State and Spatially Resolved Studies of UV-Laser Induced Desorption of Molecules from Oxide Surfaces

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ABSTRACT

Quantum state resolved velocity distributions of NO desorbing from single crystal metal and oxide surfaces after a non-thermal excitation process with UV-photons have been studied by several groups in the past. In order to achieve a "complete" experiment it is necessary to determine in addition the spatial distribution of the desorbing particles. We report on results of the determination of angular distributions of desorbing NO via a new experimental setup. Two systems have been studied in detail, i.e. NO on NiO(100) and NO on NiO(111). A model proposed before is employed to explain the experimental results, i.e. the observation of bimodal velocity flux distributions. The bimodal signal is consistent with the existence of two desorption channels which are predicted to exhibit different angular distributions. This prediction is verified with the new experimental setup. The comparison of the two crystallographic planes of NiO allows us to address the problem of the influence of the magnetic properties of the substrate onto the population of different spin states of desorbing NO molecules. Finally we shall report on results gained with a CO detection system based on a (1+1') REMPI process employing VUV photons. Here the system CO/Cr₂O₃(111) is studied. With this setup the resolution of rotational states in the desorbing particles is easy to achieve in contrast to the widely used (2+1) REMPI process of the same transition.

2. INTRODUCTION

While state resolved studies in photochemistry of gas phase systems are common standard by now¹, such studies on well characterized surfaces are still in an early stage^{2,3}. One of the simplest possible photochemical processes at the surface involving bond breaking is the disrupture of the molecule surface bond followed by desorption of the molecule⁴. Due to the rather large photodesorption cross sections for molecules desorbing from oxide surfaces^{5,6}, these system are particularly well suited to undertake state



Fig.1 Schematic representation of antiferromagnetic ordering in NiO. The (111) and (100) planes are indicated.

resolved studies. However, in order to relate the observed desorption dynamics to the adsorption system the latter has to be well characterized. In general this is not the case for adsorption systems on oxide surfaces. We have therefore spent, in recent years, some time to characterize molecular adsorption systems on the oxide films, which we have chosen as substrates instead of bulk oxide single crystals^{7,8}. The thin films have the advantage that charging in connection with electron spectroscopic investigations does not occur, and, perhaps even more importantly, the samples can be cooled easily to low temperatures. In addition, thin film oxides may be prepared with different crystallographic orientations so that the face specificity of adsorption may be studied. This is true in particular in connection with polar (111) surfaces of rock salt oxides which are thermodynamically unstable but show considerable chemical reactivity and can only be prepared as thin, well ordered films⁹. We have studied adsorption and photodesorption of NO from NiO(111) in comparison to the

same processes on NiO(100). From earlier studies we have had indications from the observed high vibrational excitations of the desorbing molecules that the desorption process is mediated via a negative ion resonance¹⁰, i.e. an NO⁻ species on NiO. Naturally, the formation of the negative ion is accompanied by electron transfer from the substrate to the molecule and the desorption of neutral molecules then implies that the electron is transferred back from the molecule to the substrate. Therefore, if the substrate is magnetic, spin polarization of the exchanged electron plays a prominent role in the process under discussion. NiO represents an antiferromagnetic substrate where the direction of magnetic order is the (111) direction as shown in Fig. 1. Consequently, we expect a spin effect for the NiO(111) surface where all spins in the surface are alligned (assuming "bulk terminated magnetism" for the surface) while we do not expect a spin effect for the NiO(100) surface where the spin directions in the surface alternate. The NO molecule carries an unpaired electron in the 2π orbital which leads to two energetically separated electronic doublet states. When the electron from the intermediately formed anion is transfered back to the substrate we may expect a nonthermal distribution in the occupation of the two spin-orbit components of the ${}^{2}\Pi_{1/2,3/2}$ states depending upon the crystallographic orientation of the substrate. In an earlier publication we reported on a spin effect¹¹ but at the time we did not have control of the substrate orientation. In the present contribution we show that there are pronounced differences between the $NiO(100)^6$ and $NiO(111)^{12}$ surface with respect to spin effects. We record our NO data with a novel experimental setup which allows the determination of angular distributions of desorbing ions. The present setup cannot only be used to study NO desorption. A VUV probe laser has been implemented to also study CO desorption with full quantum state resolution¹³. This setup has been applied to the study of CO/Cr₂O₃(111) in order to investigate the connection between adsorbate geometry and velocity flux distribution¹³.

