represents the expected $E_i$ dependence of $S_0$ in presence of two barrier distributions, associated with (100) terraces and with steps, respectively.

For the best fit two independent error function distributions are necessary, so that:

$$S^\text{total}_0 = S^\text{ss}_0 A_s + S^\text{tt}_0 A_t + K$$

where $A_s$ and $A_t$ are the relative weights of the projected areas of the nanofacets associated to steps (s) and terraces (t) seen at $\theta=31^\circ$ and $K$ is a constant, necessary to account for the non-activated channel.

I obtain $S^\text{ss}_0=0.51$, $E_{B_s}=0.25$ eV and $W_s=0.08$ eV for step heights and $S^\text{tt}_0=0.35$, $E_{B_t}=0.60$ eV and $W_t=0.20$ eV for terraces. $K$ reads ~0.05, in accord with the initial sticking coefficient measured for the non-activated channel. The abnormally high value of $E_{B_t}$ is due to non-normal incidence. Assuming normal energy scaling this value corresponds to a real value $E_{B_t}^{\text{norm}} = E_{B_t} \cdot \cos^2(45^\circ) = 0.3$ eV, which is close to the ones determined for the low index surfaces [30] and for the $S_0(E_i)$ curve of Fig. 4.16. On the other hand, $S^\text{tt}_0$ is half as large as the maximum value of $S_0$ measured on
Ag(100). The barrier at terraces is thus comparable, while the maximum sticking probability is reduced strongly with respect to flat Ag(100), resulting globally in a reduction of $S_0$ for $E_i>0.30$ eV. This result can be rationalised by assuming a reduction of the effective terrace area, as if the Ag rows close to the step edges were non-reactive.

The value of $E_{Bn}$ is correct, because it is deduced from trajectories normal to the step heights. Its average value is therefore definitively smaller than for the low index surfaces and shows the existence of an adsorption pathway related to open steps and with a reduced barrier with respect to flat Ag(100) and Ag(110).

KW data showing $S_0$ vs. $\theta$ at T=105 K are reported in Fig. 4.18. From panel A it is evident that $S_0$ has a maximum around the surface normal for $E_i=0.97$ eV, the position of which shifts towards the normal to the step heights with decreasing $E_i$. For $E_i=0.22$ eV the $S(\theta)$ curve is well peaked around $\theta=39^\circ$. These data demonstrate that at low impact energy the sticking probability at the steps is definitively larger than at terrace sites. Since the global sticking probability remains lower than for flat Ag(100), the reactivity for molecular adsorption at terrace sites must be strongly reduced, as already suggested in the analysis of Fig. 4.14.

In a previous investigation of O$_2$/Pt(533) [7] the $S_0$ dependence on $\theta$ could be described by assuming that the total sticking probability is given by the sum of two contributions, corresponding to the interaction with terraces and steps, respectively. For analogy with the analysis performed in the cited paper, I tried to fit the $S_0(\theta)$ curve of O$_2$/Ag(410) with the function:
\[ S_0(\theta) = S_{0t} A_t(\theta) \cos^{n_t}(\theta + 14^\circ) + S_{0s} A_s(\theta) \cos^{n_s}(\theta - 31^\circ) + K \]  (4.7)

where the weight factors \( A_t \) and \( A_s \) describe the projections of terrace and step nanofacets at given angle. I fitted the data at large negative and positive angles, where only one contribution is expected to be important; for the series with \( E_i = 0.97 \) eV (squares) I obtained \( S_{0t} = 0.8, n_t = 14, S_{0s} = 0.4 \) and \( n_s = 7 \). As shown in panel B of Fig. 4.18, these distributions are sharply peaked, as expected for activated adsorption (for comparison, for Ag(110) < 110 > it was found \( n_{(110)} = 6 \)). However the best fit values of \( S_0 \) are inconsistent with those obtained from the \( S_0(E_i) \) curve at \( \theta = 31^\circ \) and the sum of the two contributions (solid line) does not reproduce the experimental data, which show a maximum of \( S_0 \) at normal incidence. This failure indicates that a more complex modelling of the surface structure is needed (e.g. the edge itself cannot be neglected). For \( E_i = 0.22 \) eV I obtain, on the contrary, a reasonable fit to the data provided an increasing background at large positive angles is taken into account. Adsorption is then sharply peaked along the normal to the step heights and \( n_s \) reads 20.

I also studied the temperature dependence of \( S_0 \) for \( \text{O}_2 \) dosed on Ag(410), parametric in \( E_i \) and \( \theta \). In Fig. 4.19 the behaviour of \( S_0(T) \) is compared to the one of Ag(110) and Ag(100). All the curves correspond to molecules impinging normal to the surface with a translational energy \( E_i = 0.39 \) eV, and are normalised to the value at \( T = 100 \) K for an easier comparison. Fig. 4.20 reports, on the contrary, the \( S_0(T) \) curves recorded for \( \text{O}_2 \) molecules with \( E_i = 0.39 \) eV and \( E_i = 0.97 \) eV, impinging normally to the step heights (\( \theta = 31^\circ \), close symbols) and \( 10^\circ \) off from the normal to the terraces (\( \theta = -24^\circ \), open symbols), respectively. It is evident that:

1) The behaviour of \( S_0(T) \) is similar to the one of oxygen on Ag(110) for \( T < 350 \) K and steeper above this temperature.

2) \( S_0 \) depends little on temperature for \( T \leq 250 \) K, while it decreases above this \( T \). This effect is more evident for the 0.97 eV curves of Fig. 4.20 and is connected to the competition between adsorption and dissociation. The behaviour for Ag(100) is dramatically different, since in this case dissociation is a much less important process.

3) No significant increase of \( S_0 \) with \( T \) takes place for \( E_i \leq 0.39 \) eV (see Fig. 4.20). For the data recorded at \( E_i = 0.97 \) eV, on the contrary, a weak maximum in the \( S_0(T) \) curve is detected around 130 K. This effect is most probably due to the increased mobility of admolecules adsorbed at terrace sites, as it will be discussed in the following. I can rule out any connections with thermal generation of isolated minority defect (kinks at steps, generating (111) nanofacets), because a) this would occur at every translational energy of the molecules and b) I would expect the effect to be angle dependent, being greater when step heights are illuminated. When molecules impinge on the surface, they can diffuse and look for the active site for adsorption in the molecular or dissociated phase or they can desorb. The balance between these two competing processes determines the behaviour of the sticking coefficient vs. temperature at large \( T \). The smooth decrease of the curves in Figs. 4.19 and 4.20 indicates that above \( T = 150 \) K, temperature at which admolecules become unstable, dissociation dominates over desorption. The residence time on Ag(410) is thus long enough to allow \( \text{O}_2 \) molecules to look for the active site and dissociate. This interpretation is in accord with the similar behaviour observed for oxygen on Ag(110),
Fig. 4. 19: Temperature dependence of the sticking coefficient of O$_2$ on Ag(410) for $E_i=0.39$ eV and $\theta=0^\circ$. Data recorded on Ag(100) (dashed line) and Ag(110) (continuous line) at $E_i=0.39$ eV and normal incidence on the surface are reported for comparison. The curves are normalised at $T=100$ K for sake of clarity.

Fig. 4. 20: $S_0(T)$ recorded for $E_i=0.39$ eV and $E_i=0.97$ eV at $\theta=31^\circ$ and $\theta=-24^\circ$. The arrow indicates the critical temperature above which only dissociative adsorption takes place.

on which dissociation is believed to occur at terraces. At $T=350$ K the residence time becomes comparable to the one necessary for diffusion over the three-atom-rows wide terraces, and the decrease of $S_0$ becomes more pronounced and steeper than for Ag(110).

