Dynamical studies of UV-laser-induced NO-desorption from the polar NiO(111) versus the nonpolar NiO(100) surfaces

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We have studied the UV-laser-induced desorption of NO adsorbed on an epitaxial film of NiO(111) grown on Ni(111). The desorbing molecules were detected state selectively via a resonance enhanced ionization technique [REMPI(1+1)] using the $^2S_o'(v'=0,1,2)\rightarrow X^2Π(v''=0,1,2)$ transition as intermediate state. Our results are compared with our experiments on NO desorption from NiO(100). The similarities and differences of the results due to the different surface structure of the polar NiO(111) and the non polar NiO(100) are discussed. For both surfaces we observe bimodal velocity flux distributions independent of the rovibrational state. Due to a rotational temperature of about 400 K and a vibrational temperature of 1800 K thermal processes can be ruled out. The wavelength dependence of the desorption cross section strongly correlates with the electronic structure of the NiO indicating a surface mediated excitation process. The spin orientation in the NO molecules influences the life time of the excited state depending on the magnetic property of the NiO surface.

I. INTRODUCTION

Although there is a permanently growing number of applications for laser-induced processes at surfaces in industry and research, the principle mechanisms of these processes are still poorly understood. The best approach in order to get an insight into the elementary steps of these processes are studies using well characterized adsorbate systems on single crystal surfaces. The main mechanisms can already be obtained from studies of a simple process like the desorption of diatomic molecules. The most detailed information on the dynamics of laser induced processes so far has been obtained by experiments of the pump-probe type. Conclusions about the very short lived intermediate state can be drawn by characterizing the initial state and measuring the final state as good as possible. Probing the translational and internal state distributions of the desorbing molecules is a major part of these experiments. However, most of the numerous papers summarized in several reviews about such desorption measurements remain phenomenological as there is little knowledge about the characteristics of the adsorbate system before and after the laser experiment itself. In our paper we want to demonstrate which kind of impact the particular surface properties can have on the dynamics of the laser induced process and thus on the final state of the system.

As model systems we have chosen NO adsorbed on epitaxially grown films of NiO(100)/Ni(100) and NiO(111)/Ni(111). As is known from a variety of different surface spectroscopical methods the adsorption behavior of NO on these two surfaces is very similar. NO is weakly chemisorbed as a single species with a binding energy of 0.5 eV at nickel atoms. On both substrates the molecular axis is tilted by approximately $45^\circ \pm 15^\circ$. As will be seen later the translational movement of the center of gravity related to the bending of the molecule which is particularly pronounced for this geometry has an important impact on the dynamics of the desorption process itself. Due to the very similar binding properties of NO these systems are ideal in order to study the influence of the polarity and particular surface structure of the substrate and connected magnetic properties on the laser induced desorption behavior. We use epitaxially grown films as they can be characterized by the common electron spectroscopic methods without charging effects observed for bulk insulators. In addition, the (111) orientation can only be prepared as thin, well ordered film as it is thermodynamically unstable. Both epitaxial films are well studied. NiO is an antiferromagnetic material under the experimental conditions (Néel temperature 526 K). It consists of two different spin lattices with antiparallel spin orientations of the Ni$^{2+}$ ions as is shown in Fig. 1. Along the (100) surface the lattice spin orientation alternates. As a consequence, there is no overall spin orientation. However, in the case of the (111) surface the spins show a preferential orientation. In the following we shall present a survey of our experimental results on laser induced desorption of NO from the nonpolar NiO(100) and the polar NiO(111) together with a discussion about the main similarities and differences resulting from the different surface structure.

II. EXPERIMENTAL SETUP

The experiments were carried out in an ultra high vacuum apparatus consisting of a preparation and main chamber for the laser experiments. The preparation chamber was equipped with facilities for low energy electron diffrac-
The photons needed for this REMPI process can be generated in a relatively comfortable way which makes NO a molecule widely used in state selective laser induced desorption experiments. As NO has an unpaired electron two different spectra due to the two different spin states are obtained. The necessary tunable UV light in the 220–227 nm range was generated via frequency doubling in a barium borate (BBO1) crystal. The fundamental radiation at 440–454 nm was obtained from an excimer laser (XeCl, Lambda Physik LPX 205 i CC) pumped dye laser (Lambda Physik LPD 3002) operated with Coumarin 2 (10–15 ns pulse length, repetition rate 4 Hz). The ions were recorded perpendicular to the surface normal and the detecting laser beam via a system consisting of a repeller, a flight tube, multichannel plates (Galileo 3040, 40 mm diameter) and a phosphor screen. With the aid of the drift tube signals from scattered light were avoided. The MCP's were gated by switching them on 2 μs after firing the detection laser and running them for 40 μs. The particular detector geometry including the phosphor screen is needed for a two-dimensional imaging of the ions in order to obtain the angular distribution of the molecules as is described elsewhere. In the experiments described here we recorded the integral amount of ions reaching the detector.

