CLEAN AND MODIFIED OXIDE SURFACES: STRUCTURE AND DYNAMICS OF ADSORBED MOLECULES

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ABSTRACT. Oxide surfaces have only received little attention as compared with metal surfaces although their technical importance is equal or even greater than metal surfaces. Experimental difficulties are the major reason for this situation. Recently, via the study of thin oxide films some of the problems have been circumvented. We address in the present review various aspects in connection with the study of adsorption of molecules onto oxide surfaces. Specific aspects include:

- Molecular adsorption on the clean oxide surfaces and its influence on oxide surface states as studied by surface science techniques
- Modification of oxide surfaces by metal deposits and its influence on the adsorption behaviour as studied by surface science techniques.

Methods applied include electron spectroscopies for electronic structure studies as well as vibrational excitations, infrared spectroscopy, thermal desorption and related methods.

• Study of the dynamics of molecules in the adsorbed state via electron spin resonance spectroscopy and the quantum state resolved detection of desorbing molecules.

1. Introduction

The development of surface science during the last thirty years [1] has been enormous and was intimately connected with studies of solid metal surfaces. One of the reasons which has always been expressed was the relevance of metal surfaces for example in heterogenous catalysis [2]. While this is true, it is also a fact that in catalysis oxide surfaces play an important, if not more important role. However, this was not reflected in the world wide efforts in surface science during the last decades [3]. There are several arguments which could be put forward to rationalize this observation. One group of reasons in this respect is connected with the experimental difficulties in the application of electron spectroscopies [4-7], which are particularly important in surface science, to the study of poor electric and heat conductors. It has therefore been our goal to circumvent these problems by preparing thin, well ordered oxide films on metal substrates which do not charge upon electron impact or electron emission, and which may easily be cooled to liquid nitrogen or liquid helium temperatures [8-11]. Another group of reasons is connected with the structure of oxides where defects play a much more important role as compared with metal surfaces [3]. The structural problems are intimately related to the stability and ill defined stoichiometry of some oxide surfaces. Furthermore, there is another factor that has to be taken into account if we want to vary the crystallographic orientation of surfaces of highly ionic materials [12]. In general, there are "cleavage planes" with low surface potentials and other crystallographic orientations with high or even diverging surface potentials. While it is very hard to prepare such orientations on bulk single crystals it is rather straightforward to do so in the case of thin oxide



Fig. 3: Schematic representation of the rock salt type binary oxide type structure. The (100) surface and (111) surface with metal termination are shown



Fig. 4: LEED pattern of the NiO(100) and NiO(111) surfaces. In the case of the (100) surface the LEED pattern of the cleaved crystal as well as the thin film are shown together with schematic representations of the surfaces.

consequences for the flow of energy in the system which is intimately connected with adsorbate dynamics. Especially, if energy is deposited into the adsorbate system the question of energy dissipation determines, for example, whether a molecule remains on the surface or desorbs from it. On metal surfaces, to be more specific, energy dissipation into the substrate after excitation, for example by photons, is very effective due to the facile creation of electron-hole pairs, often leading to rapid quenching of the excitation and the excited adsorbate remains on the surface. On an oxide surface, on the other hand, due to the presence of a band gap electron-hole pair creation is energetically unfavourable thus leading to much less effective energy dissipation into the substrate, and consequently leading to large desorption yields of the adsorbed molecules. Therefore, oxides are particularly well suited to study for example photon induced desorption processes [17-23]. The high desorption cross sections allow a very efficient quantum state resolved detection of desorbing particles applying high resolution laser techniques. The interpretation of such data lead to a detailed understanding of the microscopic processes involved in the dynamics of the desorption process. We shall review such studies.

2. Experimental Aspects

The experiments are performed in ultrahighvacuum chambers which are equipped with preparation sections. There are several techniques that are used to prepare the oxide surfaces. As briefly alluded to in the introduction, oxide surfaces may be prepared by cleavage of bulk samples or via the creation of thin films. While cleavage allows the preparation of stable surfaces only, thin film preparation also includes the possibility of preparation of metastable surfaces.