### 4.5.2 HREELS experiments

HREEL spectra recorded in the low coverage limit are shown in Fig. 4.21. O$_2$ was dosed at $T=105$ K and $\theta=\theta_s$ for different $E_i$. When dosing at high translational energy, losses are present at 32-40 meV and 85 meV. At low $E_i$, on the contrary, only one loss at $\sim$40 meV is observed. Fig. 4.22 reports HREEL spectra recorded after dosing O$_2$ with $E_i=0.39$ eV at different angles of incidence. The quantity $S_0\chi$, which gives a rough estimate of the amount of oxygen stuck on the surface in the low exposure limit, is even lower than in the experiments of Fig. 4.21. The spectra are dominated by a peak at 39-40 meV and only a weak signal is present in the 80 meV region for $\theta=31^\circ$ and $\theta=-25^\circ$. The losses in the lower frequency range are caused by the adatom-surface vibrations at different sites [20], with only a minor contribution at 30 meV due to the admolecule-surface stretch. The presence of significant intensity at these frequencies proves therefore that dissociation has taken place already at $T=105$ K, contrary to what observed for flat Ag(100) and Ag(110) and in accord with the results for O$_2$ on sputtered Ag(100) [13]. The pathway leading to dissociation is little, or non, activated as the intensity is present at all $E_i$. I further note that in Fig. 4.22 the oxygen coverage (roughly proportional to the HREELS intensities) is comparable after dosing
Fig. 4.21: HREEL spectra recorded after exposing the Ag(410) surface at T=105 K to an O$_2$ beam with $\theta=\theta_s$ and different $E_i$. Only dissociative adsorption (peaks in the range 30-40 meV) is present at the lowest translational energies, while admolecules (peak at 85 meV) are observed for $E_i \geq 0.30$ eV. The O$_2$ dose, $\chi$, in the central spectra was chosen in order to keep constant the quantity $S_0\chi$. The magnification factor is 100.

O$_2$ at $\theta=31^\circ$ and $\theta=-25^\circ$, while it is slightly lower for $\theta=60^\circ$. Such observation is in accord with the behaviour of $S(\theta)$ reported in Fig. 4.18.

The higher frequency loss is due to the internal stretch of adsorbed O$_2$. At low coverage this mode appears only for $E_i \geq 0.30$ eV, indicating that molecular adsorption results from activated pathways. As it is clearly shown in Fig. 4.21, the O$_2$ internal stretch vibrates at 85 meV on Ag(410), independently of $E_i$. I remember that two O$_2$ species, at 79 and 84 meV, are present on Ag(100) at T=100 K [19,31], associated to molecules in four-fold hollow and bridge sites, respectively. Two O$_2$ moieties with exactly the same internal mode frequency were reported also for Ag(110), but the 84 meV-species is then stable only below T=100 K [31]. The result for O$_2$/Ag(410) is therefore indicative that only one O$_2$ species is stable on this surface, at variance with Ag(100) and Ag(110). The possibility that the second species is not detected by HREELS is not plausible since both moieties lie flat on Ag(100) and they are visible by HREELS. If at the step one of the two moieties were tilted, I would expect to see its internal mode even better with HREELS because of the increased component of
the dipole moment normal to the surface plane. The absence of the HREELS signal}
proofs therefore that only one moiety is present on the Ag(410) surface.
The absence of the 79 meV moiety on Ag(410) indicates either that it is destabilised
by the limited terrace width or that migration towards the steps occurs in the 20
minutes needed to record the HREEL spectrum.
In the experiment of Fig. 4.23 the surface is exposed to a high amount of oxygen
dosed with $E_i=0.39$ eV nearly normally to the step heights. The crystal, initially at 105
K, is subsequently flashed to higher temperatures. The molecular oxygen related
feature is still at 84 meV, indicating that its frequency is little or not dependent on
coverage. The O-Ag mode vibrates now at 38 meV. Such up-shift with respect to the
corresponding low-coverage experiment (fourth spectrum from the bottom in Fig.
4.21) is unlikely to be due to further adsorption in the 40 meV species. It is most
probably related to a dipolar shift of the 34 meV moiety due to the increased
coverage. At 155 K molecular oxygen has dissociated completely and a small peak
around 69 meV appears, the identification of which is not clear yet. Around room
temperature the adatom-surface vibration shifts to 34 meV, in accord with what
observed on Ag(100) [20].
Finally I notice that the ratio between the O-Ag and O-O stretch mode intensities ($I_O$
and $I_{O2}$) corresponding to $O_2$ doses with $E_i=0.39$ and $\theta\sim31^\circ$ changes in favour of $I_{O2}$
with increasing exposure (see fourth, second and first spectrum from the bottom in
Figs. 4.21, 4.22 and 4.23, respectively). Dissociation must therefore be important in
the very early stages of the adsorption process, while molecular adsorption becomes
dominant after some atomic coverage has built up.
Fig. 4. 23: HREEL spectra recorded after dosing 7.2 ML of O$_2$ with $E_i=0.39$ eV and $\theta=28^\circ$ on Ag(410) at $T=105$ K and after flashing the adlayer to higher temperatures. After each flash the sample is cooled below 110 K to record the spectrum.

Fig. 4. 24: HREEL spectra recorded after exposing the Ag(210) surface at $T=105$ K to an O$_2$ beam with $\theta=0^\circ$ and different $E_i$. Only dissociative adsorption (peaks in the range 30-40 meV) is present at all translational energies even after long doses.
4.6 Preliminary results for oxygen adsorption on Ag(210)

Preliminary HREEL spectra of oxygen chemisorption on Ag(210) are reported in Fig. 4.24. They were recorded after exposing the Ag(210) surface at T=105 K to an O$_2$ beam impinging at normal incidence with different translational energies. These experiments are therefore similar to those of Fig. 4.21, but in the present case the exposure is much longer (several ML instead of a fraction of ML, calculated here in ML of Ag(210)). Inspection of the spectra clearly tells that:

a) No peak is present around 80 meV, i.e. in the region of the internal stretch of O$_2$ molecules. This is indicative that no molecular adsorption occurs on Ag(210), independently of $E_i$, in the same conditions for which it was detected on Ag(100) and Ag(410).

b) An intense feature at 41 meV, associated to atomic oxygen, is present when dosing with $E_i$=0.09 eV and $E_i$=0.39 eV. It shifts towards a slightly smaller frequency when dosing with the maximum energy. A feature at 32 meV also grows upon dosing at $E_i$=0.96 eV.

c) A smaller peak at 55 meV is present when dosing at the lowest energy, the nature of which is not yet clarified. Such peak is present also for O$_2$ adsorption on Ag(110) at low T.

Although they are preliminary experiments, these data confirm the main result obtained for O$_2$ adsorption on Ag(410), since they show the opening of a non-activated, dissociative adsorption channel related to open steps. Moreover, both molecular oxygen species detected on flat Ag(100) [19] are destabilised on Ag(210).

4.7 Discussion on oxygen adsorption on Ag(n10) surfaces

4.7.1 Energy barriers and final adsorption states

From comparison of the $S_0(E_i)$ curve for $\theta$=31° reported in Fig. 4.17 with the HREEL spectra of Fig. 4.21 it is possible to draw a schematic picture of the oxygen chemisorption process in presence on open steps.

At the lowest investigated energy a non-vanishing sticking coefficient is measured by KW experiments, corresponding to a peak at 40 meV in the energy loss spectrum, indicative that dissociative adsorption has occurred. The non-activated channel related to the presence of open steps leads therefore to dissociative oxygen adsorption and allows an unambiguous identification of this particular defect with the active site for O$_2$ dissociation on Ag(100). This result is further confirmed by the observation of an intense O-Ag vibration around 40 meV when oxygen is dosed on Ag(210) in the same experimental conditions. The ambiguity of the results on sputtered Ag(100) is thus washed out.