In our experimental setup 20 L of NO are sufficient to reach the saturation coverage. In order to keep a constant surface coverage prior to each of the pump excimer laser pulses the sample was redosed via background pressure of 5×10⁻⁸ Torr in most of the experiments. The measured REMPI signal was corrected for the background signal. This was realized by firing the detection laser with twice the frequency of the desorption laser and subtracting the gas phase signal from the desorption signal with the aid of a boxcar integrator (SRS 245).

There is a small amount of laser-induced photoreaction of NO on NiO(111) in contrast to NiO(100). The products remaining at the surface slowly change the properties of the system, if one does not clean the crystal before each experiment by heating it to 700 K. The amount of reaction products is small enough to keep the experimental conditions constant within a given experiment.

III. RESULTS

A. Velocity flux distributions

In order to obtain the translational energy distributions of the desorbing species the probe laser was fixed to the maximum of a specific rovibronic transition of the NO. The delay between pump and probe laser was varied between 0 and 800 μs. From the signal recorded as a function of the delay time we obtain the time of flight (TOF) spectrum for the molecules in the chosen rovibrational state. As the TOF spectrum is depending on the actual geometry of the experiment, i.e., on the distance of the detection to the probe laser we transform the spectrum into a velocity flux distribution.

Figure 2 shows such velocity flux distributions for several rotational and vibrational states of the 3Σ⁺ state of NO desorbing from NiO(100) and NiO(111) after exciting them with an energy of 6.4 eV. Most striking at the first sight is the bimodal structure of the velocity flux distributions of the desorbing molecules for both substrates. Particularly remark-
B. Rotational distributions

In the case of NiO(111) the intensity change as a function of rotational excitation can be measured for a fixed velocity for which one channel is dominant. The spectra of the desorbing molecules can be recorded and analyzed assuming a Boltzmann distribution for the rotation. For this purpose the delay between pump and probe laser was fixed and the spectra were taken by varying the detection wavelength with 0.001 nm resolution. The spectra of the desorbing NO have been recorded for different excitation energies. Table I summarizes our results concerning the rotational temperatures for a velocity of 1000 m/s. For an excitation energy of 5.0 and 6.4 eV, the rotational temperature is $435 \pm 25$ K independent of the vibronic state. Changing to 3.5 eV a significant decrease of the rotational temperature is observed particularly for vibrationally excited states ($T = 750$ K).

For NiO(100) the analysis is not so easy. As the translational motion is coupled to the rotational excitation a simple recording of the spectrum at a fixed velocity would lead to wrong rotational distributions. For a Boltzmann analysis the whole integral over the intensity distribution of one particular channel has to be taken. The velocity flux distributions could not be fitted with simple Boltzmann velocity distributions or molecular beam distributions. We used a Student-$t$-distribution in order to describe the portion of slow and fast channel. From such fits we obtained rotational temperatures of $405 \pm 25$ K for the slow channel in $v^\pi = 0$. For the fast channel the rotational temperature is $260 \pm 25$ K for low rotational quantum numbers. However, for very high rotational quantum numbers ($E_{ro} > 400$ cm$^{-1}$, $J^\pi > 20.5$) the rotational temperature changes to $470 \pm 25$ K. The discussed behavior of the velocity flux distributions makes it clear that a resolution of single rotational states is necessary in order to allow any statements concerning internal state distributions.

C. Vibrational temperature, electronic population, and spin effect

Vibrational temperatures were obtained assuming Boltzmann behavior and by summing over the intensities of all rotational states for a given vibrational level. For both surfaces we find a high vibrational excitation which is in the same order of magnitude for both types of surfaces. As will be discussed later, the vibrational excitation is compatible with a change of bond length in the excited state in connection with the lifetime of the excited state. In the case of NO/NiO(100) we obtain a temperature of $1890$ K (Refs. 30–33) independent of the electronic state.