In Figure 2 three different thin film preparation techniques are compiled. At the top the most simple variety is presented, i.e. the oxidation of a metal single crystal of specific orientation leading to the growth of an oxide layer. The structural quality of the resulting layers depends on the



Fig. 6: Shapes and energies of the d-orbitals in NiO in the bulk (O_h) and at the surface $(C_{4\nu})$. The excitation energies as calculated via ab-initio calculations by Freitag and Staemmler [58] are shown in the middle panel.

3. The Clean Oxide Surfaces

3.1 SURFACE STATES

Figure 3 shows the schematic structure of a rock salt type oxide which exposes two low index surfaces, i.e. the stable cleavage (100) plane as well as the thermodynamically unstable, unreconstructed (111) plane. Figure 4 collects LEED patterns [12,14] of a cleaved as well as a thin film NiO(100) surface. Clearly, the cleavage plane yields a much sharper LEED pattern than the thin film indicating the higher defect concentration on the thin film surface. In addition, we present a thin film preparation of the NiO(111) surface [12]. The pattern is rather sharp as compared with the (100) preparation and we shall see later that this is due to the presence of stabilizing hydroxyl groups at the surface. Very similar situations can be found for CoO [32-34] as well as FeO [35,36]. Let us for simplicity consider the (100) surface in greater detail. The question is: Can we observe surface specific effects which are connected to the fact that the atoms in the surface are not fully coordinated as compared with the atoms in the bulk of the crystal? Figure 5 illustrates the octahedral coordination in the bulk and compares it with the fivefold coordination in the surface layer. It is now quite obvious that we would have to look for ligand field effects [58]. Those will be most pronounced for the Ni ions with their unfilled d-shell. We consider the situation for the d-orbitals in more detail in Figure 6. Briefly, an octahedral field splits the d-orbitals in a threefold degenerate t_{2g} - and a twofold degenerate e_g -set. Ni²⁺ carries eight electrons, six occupying the t_{2g} -set and two unpaired electrons in the e_g -set. This leads to a ${}^{3}A_{2g}$ state. The two lowest lying excited states in this octahedral field are of ${}^{3}T_{2g}$ and ${}^{3}T_{1g}$ type and are situated at 1eV and 1.81 eV, respectively. If we reduce the ligand field by taking one of the ligands off the symmetry as well as the repulsion is reduced and this splits the t_{2g}-set into an e- and a b₂-component, and the e_g-set into an a1- and a b1-component. At the same time the splitting in the d-levels is reduced and the excited states shift to lower energy and are increased in number. Therefore, it should in principle be





Fig. 9: Model of a NiO(111) surface exposing various kinds of terminations, defects and facets.

Fig. 10: O1s XPS spectra for NiO(100) (cleaved surface and thin film) and NiO(111) crystal orientations.

spectroscopy to identify excited states localized in the surface. Those may be used in turn to investigate the interaction with adsorbed molecules. Such information is very hard to obtain for example with traditional XPS investigations because the metal core hole spectra of transition metal oxides are rather complicated and congested with many particle satellites [59-60].

3.2 ADSORPTION OF MOLECULES

The surface states discussed in the previous section can be used to study the interaction of molecules with the oxide surface. This works particularly well because the ligand field states are rather localized on the ion and allow a clear assignment of the site of interaction, if they are influenced through adsorption. If we could coordinate a molecule from the gas phase to the surface Ni²⁺-ion, we would expect a shift of the transition to higher excitation energy because the ligand field is increased again. Figure 7 shows what happens when we do the experiment [58]. These experiments are performed on thin NiO(100) films because sample cooling is no problem. The lower two traces show the comparison of the relevant spectra in the appropriate energy range. Obviously, the two systems exhibit the same transitions, except for slight differences in the relative intensities, which are connected with the fact that the film has a considerably higher defect density as compared with the bulk single crystal as revealed by the LEED spot sizes shown as insets [12,14]. Such a NiO(100) film easily forms adsorbed OH groups as indicated by the sharp vibrational OH losses [12,58]. The assignment to OH losses is corroborated by the isotope exchange experiments [12] as shown by the shifted OH losses in the third trace from the bottom. However, the surface excited state is not influenced in intensity by the presence of OH indicating that the hydroxyl groups are not located on the Ni terrace sites. We rather think that the OH groups are located at defect sites. This is supported by the fact, that while OH groups adsorb easily on the NiO(100) film, there is no trace of OH on the in situ cleaved single crystal even upon exposure to