Increasing the translational energy of the beam a new feature in the atomic oxygen region (at 32-34 meV) appears in the HREEL spectra and, above $E_i$=0.30 eV, also the peak at 84 meV, fingerprint of O$_2$ admolecules, is present. Thanks to this spectroscopic information I can relate the energy barrier of 0.25 eV, deduced for normal incidence on the step heights, with the onset of molecular adsorption at steps. The assignment is straightforward, since this threshold is present for $\theta$=$\theta_s$, when step heights are well illuminated, and it is much weaker for $\theta$=0° and $\theta$=-30° (see Fig. 4.16 and Fig. 4.17).
The second energy barrier is comparable with those measured for the low Miller index Ag surfaces and for Ag(410) when $\theta \sim \theta_c$, and thus corresponds to molecular adsorption at terrace sites.

I have already underlined that only one of the two $O_2$ moieties present on flat Ag(100) is stable on Ag(410), while no significant molecular adsorption is detected on Ag(210) even after prolonged exposures. On Ag(410) the stretch energy of 84-85 meV must be associated also to admolecules decorating the step edges. This hypothesis is not unreasonable because theoretical calculations for $O_2$/Ag(110) [32] show that $O_2$ prefers to sit in the grooves and maximise the number of bonds with Ag atoms. However, also the active site for dissociation is at the step. As the molecular species is relatively stable, the molecular adsorption site and the dissociation site must be well separated by a potential energy barrier. This picture would also tentatively explain why no stable molecular adsorption occurs on Ag(210). In fact, if the terrace width is comparable with the dimensions of the molecule, the latter sees both the active site for adsorption at the step and the one for dissociation at the nearest step. It therefore makes the more energetically favourable choice.

One possibility for the location of active sites is that dissociation occurs at the upper side of the step, as reported recently for $O_2$/Pt(111) by scanning tunnelling microscopy [33], while admolecules sit at the lower side of the step. This is a reasonable hypothesis also for Ag(410). In fact my data show that the pathway for molecular adsorption at steps opens only when the step heights are well illuminated, while some dissociative adsorption is present at every angle of incidence; the upper side of the step is indeed always illuminated. I cannot deduce more precise information because the experimental apparatus available for my experiments does not allow to investigate the geometry of the adsorption site of the different oxygen moieties I have detected. STM or X-rays photoelectron diffraction would be necessary to achieve this goal.

The population of different adsorption states with increasing $E_i$ is confirmed by the different maximum coverage obtained for $O_2$ exposures on Ag(410) with increasing beam energy. Fig. 4.25 shows the $\Theta(t)$ curves for oxygen adsorption experiments performed at $T=110$ K and $\theta=31^\circ$ (i.e. for normal incidence on the step heights) with $0.25 \text{ eV}<E_i<0.97 \text{ eV}$. The curves are calculated from integration of the KW traces, weighted with the $O_2$ beam flux, and refer therefore to the total coverage expressed in ML of molecules. $\Theta_{\text{max}}$ ranges from 0.035 ML to 0.075 ML of $O_2$ but, since both adatoms and admolecules are present, the actual coverage can be up to twice as large. In spite of that, these coverages are much smaller than the density of open steps, which is expected to determine the saturation coverage. They can indeed be affected by a systematic error due to an underestimate of the flux. The physical information contained in the picture remains however still valid.

### 4.7.2 Surface disorder and concentration of minority defects

The results of HREELS and KW experiments on Ag(410) support, a posteriori, the hypothesis that surface disorder and concentration of isolated minority defects on the Ag(n10) crystals are negligible in my experimental conditions. In particular I notice that:
Fig. 4.25: Total coverage, $\Theta$, vs. exposure time for O$_2$ adsorption on Ag(410) at T=110 K. The beam impinges on the surface with $\theta$=31° and different translational energies.

a) No massive formation of (111) facets is likely to occur since: 1) this would show up in the LEED images which, on the contrary, are sharp patterns with (410) or (210) spots only; 2) no strong disorder was reported in a previous structural LEED study of Ag(410) [34].

b) For Ag(410) the miscut of 1° with respect to the nominal surface plane is not expected to cause relevant effects, since the misalignment component in the direction perpendicular to the steps gives rise to some (510) and (310) facets, which are expected behave similarly to (410). The misalignment component along the step edges, on the contrary, causes, in the worst case, the presence of one kink site every 60 step atoms and can thus influence the sticking coefficient by less than 2%, a much lower value than the smallest $S_0$ measured for O$_2$/Ag(410) (~5%). Moreover a kink on an open step corresponds to a more compact atomic configuration than the open step itself.

c) The HREEL spectra recorded for Ag(410) and Ag(210) show an amount of dissociated oxygen comparable with the one detected for oxygen adsorption at low T on heavily damaged (sputtered) Ag(100) surfaces (compare Figs. 4.21, 4.22 and 4.24 with Figs. 4.5 and 4.10 and refs. [12,13]). The dissociation probability in the low coverage limit is therefore comparable. If the physics of the O$_2$-Ag(n10) interaction were not determined by the majority defect (open step) but by isolated kinks, then their density at T=105 K on annealed Ag(410) would be similar to the one present on heavily sputtered Ag(100) at low T (a treatment which destroys the LEED pattern of the surface). This is clearly not a reasonable estimate for the density of defects of a surface with a sharp LEED pattern.

d) Isolated kinks at steps, forming (111) step segments, could be generated because open steps are thermodynamically unstable. Let’s assume that this effect is relevant for my experiment. If the active sites were generated by the thermodynamic fluctuations of the steps, their density should increase with crystal temperature and the sticking coefficient would correspondingly increase with temperature for all translational energies, as it was observed for flat Ag(100) [5].
As it is shown in Figs. 4.19 and 4.20, on the contrary, for O$_2$/Ag(410) $S_0$ decreases with $T$ for $E_i=0.39$ eV and shows a slight increase only around $T=130$ K and only when dosing O$_2$ with $E_i=0.97$ eV. This minor effect could however be due to an enhancement of the mobility of O$_2$ molecules adsorbed at terrace sites, as explained in the previous discussion. Thermodynamic fluctuations of the step shape are therefore not the determining effect for the measured sticking coefficient.

### 4.8 Conclusions

In this chapter I investigated the interaction of oxygen with defected and nanostructured Ag(100) surfaces as well as with Ag(410) and Ag(210), by means of KW measurements and vibrational spectroscopy. The data demonstrate that dissociation is induced by defects and that these defects can be safely identified with open steps.

For the sputtered surfaces I showed, in fact, that, when dosing at $T=105$ K, two oxygen adatoms moieties form, corresponding to adsorption at vacancies and at isolated kink sites. In these conditions no dissociation takes place, on the contrary, on flat Ag(100), at least in the low O$_2$ coverage limit. The dissociation probability is nicely correlated with the density of kinks estimated for nanostructured surfaces.

At high oxygen doses, when the defects are saturated, dissociation becomes a truly minor channel and molecular chemisorption dominates also for the damaged surface. Molecular adsorption occurs, then, even for the most defected surfaces.

The investigation of the O$_2$/Ag(410) and O$_2$/Ag(210) systems allows to unambiguously identify open steps with the active sites for O$_2$ dissociation and to study the dynamics of the interaction of oxygen with these defects. For both systems a non-activated, defect-related, dissociative adsorption channel is present, while on Ag(410) also molecular adsorption can occur at open steps, with a reduced activation barrier with respect low Miller index surfaces ($E_B=0.25$ eV instead of 0.37 eV).

Finally I found that reactivity is enhanced at steps and reduced at terraces with respect to Ag(100) and Ag(110), thus demonstrating that it is influenced by the limited terrace width and that the stepped surface is not a mere superposition of (100) and (110) nanofacets. The global O$_2$ uptake is thus reduced in spite of the increased reactivity of step sites.