However, for NO on NiO(111) there is a significant difference of the vibrational temperature looking at the two different spin states of NO as can be seen from the corresponding Boltzmann plots in Fig. 3. We obtain a temperature of $2050$ K for $^2\Sigma^+$ and $1600$ K for $^2\Pi$. This spin effect is only noticeable for a desorption laser energy of $6.4$ eV. In an earlier report we did not control the substrate orientation and did not search for vibrational excitation.
D. Desorption cross sections

Assuming a first order kinetics for the desorption we obtain the following equation

\[
\ln\left(\frac{N}{N_0}\right) = -\sigma \cdot n_{ph}
\]

with \( N \) being the number of molecules remaining at the surface, \( N_0 \) the initial number of molecules, \( \sigma \) the desorption cross section, and \( n_{ph} \) the number of photons impinging on the surface. The desorption cross section was measured by two different ways. The surface is covered both times with a saturation coverage. We then follow the depletion of the surface at an ambient pressure of less than \( 2 \times 10^{-10} \) Torr as a function of laser pulses. We monitor the amount of molecules left on the surface by XPS or the desorbing molecules by REMPI. Both measurements lead to the same result which means that with our REMPI measurements we detect the major species of NO adsorbed on the surface and not defect desorption.30-32

At 6.4 eV we obtain the same cross section of \((6\pm1) \times 10^{-17} \) cm\(^2\) for both systems, NO/NiO(100) and NiO(111). The cross sections are 1–4 orders bigger than those observed on metals3-24 and typical for oxide surfaces.30-32,56,57

For NiO(111) the desorption cross section was also evaluated at different wavelengths of the desorption laser. When changing to 5.0 eV the cross section changes to \((3\pm1) \times 10^{-17} \) cm\(^2\) and at 3.5 eV to \((7\pm1) \times 10^{-18} \) cm\(^2\). The wavelength dependence of the cross sections gives a clue about the excitation mechanism as will be seen in the next paragraph.

IV. DISCUSSION

A. Excitation mechanism

As is clear from the internal and translational state distributions a thermal mechanism can be ruled out for the desorption process. We now have to distinguish between direct and indirect excitation mechanisms. In direct mechanisms an electron hole pair is formed at the adsorbate itself or the atom of the surface involved in the bonding. In indirect mechanisms electron hole pairs are formed in the bulk and are coupled to the adsorbate system.58 The wavelength dependence of the desorption cross section indicates which one of the processes is dominant as it should be related to the absorption spectrum of the adsorbate or substrate.59 However, the absorption spectrum of NO on NiO is broad so that it is not distinguishable from the background consisting of the surface spectrum. However, as NO is only weakly chemisorbed we can draw some conclusions from gas phase data. The first optically allowed transition of NO is found around 5.5 eV in the gas phase. However, we already observe desorption at 3.5 eV. Yoshinubo et al.60 also found desorption of NO from NiO(111) between 1.5 and 3.5 eV by using a mercury lamp. A direct excitation of the NO is therefore less likely. This is supported by the fact that the absorption cross section in the gas phase at 5.5 eV is 2 orders of magnitude smaller than our observed desorption cross section.61

Figure 4 shows a plot of the electron energy loss spectrum (EELS) of the substrate together with our desorption cross sections and the ones from Yoshinubo et al.60 There is a strong increase of the cross sections above 4 eV which is directly correlated with an intensity increase of the substrate spectrum and the amount of photoinduced charge carrier creation in NiO as found by Powell and Spicer.62 The latter is due to charge transfer excitations in the substrate. From gas phase measurements it is known that for the capture of an electron 0.03 eV are needed to form NO\(^-\) (Ref. 63) with a cross section 2 orders of magnitude bigger than our desorption cross section observed.64 The energy needed to form other intermediates like excited NO or NO\(^+\) is much higher (>5.5 eV). As we only observe desorption of neutral NO the electron is transferred back to the surface before desorption.

B. Desorption model

The basis of the interpretation of our experimental data is given by the Menzel–Gomer–Redhead (MGR) model for
The main steps of the desorption process are described by this model as follows. The adsorbate is transferred from its electronic ground state into an excited state via a Franck–Condon type transition. The excited state can be either ionic or electronically excited. The MGR model assumes an excited state which is either repulsive in the coordinate of the molecular distance to the surface or which has a minimum at larger distances than the ground state. As a consequence, the repulsive part of the potential energy surface is reached. The movement down the repulsive part leads to a gain of kinetic energy of the molecule. As is evident from spectroscopic measurements [for example, from line width measurements for CO on Al₂O₃(111) by Jaeger et al.¹] the lifetime of the excited state is rather short, in the order of several femtoseconds. The typical travelling distance of the molecule for such a lifetime is 1 Å. The lifetime is strongly depending on the nature of the molecule-surface bonding and the electronic properties of the surface. The quenching of the excited state is done via electron-hole pair formation in the substrate and/or phonon coupling. If the accumulated kinetic energy is larger than the well depth in the ground state the molecule can desorb after the system relaxed into the ground state. In metals the quenching is much faster than in insulators. The reason for this is that in insulators like oxides a band gap has to be overcome. The experimental finding is that the efficiency of the desorption process expressed in terms of desorption cross sections is much bigger in insulators than in metals.