Fig. 13: HREEL spectra in the range of NO stretching vibrations of a CoO(111) surface exposed to NO (saturation coverage) taken at 80K surface temperature. Lower trace: Surface as prepared, i.e. with OH groups at the surface. Upper trace: spectrum after OH/OD exchange.



Fig. 14: HREEL spectra in the range of NO stretching vibrations of a CoO(111) surface as prepared and exposed to CO (saturation coverage) at different surface temperatures.

molecules considerably stronger than terrace atoms. Therefore we studied a NiO(111) film. Here the main terraces are (111) oriented, either Ni or O terminated and the facets are either (110) or (100) oriented. We note in passing that the structural quality of the NiO(111) film is better than the NiO(100) film [12]. Figure 10 collects the O1s spectra of the bulk NiO(100) cleavage plane in comparison with the O1s spectra of the NiO(100) and NiO(111) films [64]. While the O1s spectrum of the cleavage plane is a single symmetric line, the films show a shoulder at higher binding energy, which is due to the presence of OH at the surface. It is quite obvious in the spectra, taken at grazing electron exidence, that the OH concentration is considerably higher on the (111) surfaces as compared to the (100) surface. In fact, if we calculate the coverage quantitative, the OH coverage is by a factor of 3 larger on (111) as compared with (100). This shows that it is not unreasonable to assume the defects that adsorb OH are essentially NiO(111) facets. This is, of course, not a conclusive proof, but the results are, however, compatible with such an assignment. The presence of OH groups, in particular on the NiO(111) film, leads to a strong influence on the structure and reactivity of the system [12,30].

It can be shown that upon removal of the hydroxyl groups from the surface the NiO(111) surface undergoes a p(2x2) reconstruction. This reconstruction is believed to be of the socalled octopolar type as shown in Figure 11. Lacman [65] and Wolf [66] have shown that such a reconstruction stabilizes the surface considerably, i.e. more than any other reconstruction known so far. On NiO(111) this reconstruction may be removed by the exposure to water which leads to a hydroxylation of the surface [30]. CoO(111) films do not survive the heat treatment necessary to remove the hydroxyl groups but it seems the situation is similar to NiO(111) [32]. FeO(111) on the other hand behaves quite different [32,35]. Here, the p(2x2) reconstruction is stable towards exposure to water. The factors influencing the stability of the reconstruction are not clear at the moment but it is not unlikely that the varying degrees of ionicities in the systems may play a key role.



Fig. 17: Electron energy loss spectra in the range of electronic excitations in the band gap of $Cr_2O_3(111)$ at 90 K surface temperature after exposure to various gases.

acid HNO_2 is not clear at present. Another possibility would be a particular bonding of the NO in the neighbouring site, e.g. instead of nitrogen end down oxygen end down [61]. However, this is pure speculation at the moment.