### References

5 Ethylene interaction with Ag(410) and Ag(210)

5.1 Introduction

The interest in ethylene adsorption on metal surfaces is mainly due to the role played by this molecule as a test species for the investigation of the chemistry of hydrocarbons, a field which attracts much attention because of the many technological applications connected to it. The C₂H₄/Ag system is even more intriguing since silver powders are the only catalyst in the ethylene epoxidation reaction. Although experiments performed in ultra high vacuum failed, so far, in producing epoxide, they lead to a quite complete characterisation of the interaction of C₂H₄ with Ag faces [1]. In spite of the large attention devoted to this subject, the ethylene reactivity at defect sites was relatively poorly studied. Microcalorimetric measurements showed that C₂H₄ initially adsorbs on Pt(211) as quad-σ-acetylene and, at higher coverage, as ethylidyne (C-CH₃), while on the more corrugated Pt(311) only ethylidyne (C-CH₂) forms [2].

As already mentioned in Chapter 2, previous studies showed that, at a crystal temperature T=105 K, ethylene adsorbs on Ag(100) in different states, depending on the translational and vibrational energy of the gas-phase molecules: a physisorbed state (metastable at this T) [3], a π-bonded state, which is translationally activated [4, 5], and at the highest nozzle temperatures a more strongly bound, undissociated state coupled with radical formation [4].

Recent local density approximation (LDA) calculations [6] did not find any stable chemisorption state for C₂H₄ on Ag(100), contrary to experimental results. They suggested that the experimentally observed states might be related to defects, as it is the case for C₂H₄ on aluminium [7]. The unexpected barrier for ethylene adsorption into the π-bonded state on Ag(100) could then be linked to the energy required for the creation of a defect at which the molecule can stick with high enough binding energy to be stable still at 100 K.

On this theoretical and experimental basis I decided to investigate the interaction of ethylene with the defected Ag(410) and Ag(210) surfaces. Indeed I found that open steps remove the translational barrier to adsorption into the π-bonded state. This result is in accord with what suggested by theory and confirms an increased reactivity of step sites for C₂H₄ adsorption. Moreover this is the only stable adsorption state observed on Ag(410), since neither more strongly bound states nor radical formation are detected. The existence of open steps seems therefore not to catalyse any significant dissociation of the ethylene molecules, contrary to what reported in the previous chapter for O₂ [8].

For C₂H₄/Ag(410) I will also show a complete characterisation of the sticking coefficient, S, with respect to translational energy, angle of incidence and crystal temperature and the existence of an adsorbate-assisted adsorption mechanism for physisorbed ethylene.
5.2 Experimental

Experiments were performed in the UHV apparatus described in Chapter 3, using the same Ag(410) and Ag(210) crystals employed to investigate O$_2$ adsorption. In both cases the scattering plane is now defined by the normal to the surface and the $<\hat{1},n,0>$ direction. The surface was prepared by sputtering with Ne$^+$ ions and annealing to $T=700$ K and the supersonic molecular beam was collimated to a spot diameter of 2 mm at the crystal for KW measurements and of 8 mm for HREEL Spectroscopy. The translational energy, $E_i$, of the impinging molecules was varied from 0.10 eV to 0.83 eV both by seeding C$_2$H$_4$ in helium (3% of C$_2$H$_4$) and by heating the nozzle up to $T_N=870$ K.

The final adsorption state of ethylene was characterised by HREELS. In order to enhance the surface sensitivity under dipole scattering conditions, spectra were recorded at grazing incidence (63°) and low electron energy ($E_e=1.7$ eV). The energy resolution of 7 meV of the spectrometer was chosen as a compromise between the resolution and the count rate on stepped surfaces.

When dosing ethylene with a hot nozzle the possibility that significant fragmentation occurs inside the nozzle itself must always be considered. In this case, in fact, it would be impossible to distinguish if the fragments detected on the surface are due to the interaction of ethylene with the surface or if they were already present in the supersonic molecular beam.

In my experiments the occurrence of significant pyrolysis inside the hot nozzle can be excluded on the basis of the following arguments:

1) No radicals are detected on the Ag(410) surface when a pure ethylene beam is dosed with $T_N=870$ K, at variance with what observed on Ag(100) [4]. If the radicals were produced inside the nozzle, they would be present on both surfaces.

2) The composition of the C$_2$H$_4$ beam at different $T_N$ was measured and compared with the HREELS results obtained for Ag(100), on which radicals are observed when dosing at $T_N>850$ K. I employed the Extranuclear quadrupole mass spectrometer (in line of sight with the beam) to detect the signal of a chopped beam. The energy of the electrons in the ioniser was chosen to be 16 eV, i.e. immediately above the ionisation threshold, in order to increase the sensitivity to small changes in the spectrum. All the mass spectra are dominated by the mass 28 (M28) signal at all nozzle temperatures, but the relative abundance of masses 26 (M26) and 27 (M27), corresponding both to the normal fragmentation pattern of ethylene and to de-hydrogenated species, increases with $T_N$. The M26 and M27 intensities, normalised to the M28 peak intensity ($I_{M28}$), are plotted in Fig. 5.1 vs. $T_N$. I note that the M27 signal remains constant up to $T_N=600$ K and increases by $\sim$20% ($\sim$1.5% of $I_{M28}$) between 600 K and 910 K, while the M26 signal doubles (increase of $\sim$5.5% of $I_{M28}$) passing from $T_N=RT$ to $T_N=929$ K. Since the latter growth is approximately linear in $T_N$, it corresponds to an increase of only 1% of $I_{M28}$ between $T_N=850$ K and $T_N=929$ K, i.e. in the range of nozzle temperatures in which radical adsorption is detected in the HREEL spectra of C$_2$H$_4$/Ag(100). If the concentration of radicals in the beam grew with increasing $T_N$, they would appear in the energy loss spectrum at all nozzle temperatures, and not only above 850 K. Moreover, the increase of the M26 signal is comparable to the density of vibrationally excited molecules, and is probably due to this
effect. I can therefore conclude that the amount of radicals present in the beam is negligible and does not affect the validity of my results.

Fig. 5.1: Intensity of masses 26 and 27 as a function of nozzle temperature. The intensities are deduced from the QMS spectra of a pure ethylene beam and normalised to the M28 signal.

5.3 Data presentation

5.3.1 \(\text{C}_2\text{H}_4/\text{Ag}(410): \) analysis of the KW traces

Fig. 5.2 shows the QMS trace of the \(\text{C}_2\text{H}_4\) partial pressure in the main chamber during a KW experiment performed at a crystal temperature \(T=110\ \text{K}\), with \(E_f=0.36\ \text{eV}\) and \(\theta=\theta_s\). Following the procedure described in paragraph 3.2.3, at time \(t=t_0\) the molecular beam enters the UHV chamber; at \(t=t_1\) the inert flag placed in front of the crystal is removed and the beam hits the active surface of the sample. The drop of the \(\text{C}_2\text{H}_4\) partial pressure, due to the pumping action of the surface, indicates that adsorption is occurring and gives a direct measurement of the total sticking probability, \(S\), as a function of coverage. The behaviour of \(S\) is qualitatively different from the one observed for \(\text{O}_2/\text{Ag}(410)\) (see Fig. 4.14), since the sticking coefficient increases with coverage from the initial value, \(S_0\), up to a maximum value, \(S_{\text{max}}\).

At \(t=t_2\) the inert flag intercepts the beam again. The observed increase in the QMS trace corresponds to desorption of molecules in a metastable state; it indicates that, at \(T=110\ \text{K}\), physisorption is important on \(\text{Ag}(410)\), as it was the case for \(\text{C}_2\text{H}_4/\text{Ag}(100)\) [3]. When exposing the crystal to the \(\text{C}_2\text{H}_4\) beam for a second time (\(t=t_3\)) the shape of the QMS trace is radically different: \(S\) immediately reaches its maximum value which, at this temperature, is slightly higher than \(S_{\text{max}}\). Such behaviour does not change for further exposures and suggests that the adsorption process on the partially covered surface is different from sticking on bare \(\text{Ag}(410)\). When the beam is intercepted, desorption occurs, indicating that the extra coverage of ethylene is in the metastable, physisorbed state.