3. EXPERIMENTAL SETUP

The experiments were performed under UHV conditions as outlined elsewhere¹²⁻¹⁴. Fig.2 shows the schematic experimental setup for fully quantum state and spatially resolved desorption studies¹²⁻¹⁴. The surface is illuminated by a laser of 15 nsec pulse width and the power is of the order of a few mJ cm⁻². A well defined time after the desorption laser has been switched off a probe laser is fired parallel to the surface. The probe laser forms a laser sheet which is used to induce a (1+1) REMPI process via the $A^2\Sigma^+$ state starting from a well defined rotational-vibrational state. The ions are repelled by a repeller plate into a flight tube which at the end carries a multichannel plate and a phosphor screen. The ions produced in the laser sheet are imaged onto the phosphoric screen and the image is stored via a CCD camera onto a video recorder. In Fig.3 a distribution of NO desorbing from a NiO(111) surface in the ground vibrational state with rotational quantum number J=5.5 is depicted. A cut through this distribution parallel to the surface normal represents the velocity flux distribution from 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^{5,6}. For CO we have used a (1+1') REMPI process involving excitation from the $X^{1}\Sigma^{+}$ state to the $B^{1}\Sigma^{+}$ state and subsequent ionization, as outlined by Zacharias and collaborators¹⁵. In contrast to the excitation where the light from the excimer pumped dye laser can be



Fig.2 Experimental setup Fig.3 Spatially resolved distribution of desorbing NO





Fig.4a Ground and excited state potentials involved in Fig.4b Angular dependence of the ground state the excitation as a function of the distance potential molecule-surface and the NO bond distance

used directly, in the case of CO the radiation must be frequency tripled in a rare gas cell before it can be used for the (1+1')REMPI process. The use of the (1+1')REMPI process is advantegous as it gives access to rotational resolution for the desorbing CO molecules¹³ which is not possible with the often used (2+1)REMPI process¹⁶.

4. CALCULATIONAL DETAILS

In order to analyse our data we have performed model calculations assuming ground and excited state potentials sketched in Fig.4a¹⁷. Both potentials exhibit minima. In addition to the dependence on the distance the potentials exhibit a pronounced angular dependence as sketched in Fig.4b. The strong polar



Fig.5Geometry of the adsorbed NO molecule on NiO(100)

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 desorption, vibrational and NEXAFS data⁷.

The molecule is bound by 0.5 eV atop a Ni ion¹⁸ N-end down, and the molecular axis is tilted by 45° with respect to the surface normal. A schematic geometry is shown in Fig.5. The excited state potential has been deduced from ab-initio calculations¹⁹ where the NO⁻ interacts with a NiO₅-cluster. While the excitation process as well as the deexcitation process are described quantum mechanically the propagation on the excited state potential as well as

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on the ground state potential is determined via quasi classical trajectory calculations.

We have assumed that the process proceeds according to the socalled MGR model²⁰ and related models²¹. In this model the system is excited within a Franck-Condon transition to the excited state. There it feels in our case a force towards the oxide surface due to the electrostatic attraction between NO⁻ and Ni²⁺. After a certain time of propagation on the excited state potential the system relaxes back onto the ground state potential. In case the molecule has accumulated enough kinetic energy in the excited state it will escape the ground state potential minimum and desorb. For the dynamics of the adsorbed molecule it is important to realize that the hindered rotational process the molecule performs is coupled to a translational motion of the center of gravity. In the simplest limit the wavefunctions $\Psi(\underline{r},\underline{k})$ describing such a motion would be

 $\Psi(\underline{r,k}) = Y_{\underline{l,m}}(\Theta,\phi) \exp(i\underline{kr})$ where the spherical harmonics describe the rotational motion and the plane wave the translational motion²². Thus the motion may be classified according to motion towards the surface and away from the surface and we may analyse the escaping molecules accordingly⁶.

5. RESULTS AND DISCUSSION

Fig.6 shows two sets of velocity flux distributions accumulated for desorption from NiO(100)⁶ and NiO(111) 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 discrepencies which we briefly summarize:

- The molecules on both surfaces are highly vibrationally excited. i)
- Translational and vibrational degrees of freedom are decoupled in both cases. ii)
- Rotational and translational degrees of freedom are strongly coupled for NO/NiO(100) but weakly iii) if at all for NO/NiO(111).



Fig. 6 Velocity flux distributions for NiO(100) (right panel) and NiO(111) left panel

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iv) There are two channels in the velocity flux distributions which we call slow and fast channels in both cases. The relative populations 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.

A very significant observation is the vibrational excitation in both cases. It indicates that the anion mediated mechanism is active in both cases. Because the anion has a longer nitrogen-oxygen equilibrium distance²³ the relaxation back to the ground state potential with a shorter bond length induces the strong vibrational excitation. The population of the various vibrational states is very similar in both cases and compatible with a Franck-Condon simulation on the basis of a harmonic oszillator NO⁻ potential as shown elsewhere⁶. The proposal for an ion mediated mechanism is supported by measurements with wavelength dependent excitation. Fig.7 shows the photodesorption cross sections as a function of wavelength. The unfilled dots are from the work of Yoshinubo et al.^{24,25} Superimposed are two experimental results: On one hand the ELS spectrum¹⁸ and on the other hand the photoinduced charge carrier concentration in bulk NiO as determined by Powell and Spicer²⁶. It is quite obvious that at the edge of the charge transfer gap of NiO close to 4eV 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

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Fig.7 Photoinduced desorption cross-section for various photon energies. Superimposed is the ELS spectrum of pure NiO(100). Beneath we show the photoinduced charge carrier concentration in NiO.