Another interesting, but rather different case of a transition metal oxide surface is represented by the Cr₂O₃(111) surface [37-39], the structure of which is schematically shown in Figure 15. The two possibilities of oxygen and metal termination are indicated. We have previously looked at adsorption on this surface and know that this system is characterized by an electronic excited surface state. Upon interaction with various molecules from the gas phase, this state was considerably influenced in its intensity. We have studied the corresponding energy range again in more detail. Figure 16 shows the electron energy loss spectra up to about 2.5 eV loss energy. Three features are found at 1.2 eV, 1.4 eV, and 1.75 eV. We have argued before [37-39] that the losses above 1.5 eV are due to excitation of the Cr^{3+} -ions in Cr_2O_3 . In fact, the loss at 1.75 eV is due to the excitation from the ${}^{4}A_{2g}$ ground state of Cr^{3+} to the ${}^{2}E_{g}$ and ${}^{2}T_{1g}$ states, i.e. the famous ruby line. The losses at lower energies cannot be due to transitions on Cr^{3+} -ions in a regular bulk $Cr_{2}O_{3}$ ligand field. One possibility would be the assignment of the band to the excitation of Cr3+-ions in a reduced ligand field, a situation encountered at the surface of Cr₂O₃ similar to the discussion for NiO given above. Another possibility is that the transitions occur on Cr2+-ions present in the surface as discussed earlier [37-39]. An argument in favour of a charge reduced state is the electrostatic stabilization the polar Cr₂O₃(111) surface experiences in this case [37-39]. A definite assignment is not straightforward and it is even more involved if we realize that the relative intensities of the 1.2 eV/1.4 eV losses with respect to the 1.75 eV loss change with surface temperature as shown in Figure 16. This latter effect may have several reasons, including magnetic as well as dynamic effects, i.e. atomic motion in the surface. It is clear, however, that the low energy losses are localized in the surface region because they are very sensitive towards the presence of adsorbates. Figure 17 shows the loss region for several adsorbates on Cr₂O₃. In some cases the vibrational losses of the adsorbates are observed (arrows). The 1.2 eV/1.4 eV loss is

quenched in all cases. In the case of the O_2 adsorbate the situation is more complicated. The extra features are connected with molecular oxygen on the surface. However, the definitive assignment is not straightforward. O_2 desorbs from the surface between 180 K and 210 K with two maxima in the TD spectra [39]. After the desorption has taken place the two extra features are gone but the 1.2 eV and 1.4 eV losses are still quenched [41]. The vibrational loss spectrum indicates the presence of a species with vibrational frequency around 1000 cm⁻¹ which we have assigned before [39] to the formation of a chromyl species. After flashing the surface the 1.2 eV and 1.4 eV losses reappear. Obviously, the Cr_2O_3 has a rich surface chemistry which may be interesting to study in more detail in the future.

The last example is dedicated to an oxide surface with completely different properties. Al,O, represents a material which is much less reactive as compared with the transition metal oxides discussed above. However, it is a prototype material that is used as support for dispersed metal catalysts and it is particularly interesting to study its adsorption properties before we deposit metals onto this surface [15,55-57]. This system is grown on a NiAl(110) single crystal surface as a thin (5 Å) very well ordered oxide film as judged by the SPA-LEED pattern with very sharp spots [55-57]. This system has been chosen to represent a support material. Figure 18 shows the global pattern and a close up indicating the double diffraction spots of the thin film [68]. Band structure measurements point to a hexagonally ordered first layer [55,68], and ISS shows that the surface is oxygen terminated [15]. HREELS measurements indicate the presence of γ -Al₂O₃ with three phonon losses in contrast to α -Al₂O₃ with two phonon losses [55]. The HREEL spectrum of the clean surfaces is shown in Figure 19 at the top. We have studied CO adsorption onto such an Al₂O₃ surface [68,69]. Figure 20 shows TD-spectra for different exposures. There are four features discernable in the data. The monolayer saturates at about 1 L. There are two different features in the monolayer regime with desorption maxima at 67 K and at 58 K. This corresponds to adsorption enthalpies of 0.17 eV and 0.14 eV, respectively. A typical adsorption enthalpy of the same order of magnitude for a CO-metal adsorbate, i.e. CO/Ag(111), has been determined to be 0.17 eV [70]. Before the multilayer desorption peak at 38 K appears there seems to exist a fourth feature with maximum desorption temperature around 45 K. It is not clear at present whether the latter feature corresponds to a bilayer or another intermediate state of the adsorbate. The multilayer adsorption enthalpy of 0.08 eV is close to the heat of condensation [71].

Knowing these TD spectra we can ask what is the relation between temperature and CO pressure to maintain the CO coverage as found in the UHV experiment, even at elevated temperature? Take for example the most strongly bound species in the monolayer. A simple estimate shows [8,72] that for T = 500 K the most strongly bound species needs a CO pressure of about 1 bar. To keep the other species, desorbing at 58 K, at the surface we would have to increase the CO pressure to 290 bar. We note in passing that such estimates may be interesting with respect to certain questions in catalysis.