Fig. 5.3 reports the total coverage, \(\Theta\), as a function of time. It is calculated from integration of the KW trace of Fig. 5.2, weighted with the beam flux, and is expressed...
Fig. 5.2: QMS trace of the C₂H₄ partial pressure during a KW experiment performed on the Ag(410) surface at T=110 K. The beam impinges normally onto the steps heights (θ=31°) with Eᵢ=0.36 eV. Three subsequent adsorption cycles are shown.

in ML of Ag(410). The arrows correspond to the times t₁, t₂ and t₃, i.e. to the instants when the beam strikes on the sample for the first time, when it is intercepted and when it hits the surface again. During the first exposure, the increase of the total coverage is very fast in the first 10 sec and much slower later. For an exposure time Δt>10 sec, in fact, the slope of the Θ(t) curve is zero within the experimental error.
affecting the determination of the background. The decrease of $\Theta(t)$ at $t=t_2$ gives an estimate of the amount of ethylene desorbed from the surface, i.e. of the metastable coverage at $T=110$ K, which reads $\sim 0.02$ ML.

From the analysis reported in Figs. 5.2 and 5.3 I note that the first shot, corresponding to the interaction with the bare surface, is characterised by co-adsorption of a metastable physisorbed state, promptly desorbed as the shutter is closed, and of a stable chemisorbed state. For the former an adsorbate-induced adsorption mechanism is observed. It is due to the presence of the stable chemisorbed species and it causes the increase of $S$ with coverage. The population of chemisorbed ethylene almost saturates after the first exposure, since no increase is detected in the coverage of the stable species upon further dosing. Shots other than the first correspond therefore to metastable adsorption into the physisorbed state on a surface pre-covered with chemisorbed ethylene. The substantial reproducibility of these traces indicates that we are now observing physisorption-desorption cycles. Moreover the initial $S$ value in the second and third shots is slightly larger than $S_{\text{max}}$, indicating that the latter corresponds to the sticking of physisorbed ethylene on a surface saturated with chemisorbed molecules.

A deeper insight in the adsorbate-induced mechanism observed in the trace of Fig. 5.2 is gained form Figs. 5.4 and 5.5. The former one reports the behaviour of $S$ vs. ethylene coverage for the three cycles of the experiment of Fig. 5.2. Panel A refers to the first exposure, panel B to $S$ as a function of the variation of coverage, $\Delta \Theta$, during the second and third adsorption cycles. As it is evident, while in the first shot $S$ initially increases with $\Theta$, in the subsequent ones it immediately reaches the maximum value and remains constant until saturation. Within experimental error, it has therefore the rectangular shape predicted by the Kisliuk model for physisorbed systems; the molecules can therefore stick also on already occupied sites. The shape of the $S$ curves confirms that the increase of $S$ with coverage is present only when physisorption occurs on a surface pre-covered with chemisorbed ethylene.

![Fig. 5.4: Coverage dependence of the sticking probability calculated from the QMS trace of Fig. 5.2. Panel A: $S(\Theta)$ for the first exposure. The increase of $S$ with coverage is evident. Panel B: behaviour of $S$ vs. the variation of total coverage, $\Delta \Theta$, for the second and the third shots. The rectangular shape of the $S(\Delta \Theta)$ curves is expected for physisorbed systems.](image-url)
Letizia Savio Chapter 5

Fig. 5.5: Behaviour of $S(\Theta)$ for C$_2$H$_4$ on Ag(410) in different experimental conditions. Panel A: pure C$_2$H$_4$ beam with $E_i=0.10$ eV, $T=110$ K and $\theta=\theta_s$ (continuous line) and $\theta=-59^\circ$ (dashed line). Panel B: seeded beam with $E_i=0.36$ eV, $T=112$ K and same angles of incidence as in panel A. Panel C: seeded C$_2$H$_4$ beam with $E_i=0.36$ eV, $T=136$ K and $\theta=\theta_s$. The adsorbate-induced effect, particularly evident for the seeded beam at 110 K, suddenly disappears at higher temperature.

Fig. 5.5 shows $S(\Theta)$ for C$_2$H$_4$ molecules impinging respectively normal to the step heights ($\theta=31^\circ$) and with the step heights in the shadow ($\theta=-59^\circ$). The traces in panel A correspond to a pure ethylene beam with $E_i=0.10$ eV, those in panel B to a seeded beam with $E_i=0.36$ eV. In both cases the crystal temperature is 110 K; the higher coverage achieved in panel A is due both to the larger sticking coefficient and to the larger flux of the pure beam. Panel C shows the same KW experiment of panel B (continuous line) performed at $T=136$ K, at which temperature the metastable physisorption coverage is negligible (no desorption is observed immediately after intercepting the beam). It is apparent that:

a) the increase of $S$ with coverage is quite small for the pure beam and relevant for the more energetic one;
b) the apparent saturation coverage is higher when the molecules hit against the step heights ($\theta=31^\circ$) than when they are shadowed ($\theta=-59$) (see panel B);

c) when dosing at higher temperatures (panel C) $S(\Theta)$ is initially flat and decreases for $\Theta>0.015$ ML. This behaviour probably results from the competition between the increase induced by the presence of pre-adsorbed ethylene and the reduced lifetime of physisorbed molecules on the surface. If this is the case, ethylene chemisorption is mediated by a physisorbed precursor.

5.3.2 $\text{C}_2\text{H}_4$/Ag(410): sticking probability

The $S_0$ and $S_{\text{max}}$ values measured at $T=110$ K and $\theta=0^\circ$ are plotted vs. $E_i$ in Fig. 5.6 (closed and open symbols, respectively). $E_i$ is varied from 0.10 eV to 0.83 eV by using both a pure (circles) and a seeded (squares) $\text{C}_2\text{H}_4$ beam. For $E_i=0.36$ eV both symbols are present, since this translational energy can be obtained with a seeded beam at $T_N=300$ K as well as with a pure beam at $T_N=870$ K. In the latter case, however, the ethylene molecules are also vibrationally and rotationally excited.

![Fig. 5.6: Behaviour of $S_0$ (closed symbols) and $S_{\text{max}}$ (open symbols) as a function of the translational energy for $T=110$ K and normal incidence on the Ag(410) surface. Circles and squares indicate that either a pure or a seeded $\text{C}_2\text{H}_4$ beam has been employed.](image)

From comparison of $S_0(E_i)$ and $S_{\text{max}}(E_i)$ it is evident that:

a) Both curves decrease with increasing $E_i$, as it was the case on the flat Ag(100) surface [3] and as expected for non activated systems.

b) The difference between $S_0$ and $S_{\text{max}}$ is small at low $E_i$ and increases with translational energy. For $E_i=0.8$ eV the maximum of $S$ is four times larger than its initial value.

c) For $E_i=0.36$ eV the adsorption probability is slightly lower for internally hot than for cold molecules. For $\text{C}_2\text{H}_4$/Ag(100) the effect was larger and it was ascribed to the influence of rotations in inhibiting the sticking probability [3]. The same mechanism holds also for Ag(410), although with a reduced efficiency.
Letizia Savio
Chapter 5

Fig. 5.7 reports the dependence of $S_0$ (panel A) and $S_{\text{max}}$ (panel B) on the angle of incidence of C$_2$H$_4$ molecules, at a crystal temperature of 110 K and parametric in $E_i$. The three series of data correspond to a pure (circles) and a seeded (squares) ethylene beam with the nozzle at 300 K ($E_i=0.10$ eV and $E_i=0.36$ eV, respectively) and to a pure beam (diamonds) with the nozzle at 870 K ($E_i=0.36$ eV). At given translational energy, the shape of $S_0(\theta)$ and $S_{\text{max}}(\theta)$ is quite similar, although opportunely scaled: both curves are approximately constant for $-50^\circ \leq \theta \leq 60^\circ$ at all $E_i$, except for a slight increase around $\theta=-40^\circ$. When $\theta<-50^\circ$ the curves drop rapidly, showing therefore an asymmetric behaviour (no change is detected in the range $50^\circ<\theta<60^\circ$). The sticking coefficient shows thus a very weak angular dependence for those angles at which the step heights are illuminated and drops as soon as they are shadowed. At $\theta=-50^\circ$, in fact, molecules impinge at $+81^\circ$ on the step heights, while for $\theta\leq-60^\circ$ only the terraces are exposed to the beam. At $\theta=+60^\circ$, on the contrary, step heights are still well illuminated by the molecular beam at an angle of $29^\circ$.