results compatible to the proposed mechanism. The chosen potentials in connection with the computer simulations allow a qualitative interpretation of all basic Very observations: 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 translational of and rotational motion is connected with the angular dependence of the potentials^{17,27} involved. The faster a molecule moves in the desorption channel the more has it felt the

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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_z component to the total linear momentum. This leads to a larger angle relative to the surface normal. The computer simulations qualitatively indicate that this is sufficient to explain the observations. There is, yet, one more detail we would like to comment on. As already alluded to in the introduction, NiO is an antiferromagnetic substrate, and we may expect a spin effect especially for the (111) plane. In fact, for the NiO(100) surface, Mull et al.⁶ have already published that there is no detectable spin effect, i.e. there is no nonthermal relative Fig.8 Boltzmann plots for the vibrational excitation in population of the ${}^{2}\Pi_{3/2}$ and ${}^{2}\Pi_{1/2}$ states. In the case of the NiO(111) surface, however, a small





spin effect can be detected¹². Summing over all rotational levels for a given vibrational level separately for the two electronic states we can determine vibrational temperatures as shown in Fig.8.

We obtain different temperatures for the two electronic states of NO, i.e. T_{vib} =2050K for the $2\Pi_{3/2}$ state, and T_{vib} =1600K for the ${}^{2}\Pi_{1/2}$ state. This should be compared with a single vibrational temperature T=1850 K for the NiO(100) surface. Interestingly the effect on NiO(111) is only detectable for a desorption laser energy of 6.4eV. While we do not yet understand all details of the process, the observation may be qualitatively interpreted: Before desorption the electron on the NO anion has to be transfered back. Whether a neutral NO molecule in the ${}^{2}\Pi_{3/2}$ or ${}^{2}\Pi_{1/2}$ state is formed depends on the magnetic moment in the substrate. We would envision that the two channels involve different life times of the anion. This in turn should lead to different vibrational temperatures as observed experimentally. Thus it is felt that the model we currently have for understanding the desorption dynamics of NO from different planes of NiO allows us to qualitatively rationalize most of the experimental findings for basically all degrees of freedom of the desorbing particles.

It is important to extend the desorption studies from NO as a probe molecule to other systems such as CO. We have already realized a set up to detect desorbing CO molecules via a (1+1') REMPI process involving VUV photons. The setup used is described in detail in ref.(13). We have investigated the system $CO/Cr_2O_3(111)^{12}$, where we know from our electron spectroscopic investigations that the molecule is oriented more or less parallel to the surface plane^{28,29}. In this case there is no pronounced translational motion of the center of gravity of the molecule. Consequently, we do not expect a pronounced bimodality of the velocity flux distributions. Fig.9 shows the rotationally resolved spectrum of desorbing CO just to proove the quantum resolution in this case.



Rotation-vibration spectrum of CO desorbing from Cr₂O₃(111). Fig.9

There is a clear differentiation between P and R branch for v=0. In addition we see the v=1 branches. From the population it is obvious that the CO molecules are strongly vibrationally excited. The velocity flux distribution (Fig.10) are bimodal in v=0 but not in v=1, indicating that in the CO case the bimodality in v=0 is due to a thermal channel.



Fig.10 Velocity flux distributions for the system $CO/Cr_2O_3(111)$. Two sets of data for varying rotational quantum numbers in two vibrational states are shown.

The desorption temperature for this system is $T_{max}=160K$ which is only 60K above the surface temperature. It is not inconceivable that the laser _ induced heating produces a temperature jump of 30K so that part of the molecules desorb thermally. In this case the desorption mechanism is not yet clear. Wave length dependent measurements have to be undertaken. On the other hand CO⁻ is not as easily formed compared with NO⁻³⁰. However, the present investigations have been done with a desorption laser energy of 6.4eV. With this energy we are in the range of the $a^3\Pi$ state of excited CO^{31} . Even though the excitation of this state is optically forbidden in the gas phase the antiferromagnetism of Cr₂O₃, connected with the open shells of the Cr ions, may render this process allowed. The $a^3\Pi$ state on the other hand has a carbon-oxygen bond distance²³ about 7% longer than in the ground state. The involvement of such a state would then easily explain the observed strong vibrational excitation. The ELS spectra³² of CO on Cr₂O₃ indicate excitations in the proper energy regime so that this mechanism must be considered a real possibility. If it were the correct mechanism it could involve the excitation of the molecule directly via electron-hole pair creation although this process

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could be substrate mediated as well. Further studies in this direction are under way.

6. SUMMARY AND CONCLUSIONS

For the system NO/NiO we have performed fully quantum state and spatially resolved desorption studies. From the accumulated evidence the mechanism is negative ion mediated, explaining qualitatively all observations covering all degrees of freedom of the desorbing molecules including a small spin effect which is detected for NO/NiO(111). This effect is explained via the antiferromagnetism of the substrate and the particular orientation of the (111) plane being perpendicular to the principal axis of magnetic orientation. We show that CO/Cr₂O₃ desorption studies may be done fully quantum state resolved. It is discussed whether the intermediate is a molecule similar to CO in the $a^3\Pi$ state. This would explain the -

high vibrational excitation but it would imply that the excitation could be localized on the adsorbed molecule.

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