In Figure 21 we show the EL-spectrum (Ep = 18 eV) of a CO multilayer on the γ -Al₂O₃(111)/NiAl(110) substrate. In the lowest trace we see on the left the elastic peak, and, due to the relatively low resolution, only a slight indication of the Al₂O₃ phonons (see ref. [55] for a well resolved phonon spectrum) followed by the CO vibrational stretch loss in the ground state. At 6 eV (note the change in energy scale) losses due to excited states start. The assignment of the spectrum is rather straightforward for the adsorbate because it compares favourably with the gas phase, shown for comparison [73]. A detailed assignment of the progressions is shown in the inset. In the following we shall consider in more detail the optically forbidden (but in electron scattering allowed) progression of the a³Π state. The population of the a³Π state involves primarily the excitation of a 5 σ electron into the 2 π orbital.



Fig. 24: Comparison of electron energy loss spectra $(a^{3}\Pi)$ of CO on $Al_{2}O_{3}(111)/NiAl(110)$ with spectra of CO on Ag(110) at T = 35 K as a function of exposure.

Figure 22 shows a set of EL-spectra of this excitation as a function of coverage. Clearly, as has been discussed in detail in a previous paper [69], there is a pronounced intensity of this excitation visible in the monolayer regime. The line width at 0.2 L exposure is rather large but the remaining structure allows us to fit (least square) a single Franck-Condon distribution to the peak. The TD spectra at this dose suggest the presence of a single species. Increase to 0.3 L leads to the appearence of a peak at 58 K desorption temperature in the TD spectra. This new state should have its own characteristic Franck-Condon distribution. The fit therefore shows two distributions: one due to the one determined from the 0.2 L exposure, which was then fixed as far as parameters are concerned, and a second one which was optimized to fit the total progression at 0.3 L exposure. This second progression is clearly shifted with respect to the first one by 170 meV as indicated by the line. At 1 L exposure the multilayer progression starts to contribute. It is only shifted by 25 meV with respect to the second progression. In total, the multilayer signal is shifted with respect to the most strongly bound excitation by 195 meV.

This leads to the following immediate conclusions: The ground state of the most strongly bound state is stabilized through interaction with the substrate by 0.19 eV, i.e. with respect to the multilayer by 0.11 eV. Since the excitation energy for the monolayer species is by 0.195 eV larger compared with the multilayer the excited state must be destabilized by 0.085 eV. One reason for this destabilization may be the expected stronger repulsion between molecule and substrate because population of the 2π orbital increases the average size of CO and leads to a more pronounced Pauli repulsion between CO and the top oxygen layer of the substrate which behaves electronically like a layer of rare gas atoms (Ne $\Leftrightarrow O^2$ -). Since the CO molecule is physisorbed on Al₂0₃ we have assumed in this case that the potential energy well of the a³II state is very similar to the gas phase. We can provide evidence for this by performing a Birge-Sponer analysis for the multilayer progression. This is done in Figure 23, where the spacing between neighbouring vibrational quanta is plotted as a function of the vibrational quantum number. From the fit we can





Fig. 25a Quasi three-dimensional intensity distribution of the system $Pt(0.5\text{\AA})/AL_2O_3(111)/NiAl(110)$ in the neighbourhood of the (0,0) reflex.

Fig. 25b: One-dimensional line profiles at two Pt coverages and two different substrate temperatures. A line fit is shown for the bottom profile.

10 and 30 Å which leads us to estimate the number of Pt atoms per cluster to vary between 20 and 50 atoms. In comparison with a previous STM study of $Ag/Al_2O_3/NiAl(110)$ where Ag clusters were only found on step edges (see Figure 26b [8]), the random distribution of Pt indicates the presence of a stronger interaction between Pt and the oxide film and a smaller diffusion length. Upon heat treatment of the layer the widths of shoulders decrease and the oxide reflexes lose more intensity (Figure 25b, top). This indicates a further structural modification of the substrate. Parallel to the structural changes observed with LEED we have monitored the line shapes and intensities of the optical phonons of the substrate as shown in Figure 19. The phonons of the system broaden and are strongly attenuated when we reach 1 Å Pt coverage [10].