The drop of the $S_0$ and $S_{\text{max}}$ values for $\theta<-50^\circ$ cannot be due to a not perfect alignment of the beam causing part of it to miss the sample, since the beam was carefully centred with respect to the crystal before starting the experiments. Moreover I notice that the change in the illuminated area of the sample (proportional to $(\cos\theta)^{-1}$) between normal incidence and $\theta=-50^\circ$ is 28 %, while the observed drop from the maximum to the minimum value of the $S_0(\theta)$ and $S_{\text{max}}(\theta)$ curves is larger. I can therefore safely ascribe the drop in the sticking coefficient to a true effect related with the missing illumination of the step heights at $\theta=-60^\circ$.

The angular dependence of $S_0$ and $S_{\text{max}}$ indicate that basically total energy scaling occurs when step heights are exposed, as it is expected for non activated adsorption systems, and suggests that the active site is at the step height or at the lower edge of the step.

![Fig. 5.7: Angular dependence of $S_0$ (panel A) and $S_{\text{max}}$ (panel B) at $T=110$ K and different translational and internal energies of the C$_2$H$_4$ beam.](image-url)
I also investigated $S_0$ and $S_{\text{max}}$ as a function of the crystal temperature, parametric in translational energy and angle of incidence. A direct comparison of the behaviour of $S_0$ and $S_{\text{max}}$ as a function of temperature is shown in Fig. 5.8. The data points refer to a seeded ethylene beam dosed at $\theta=\theta_s$ with $E_i=0.36 \text{ eV}$, i.e. to experimental conditions in which the adsorbate-induced adsorption mechanism is particularly efficient. The curves clearly show that $S_0(T)$ and $S_{\text{max}}(T)$ coincide for $T>130 \text{ K}$ but are radically different before. $S_0$ is almost constant up to $\sim140 \text{ K}$, then decreases rapidly between 140 K and 160 K. $S_{\text{max}}$, on the contrary, starts decreasing as soon as the crystal temperature increases by a few degrees. In both cases some residual adsorption, probably at minority defect sites, persists up to 220 K, when it definitely drops below the sensitivity of the KW method ($\sim2 \%$). The dramatic difference at low T can be explained by the different amounts of chemisorbed and physisorbed ethylene which contribute to the measured values and gives an estimate of the relative abundance of the two species. This point requires however a deeper discussion which will be developed in the following.

Results for other exposure conditions are summarised in Fig. 5.9: panels A and B show the $S_0$ and $S_{\text{max}}$ values, respectively, obtained dosing $C_2H_4$ at $\theta=\theta_s$, panels C and D report the same quantities for ethylene doses performed at $\theta=-40^\circ$, i.e. $26^\circ$ off the normal to the terraces and grazing to the steps. In all panels circles refer to a pure $C_2H_4$ beam with $T_N=300 \text{ K}$ ($E_i=0.10 \text{ eV}$), squares to a seeded beam dosed at the same $T_N$ ($E_i=0.36 \text{ eV}$), and diamonds to a pure beam with a nozzle temperature of 870 K ($E_i=0.36 \text{ eV}$). These data confirm that $S_0(T)$ and $S_{\text{max}}(T)$ behave very differently at low T for high impact energies, while for low $E_i$ the difference is small.

![Comparison between the $S_0(T)$ and $S_{\text{max}}(T)$ curves (closed and open squares, respectively) recorded at $T=110 \text{ K}$ and $\theta=\theta_s$ for a seeded ethylene beam with $E_i=0.36 \text{ eV}$.](image)
Fig. 5.9: Dependence of $S_0$ and $S_{\text{max}}$ on surface temperature $T$, for different translational and internal energies. Panels A and C report the $S_0(T)$ curves recorded at $\theta=31^\circ$ and $\theta=-40^\circ$, respectively; panels B and D show the behaviour of $S_{\text{max}}(T)$ at the same angles of incidence. The error bar is displayed in the lower panels only.
5.3.3 HREELS experiments

HREELS experiments were performed both on Ag(410) and Ag(210) for different angles of incidence. Fig. 5.10 reports spectra recorded after dosing ethylene with different beam energies on the Ag(410) surface at T=105 K. The angle of incidence is $\theta=29^\circ$ (nearly normal to the step heights) for the spectra in panel A and $\theta=-45^\circ$ ($31^\circ$ off normal to the terraces and grazing to the steps) for the lower spectra in panel B. The upper spectrum in panel B refers to a $\text{C}_2\text{H}_4$ exposure performed at $\theta=0^\circ$ with vibrationally excited molecules. All spectra are dominated by a peak around 125 meV, independently of the dosing conditions. This vibrational energy is slightly larger than the one reported for $\pi$-bonded ethylene on clean and oxygen precovered Ag(110) [9] and on Ag(100) at $E_i\leq0.36$ eV and $T_N<850$ K [4]. The effect of annealing the ethylene layers of Fig. 5.10 to 155 K is shown in Fig. 5.11 for the cases corresponding to $E_i=0.10$ eV and $\theta=31^\circ$ and to internally excited molecules dosed at normal incidence. In both spectra the feature at 125 meV is no longer present. The behaviour of $\text{C}_2\text{H}_4$ layers is therefore independent of dosing conditions, confirming that the adsorption state is always the same.

Fig. 5.12 reports ethylene adsorption experiments performed dosing 0.16 ML of gas with $E_i=0.10$ eV on the Ag(210) surface at T=105 K. The angle of incidence is $\theta=26^\circ$ ($7.5^\circ$ off normal to the step heights) in panel A and $\theta=-28^\circ$ ($1.5^\circ$ off normal to the
The lower spectrum refers to pure ethylene dosed with $E_i=0.10$ eV and at $\theta=29^\circ$, the upper one to vibrationally excited ethylene dosed with $E_i=0.36$ eV and at $\theta=0^\circ$. In both cases the feature at 125 meV, corresponding to the $C_2H_4$ wag mode, has disappeared, indicating that no more ethylene is present on the surface.

A loss feature at 120 meV was detected for ethylene adsorption on flat Ag surfaces and ascribed to the wag mode of $\pi$-bonded ethylene [4,9]. From comparison with the low Miller index planes and with the wag mode frequency reported for the gas phase (118 meV [10]) I can safely assign the 121-125 meV mode to the $C_2H_4$ wagging motion. The nature of the energy loss around 38 meV in the spectra of Figs. 6.10A and 6.12 is, on the contrary, more controversial. Such frequency is suitable for the $C_2H_4$ vibration against the surface, the dipole moment of which might be enhanced for molecules adsorbed at steps. Alternatively it might be due to some atomic oxygen contamination. As demonstrated in Chapter 4, in fact, a non-activated dissociative adsorption channel is open for $O_2$ on Ag(410). It is therefore hard to say which assignment is correct. After annealing the Ag(410) surface to 155 K (see lower spectrum in Fig. 5.11), in fact, some intensity is still present in the 38 meV region although ethylene has desorbed completely. On the other hand, the 37 meV feature of Fig. 5.12 is removed together with the $C_2H_4$ wag mode peak upon annealing Ag(210) to 159 K. A possible explanation to this contradictory behaviour is that the observed...
Fig. 5.12: HREEL spectra recorded after dosing ~0.16 ML of C₂H₄ with Eᵢ=0.10 eV on the Ag(210) surface at T=105 K (bottom spectra) and subsequently annealing the layer to 159 K (upper spectra). Panel A: θ=26°, panel B: θ=−28°.