The broadening and attenuation of the phonons (Figure 19) is connected with the formation of a metallic Pt film on the dielectric substrate. Such a behaviour has also been observed before for other systems [40]. As may be deduced from the degree of attenuation of the Al_2O_3 phonons as shown in the inset in Figure 19, a single monolayer of Pt leads to an almost complete quenching of the phonon losses indicating the formation of a 2 Å film with the response of a metal.

Although the interaction of Pt with the Al_2O_3 substrate is considerable already, there are systems where the deposited metal directly reacts with the substrate if elevated temperatures are chosen. A typical such situation is encountered in the study of alkali metals or alkali earth metals with transition metal oxides. At low temperatures we can grow an alkali monolayer which is associated with the observation of a workfunction minimum. Upon increasing the layer thickness we eventually form a metallic overlayer. For Na on NiO(111) we show in Figure 27 a series of XPand Auger spectra for increasing Na coverage [31]. Across this coverage series the workfunction varies by about 3 eV as indicated in the figure. Interestingly, the observed chemical shift for the Na1s ionization is very small in contrast to the shift observed in the NaKLL Auger spectra. A detailed analysis shows that the former is due to an accidental compensation of initial and final



Fig. 27: Na1s XP-spectra (left panel) and Auger NaKLL spectra (right panel) of the system Na/NiO(111) at different Na coverages as given by the value of the workfunction change ($\Delta \Phi$). The workfunction changes linearly to -2.2eV, passes through a minimum and reaches a satuartion value (close to the one of bulk metal) at -2eV.

4.2 ADSORPTION ON METAL MODIFIED OXIDE SURFACES

The adsorption properties of the thin Pt film are in certain aspects very similar to a Pt(111) surfaces as is revealed via HREELS and TDS. Figure 28a shows the HREEL-spectra of the Pt/Al2O3 system dosed to saturation with CO for various Pt coverages. The observed stretching frequency indicates CO molecules bound on-top on the surface [75]. At higher Pt coverages the band shifts and a second feature appears in the range of bridging CO sites. Due to the relatively low resolution we cannot decide at present how many different chemical species contribute to the broad feature present at the lowest Pt coverage. The existence of several species is very likely and also revealed through TDS measurements. A series is shown in Figure 29. There is a broad structure between 350 K and 550 K which shifts its maximum towards 450 K as the Pt coverage increases, and at high Pt coverage we find features known from TD spectra taken on Pt(111) [76] and stepped Pt(335) [77] surfaces shown for comparison. However, there is a pronounced TDS feature slightly above a desorption temperature of 150 K which is not compatible with CO desorbing from metallic Pt. On the other hand we have found for CO desorbing from transition metal oxide surfaces maximum desorption temperatures between 100 K and 200 K [12,14,39]. It is therefore not unlikely that these CO species desorb from sites where a Pt atom has been incorporated into the first layer of the Al₂O₃. By comparison with the clean NiAl(110) substrate and the completely Al_2O_3 covered NiAl(110) which are included in Figure 29 it is clear that the desorption maximum around 150 K cannot be connected with the metallic NiAl(110) substrate. An investigation of the chemical shift of the Pt/Al₂O₃ system measured via XPS reveals that the Pt is oxidized when it diffuses into the substrate [78]. One may speculate that the defect structure of the γ -Al₂O₃ substrate helps to facilitate the diffusion of the relatively smaller Pt ions into the quasihexagonal top oxygen layer of the Al₂O₃. Interestingly, the results on the model system may be compared with infrared spectra obtained for an Al₂O₃ powder sample impregnated with varying amounts of Pt. As is shown in Figure 28b two groups of bands grow as the Pt coverage (mass: ma)





Fig. 29: Thermal desorption spectra of CO desorbing from Pt($x\dot{A}$)/Al₂O₃(111) /NiAl(110). For comparison the TD spectra taken from the literature [76,77] are included. The two spectra at the bottom refer to the clean NiAl(110) substrate and the clean Al₂O₃(111) /NiAl(110) system.