Intensity is mainly due to C₂H₄ adsorption with a minor contribution of oxygen contamination.

I notice that complete desorption of the physisorbed molecules occurs in a few seconds after the end of the dose at 105 K, while a HREEL spectrum requires at least 15 minutes to be recorded. Only stable species are therefore detected in the vibrational spectra. The presence of a loss peak even after dosing ethylene at the lowest energy leads therefore to the unambiguous conclusion that ethylene chemisorption on Ag(n10) surfaces is a non-activated process, contrary to what reported for Ag(100) [4]. The analysis of adsorption cycles further confirms this statement: at T=105 K and Eᵢ=0.10 eV they are not reversible on Ag(410) (the second shot is different from the first one) and reversible on clean Ag(100) [3], thus indicating that on the latter surface only physisorbed molecules are present in such conditions.

Comparing the upper spectrum in Fig. 5.10B with the other ones it is evident that no substantial changes in the spectra occur with increasing Eᵢ and Tᵢ, while dramatic changes were observed on Ag(100) in the same experimental conditions [4]. The independence of the adsorption state from dosing conditions is also confirmed by the HREEL spectra of Fig. 5.11 in which the disappearance of the C₂H₄ wag after flashing to 155 K indicates that complete desorption has occurred either for molecules dosed with Tᵢ=RT or with Tᵢ=870 K. No ethylene or radical related losses are detected upon annealing to 155 K even upon prolonged exposure (~6 ML) of a vibrationally excited pure beam of ethylene, at variance with what observed on Ag(100). The stable ethylene species detected on Ag(410) is therefore identified with molecules in the π-bonded state.
I also performed some HREELS experiments dosing ethylene at low $E_i$ on an atomic oxygen precovered Ag(410) surface. Upon ethylene adsorption an increase of the peak intensity with respect to the corresponding exposure on the clean surface is observed and the vibrational frequency of the wag mode remains unchanged. This behaviour is in accord with what previously reported for Ag(100) [4] and Ag(110) [9] in the same experimental conditions.

5.4 Discussion

5.4.1 Characteristic desorption time and physisorption energy

The increase in the $\text{C}_2\text{H}_4$ partial pressure shown by the QMS trace of Fig. 5.2 is indicative of the presence of metastable species on Ag(410). The desorption of physisorbed ethylene occurs with a characteristic decay time, $\tau_{\text{des}}$, which can be calculated from the desorption curve, $f(t)$, through the formula:

$$f(t) = k e^{-\frac{t}{\tau_{\text{des}}}}$$

(5.1)

Fig. 5.13 reports the desorption curve resulting from averaging over 8 measurements performed by exposing the Ag(410) surface at $T=110$ K to a pure $\text{C}_2\text{H}_4$ beam with $E_i=0.10$ eV. Such experimental conditions correspond to the maximum metastable coverage. The single traces were normalised to unity before being averaged. The solid line is the best fit to the data obtained using the function (5.1), from which $\tau_{\text{des}}=0.8$ sec is determined.

This information allows to calculate the physisorption energy of $\text{C}_2\text{H}_4$ molecules on Ag(410), through the law:

$$E_{\text{phys}} = kT \ln \nu \tau_{\text{des}}$$

(5.2)
Assuming the pre-factor $\nu = 10^{12}$, as for Ag(100), and using the previously estimated value of $\tau_{\text{diss}}$, I obtain $E_{\text{phys}} = 0.25$ eV, in accord with the one determined for the flat Ag(100) surface [3] and with typical values expected for physisorbed hydrocarbons [11]. Moreover, I note that changing $\nu$ by a factor of 10 modifies the value of the physisorption energy only by 0.02 eV, leaving my conclusion unaltered. Therefore the presence of open steps does not affect the physisorption energy of ethylene on the Ag(100) surface.

### 5.4.2 Sticking probability and adsorbate-assisted adsorption

Inspection of Figs. 5.2, 5.4 and 5.5 indicates that the adsorption probability of ethylene on Ag(410) initially increases with coverage. The importance of this effect grows with $E_i$ and decreases with $T$. At $T=136$ K, in fact, $S(\Theta)$ is similar to a step function, indicating that the increase is counterbalanced by the reduced lifetime of physisorbed molecules on the surface.

Such effect, commonly called adsorbate-assisted adsorption, has been previously reported for several systems, like CO/Cu(110) [12], NO/W(110) [13], ethane/Ir(110) [14], ethane/Pt(111) [15], rare gases on metal surfaces [16,17], and CO/Zn-ZnO [18]. Different explanations have been proposed, ranging from analytical models to Monte Carlo simulations and trajectory calculations. In the first case several modifications of the Kisliuk model for physisorption have been developed, e.g. including the coverage dependence of the heat of adsorption [13] or accounting for different adsorption probabilities on clean and covered parts of the surface [19,17] and for islands formation [16]. Monte Carlo simulations [20,21] found that this mechanism can be explained by the higher efficiency of the energy transfer when a gas-phase molecule hits an adsorbate of the same mass than when it strikes a heavier substrate atom, i.e. by a reduction of the mass-mismatch, $\mu = m_{\text{adsorbate}}/m_{\text{substrate}}$. Finally, some trajectory calculations [15] demonstrated that the enhancement of adsorption by pre-adsorbates can be related to a modification of the corrugation of the surface and this model was successfully applied to the ethane/Pt(111)-S system.

For C$_2$H$_4$/Ag(410) the first explanation can be ruled out, since the heat of adsorption decreases with increasing coverage. In fact a low temperature shoulder in the desorption peak of ethylene is observed experimentally, while an increase would be necessary to enhance the sticking probability. Moreover the possibility of different lifetimes on the clean and covered parts of the surface might explain the disappearance of the effect with increasing temperature but not why it vanishes at low translational energy.

A model taking into account the reduction in mass mismatch with increasing coverage, due to the higher probability that an incident C$_2$H$_4$ molecule strikes against another ethylene molecule (mass 28) instead than against a silver atom (mass 108), explains indeed the behaviour of $S(\Theta)$ both with increasing $E_i$ (see Fig. 5.6) and adsorption temperature (see Fig. 5.5). The qualitative picture for the physisorption process is draw in Fig. 5.14: at low $E_i$ the C$_2$H$_4$ molecule needs to loose a small amount of energy to get trapped and physisorb on the surface, so that there is not much difference in striking an Ag atom or another adsorbed molecule. For high $E_i$, on
the contrary, the amount of energy to be lost by the impinging molecule to get trapped and physisorb is large and the efficiency of the energy transfer becomes important. This picture explains also the increasing difference between $S_{\text{max}}$ and $S_0$ with $E_i$ (see Fig. 5.6). After the total equilibrium coverage of chemisorbed plus physisorbed molecules is achieved, desorption sets in and the coverage cannot increase further, thus causing $S$ to drop rapidly to zero.

This simple model states therefore that initially ethylene chemisorbs at steps, possibly through a physisorbed precursor. This hypothesis is reasonable since at low $E_i$ no chemisorption occurs on flat Ag(100). $\text{C}_2\text{H}_4$ physisorption probability is then increased because of the favourable energy exchange mechanism with chemisorbed $\text{C}_2\text{H}_4$. The adsorbate-assisted adsorption involves therefore ethylene molecules physisorbed in presence of the chemisorbed species.

Finally, let’s address the different behaviour of $S_0$ and $S_{\text{max}}$ vs. $T$. As shown in Figs. 5.8 and 5.9, the initial sticking coefficient remains stable up to ~140 K and drops thereafter, while $S_{\text{max}}$ decreases monotonously with increasing $T$. Above 130 K, a temperature at which the lifetime in the physisorption well becomes shorter than the measuring time with the KW method, the two curves become indistinguishable. Since 140 K corresponds to the desorption temperature of $\pi$-bonded ethylene and since the residence time of physisorbed species decays exponentially with $T$, the constant value of $S_0(T)$ for $T<140$ K indicates that initially only chemisorption occurs. This behaviour does not exclude, in principle, that the chemisorption process can be mediated by a physisorbed precursor. In fact, until the lifetime of the precursor is longer than the time needed to the trapped molecule to diffuse and find the active site for chemisorption (i.e. the step), no decrease in the $S_0(T)$ curve is expected. $\text{C}_2\text{H}_4$
molecules physisorb then on an already partially covered surface, giving rise to the adsorbate assisted adsorption mechanism. Therefore $S_0$ roughly corresponds to the initial adsorption probability in the chemisorbed state. The adsorption probability of the physisorbed species, on the contrary, increases with coverage and passes from the initial vanishing value to a maximum value, which is approximately $S_{\text{max}}$. Coherently with the adsorption model proposed above, this effect is large for energetic molecules and vanishing for $E_i=0.10$ eV.

### 5.4.3 Effect of rotations on sticking probability

Let's now compare the behaviour of the sticking probability measured for C$_2$H$_4$ on Ag(410) with the one reported for the C$_2$H$_4$/Ag(100) system [3]. Firstly I note that a translational energy $E_i=0.36$ eV can be obtained either by using a pure beam with a hot nozzle ($T_N=870$ K) or a seeded beam with the nozzle at room temperature (see Fig. 6.6). The two mixtures have quite different internal energies (~0.21 eV for pure C$_2$H$_4$, 0.005 eV for seeded C$_2$H$_4$) and, in particular: i) the rotational temperature is $T_{\text{rot}}=110$ K for the pure gas and $T_{\text{rot}}=12$ K for the seeded one (see ref. [3]); ii) a significant part of molecules is in the first excited vibrational state in the former case and in the fundamental state in the latter one.

For ethylene adsorption on Ag(100) the sticking probability for molecules with $E_i=0.36$ eV reads 0.38 if C$_2$H$_4$ is dosed with a cold seeded beam and 0.15 if a pure beam of hot molecules is employed [3]. Such dramatic drop was ascribed to the effect of rotations. In fact ethylene molecules physisorb on Ag(100) with the C-C axis parallel to the surface; cartwheel rotational motion decreases the time molecules spend with their axis parallel to the surface and prevents them from coming close enough to the surface plane to get trapped into the physisorption well. The probability of being reflected back to the gas phase is thus increased.

On Ag(410) this effect is present but it is heavily reduced, since the decrease in the sticking probability is only ~5% for $S_0$ and ~7.5% for $S_{\text{max}}$. The larger drop of $S_{\text{max}}$ is expected because of the larger contribution of physisorbed molecules in determining this quantity. Rotations therefore affect also the physisorption process of ethylene on Ag(410), although to a much lower degree than they do on flat Ag(100). Therefore, this is not a major effect in the characterisation of the adsorption process.

### 5.5 Conclusions

In this chapter I have shown results for ethylene adsorption on Ag(410) and Ag(210). Both a physisorbed and a chemisorbed species adsorb on these surfaces at $T=110$ K. Contrary to what reported for Ag(100), no energy barrier is present for C$_2$H$_4$ chemisorption even at the lowest $E_i$. This effect is attributed to the increase of the surface reactivity caused by the presence of steps, and supports the theoretical suggestion of A. Dal Corso et al. [6] that no stable state exists on defect-free Ag(100).

Moreover ethylene chemisorbs on Ag(410) only in the $\pi$–bonded state and no dissociation occurs, contrary to what reported for oxygen in the previous chapter. The more stable, undissociated species and the radicals observed on Ag(100) when dosing vibrationally hot molecules do not form on Ag(410), when dosing at the same
energies. Since (100)-like sites are present on Ag(410) my result strongly suggests a reduced reactivity due to the limited terrace width also for ethylene. For C$_2$H$_4$/Ag(410) the angular dependence of the sticking probability indicates a total energy scaling mechanism, as long as steps are illuminated by the beam. When the latters are shadowed, the sticking probability drops, thus confirming the role of steps in ethylene adsorption. Finally, an adsorbate-assisted adsorption mechanism is observed for C$_2$H$_4$ physisorption in presence of the chemisorbed species. It is explained in terms of reduction in mass mismatch between the molecule and the substrate with increasing coverage.

References

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6 Conclusions

This thesis reports on a complete study of the role of defects in the interaction of oxygen and ethylene with silver surfaces, performed by energy and angle resolved adsorption experiments and by monitoring the final adsorption state by vibrational spectroscopy. My results confirm that defects may play a pivotal role in catalytic reactions. The investigation of gas-surface interaction and of simple catalytic processes on defected single crystal surfaces is therefore significant in overcoming the structure gap present between laboratory experiments performed under controlled conditions and industrial reactions.

The major findings of my investigation are:
1) Defects are the rate-limiting step in the dissociative adsorption process of oxygen on Ag(100). This is demonstrated by the opening of a dissociative adsorption channel at T=105 K for sputtered or stepped Ag crystals. The study of the Ag(n10) surfaces allows to unambiguously identify open steps with the active sites for dissociation through a non-activated channel.
2) On Ag(410) a channel leading to molecular oxygen adsorption at steps is present. This pathway is activated with a significantly reduced energy barrier with respect to flat Ag surfaces.
3) Only one of the two molecular oxygen moieties present on Ag(100) is detected on Ag(410), while no molecular adsorption is observed on Ag(210). The presence of at least one complete (100) unit cell is therefore essential to stabilise non-dissociative adsorption.
4) The sticking coefficient of O₂ on Ag(410) is increased at step sites and reduced at terraces with respect to flat Ag(100). Ag(410) is therefore more complex than the mere superposition of (100) and (110) nanofacets.
5) Open steps remove the translational energy barrier for ethylene chemisorption into the π-bonded state present for Ag(100). No more strongly bound states are however observed, contrary to the case of C₂H₄/Ag(100).
6) An adsorbate-assisted adsorption mechanism is detected for ethylene molecules physisorbed on Ag(410) when the surface is pre-covered with chemisorbed ethylene. It is explained with the reduced mass mismatch between the reactant and the substrate.
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A Publication list


8) "The role of steps and terrace width in gas-surface interaction: O2/Ag(410)". L. Savio, L. Vattuone and M. Rocca, Phys. Rev. Lett. 87, 276101 (2001).*

9) "Dynamics of the gas-surface interaction in presence of well defined defects". M. Rocca, L. Savio, L. Vattuone. Invited article. Accepted for publication on Surf. Sci.*

10) "Formation of channels for oxygen migration towards subsurface sites by CO oxidation and growth of the surface oxide phase on Ag(001)". L. Savio, L. Vattuone, M. Rocca, F. Buatier de Mongeot, S. Lizzit, G. Comelli, A. Baraldi and G. Paolucci. Submitted.

11) "Ethylene interaction with Ag(410) and Ag(210)". L. Savio, L. Vattuone and M. Rocca. In preparation.

12) "Dynamics of the O2 interaction with stepped and damaged Ag surfaces". L. Savio, L. Vattuone and M. Rocca, invited article for J. of Phys. C. In preparation.*

* The articles marked with * are part of this thesis.