Fig. 30: C1s XPS spectra of the system $Pt(xÅ)/Al_2O_3(111)/NiAl(110)$ exposed to CO to saturation at various Pt coverages and substrate temperatures.

5. Dynamics and Desorption of Molecules from Oxide Surfaces

As alluded to in the introduction the study of the dynamics in adsorbates has gained increasing interest in recent years. Several methods have been used to investigate the dynamics of interaction between gas phase molecules and solid surfaces. To gain information directly about microscopic processes in the adsorbate layer scattering methods have been employed [79]. Direct spectroscopic evidences on such processes are limited to infrared investigations up till now [80,81]. It is therefore interesting to establish other complementary spectroscopic methods for such studies. Electron spin resonance in principle holds the potential to provide information on dynamics by studying the temperature dependent line shapes [24-26]. We review our efforts in this field in section 5.1. Section 5.2 summerizes studies of photon stimulated desorption from oxide surfaces [17-23]. The desorbing particles are state specifically detected in this case and a detailed understanding of the desorption dynamics can be achieved.

5.1 ELECTRON SPIN RESONANCE SPECTROSCOPY OF ADSORBED MOLECULES

Typical time scales for molecular motion are of the order of 10⁻⁷ to 10⁻¹¹ s. Electron spin resonance spectroscopy (ESR) is the spectroscopic technique operating in this time domain [82]. The first ESR experiment on a single crystal surface has been published by Baberschke and his group [83,84]. However, they found that submonolayers of molecules on metal surfaces do not give rise to a detectable ESR signal because the coupling of the unpaired spin to the conduction electrons





Fig. 33: UHV-ESR spectra of the system $NO_2/Al_2O_3(111)/NiAl(110)$ at various NO_2 coverages.

Fig. 34: UHV-ESR spectra of the system $NO_2/Al_2O_3(111)/NiAl(110)$ at the given coverage for various surface temperatures.

caused by the reaction of the paramagnetic NO2 monomers to diamagnetic N2O4 dimers. If the annealing procedure is repeated for moderate coverages for longer time intervals the decrease of line widths stops at a given value and only the line intensities decrease. At very low coverages this decrease in line width is not observed because the line width has reached is lowest limits already directly after adsorption. In this limiting case the dipolar interaction contribution is small compared to other contributions, e.g. those given by the interaction of the individual molecule with the substrate. The observed spectra have been simulated on the basis of two main considerations: One consideration is connected with the distribution of orientations in the sample, i.e. it could be either anisotropic or isotropic. The other consideration is concerned with the dynamics of motion of the molecules. To see this we resort to Figure 34. ESR spectra of a submonolayer coverage are taken at different surface temperatures. The fits shown in the figure represent distributions of threedimensionally randomly oriented and static molecules. It is quite obvious that the fits are of better quality for the higher temperatures. This should not be the case if the deviations at lower temperatures corresponded to molecular motions, not taken into account by the fits. If on the other hand a molecular motion became unfrozen in the time window of the experiment the deviations from the static distribution should become larger with increasing temperature, eventually leading to motional narrowing of the lines. The simulation at highest temperature represents a static and isotropic distribution. The question is: What causes the deviations at lower temperatures? A possible answer is: A fraction of the molecules is oriented when they adsorb on the surface. This would explain the deviations. Upon raising the temperatures the contribution from the oriented molecules are removed from the distribution. This desorientation is an irreversible process. By cooling down to 35 K after annealing the adsorbate, the threedimensional randomly oriented and static distribution fits the spectrum quite well as is obvious from the lowest trace in Figure 34. Summarizing the results show the consequences of molecular motion: Diffusion is clearly visible through the dimerization of NO2 monomers. However, no rotational motion of the molecules can be detected below 100 K in the time window of the experiment. Thus, the upper limit of the time

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Fig. 37: Velocity flux distributions for NiO(100) (right panel) and NiO(111) (left panel)

the surface. With the laser sheet technique this distribution may in principle be recorded in one shot. In addition the distribution contains the angular information which may be deduced. Such spatial distributions may be recorded if the sensitivity for the particular molecule is large enough to allow excitation in a laser sheet. This is not the case for carbonmonoxide. In this case the velocity flux distributions have to be determined via line scan excitation and delay time variation [18,19]. Figure 37 shows two sets of velocity flux distributions accumulated for desorption from NiO(100)[18] and NiO(111) [21] surfaces. The left panel collects data for a given rotational quantum and varying vibrational excitation for both surfaces, while the right hand panel contains velocity flux distributions for the first vibrational excited state and varying rotational quanta. Obviously, there are similarities and discrepancies which we briefly summerize:

- i) The molecules on both surfaces are highly vibrationally excited.
- ii) Translational and vibrational degrees of freedom are decoupled in both cases.
- iii) Rotational and translational degrees of freedom are strongly coupled for NO/NiO(100), but weakly if at all for NO/NiO(111).
- iv) There are two channels in the velocity flux distributions which we call slow and fast channels in both cases. The relative population of the two channels are very different in both cases.
- v) The angular distributions indicate a strong peaking for the fast channel along the surface normal and a wide angular distribution for the slow channel.

In order to analyse our data we have performed model calculations assuming ground and excited state potentials sketched in Figure 38a [94]. Both potentials exhibit minima. In addition to the dependence on the distance the potentials exhibit a pronounced angular dependence as sketched in Figure 38b. The strong polar angle dependence leads to the tilting of the NO axis and the considerably weaker azimuthal dependence allows the molecule to rotate rather easily about the Ni-N bond. Some of the parameters for the ground state potential we know from experimental thermal





Fig. 39: Photoinduced desorption cross-section for various photon energies. Superimposed is the ELS spectrum of pure NiO(100). Beneath we show the photoinduced charge carrier concentraction.

Fig. 40: Boltzmann plota for the vibrational excitation in the lowest electronic states of NO.

very similar in both cases and compatible with a Franck-Condon simulation on the basis of a harmonic oszillator NO⁻ potentials as shown elsewhere [18]. The proposal for an ion mediated mechanism is supported by measurements with wavelength dependent excitation. Figure 39 shows the photodesorption cross sections as a function of wavelength. The unfilled dots are from the work of Yoshinubo et al. [100,101]. Superimposed are two experimental results: On one hand the ELspectrum [58] and on the other hand the photoinduced charge carrier concentration in bulk NiO as determined by Powell and Spicer [102]. It is quite obvious that at the edge of the charge transfer gap of NiO close to 4 eV the cross section starts to increase. However, the increase does not correlate with the excitation probability but rather with the observed linear increase in charge carrier concentration. In the simplest picture the electron current at the adsorbate is proportional to the charge carrier concentration, and thus to the production of NO⁻. Since, however, the photodesorption cross section should increase proportional to the production of NO⁻, we find the present results compatible to the proposed mechanism. The chosen potentials in connection with the computer simulations allow a qualitative interpretation of all basic observations: Very briefly, for example, the bimodality in the velocity flux distributions has to do with the distance relative to the surface where relaxation occurs, and the direction of the k-vector directly after the excitation. The relative population of the fast and slow channels is connected with the life time of the excited state. If we assume the same excited state potentials for the (100) and (111) faces, the observation of changes in the relative populations indicate different life times of the excited states in the two cases. Finally, the coupling of translational and rotational motion is connected with the angular dependence of the potentials [94,103] involved. The faster a molecule moves in the desorption channel the more has it felt the action of the angle dependent potential. Thus, a molecule with large linear momentum will also exhibit higher angular momentum, i.e. population of high rotational quanta. The change in angular distribution in the fast versus the slow channels may be rationalized rather simply: The molecules contributing to the slow channel exhibit a smaller k, component to the total linear momentum. This leads to a larger angle relative to the surface normal The computer spectroscopy, may be applied on submonolayer coverages. This is not possible for metal surfaces. Also desorption dynamics can be studied very efficiently because energy dissipation is much slower on oxide surfaces as compared with metal surfaces. This is true, in particular, for the case of photon stimulated processes.

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