The desorption process does not need to run like a MGR type. The Antoniewicz model assumes that the excited state has a minimum at shorter distances to the surface than the ground state.¹ Gortel describes the desorption via a wave-packet formalism.¹⁰ The main idea in all models is that the kinetic energy necessary to escape the surface is gained by moving down the slope of the potential energy surface in the excited state.

In the following we would like to summarize our present view of the states involved in NO desorption from NiO surfaces.

The ground state of NO on NiO(100) as well as on NiO(111) is weakly bonding with a well depth of approximately 0.5 eV known from TDS (Ref. 36) and the minimum is located at about 2.5 Å distance from the surface, according to the calculations by Pöhlchen, Staemmler, and Wasilewski.⁷⁰ NO is bound with the nitrogen atom to a Ni ion in the surface and the molecular axis is tilted by approximately 45° with respect to the surface normal. The potential energy diagram for the ground state is shown schematically as the lower hypersurface in Fig. 5. Two normal coordinates have been considered, i.e., the potential energy of the entire molecule upon motion towards the surface as alluded to above and also the stretching vibration within the NO molecule. In the latter case, HREELS data³⁶ suggest that the bond length does not change much from the gas phase value upon adsorption on the surface. Moreover, an educated guess about the excited state is shown in Fig. 5 (the upper hypersurface). As will be shown elsewhere in detail calculations suggest¹¹ that the excited state exhibits a minimum which is located at smaller molecule surface distances. Briefly, the reason is the formation of a negative intermediate ion⁸ which is attracted and thus pulled inward by the Ni cations. The calculation indicates that the minimum in the excited state is of the order of 5 eV and thus deeper than in the ground state with respect to the molecule surface separation. In addition, the NO bond distance is larger in NO⁻ with respect to neutral NO which has also been taken into account in Fig. 5.

The specific desorption model used here thus contains elements of the three general models discussed earlier. Consequently the process observed will be characterized by a certain degree of complexity as will be discussed later.

C. Life time of the excited state and the influence of the magnetic properties of the surface on the spin effect

The high excitation of the vibration of the desorbing molecules is a further indication of the NO⁻ formation.³¹ As a consequence of the formation of NO⁻, the bond length of NO changes in the excited state with the minimum of the potential energy surface of the NO stretching coordinate being located at a larger distance (Fig. 5) Assuming a Franck–Condon-like transition into the upper potential energy surface the excitation leads to a noneigenstate of the excited system. The propagation of this noneigenstate may be described by solving the time dependent Schrödinger equation. The final state population of the NO vibration after the desorption then is a consequence of the average life time of the excited state. Assuming a bond length like gas phase NO⁻ we obtain the experimental determined vibrational population for a life time of several 10⁻¹⁴ s.³¹

As was mentioned, the vibrational temperatures of NO showed a dependence on the electronic state for NiO(111) while we did not observe a spin effect in NiO(100). As this is only observed for an excitation energy of 6.4 eV, all details of the process are not understood so far, but we may interpret the observation qualitatively as follows. As mentioned at the beginning, NiO is an antiferromagnetic material with two different spin lattices of antiparallel spin orientations of the Ni²⁺ ions. The desorption mechanism involves a transfer of...
an electron. The spin orientation of the transferred electron relative to the lattice orientation is important. Along the (100) surface the lattice spins are oriented with alternating spins, i.e., no overall spin orientation. In the case of the (111) surface the spins show a preferential orientation. If the spin of NO is equal to the lattice orientation the electron can be integrated easier than in the case where they are different. As a consequence, the life times are different for the two channels leading to different vibrational temperatures as observed experimentally. Of course, at this point it is only a handwaving argument.

D. Bimodal velocity distributions and the impact of binding geometry

Thus far we did not discuss the propagation within the potential of the excited state. As we will show, the geometric orientation of the molecules is important for this aspect. On both surfaces the NO is tilted by an angle of about $45 \pm 15^\circ$ against the surface normal. The molecule can undergo a degenerate bending vibration and azimuthally rotates freely about the surface molecule bond as indicated in Fig. 6, where we show the angle dependent part of the potential. Normally such motions are relatively low in energy which means that they are noticeably excited at the temperatures used in our experiments. In our previous model calculations we have treated the adsorbed state as a hindered rigid rotor and the excited state as a repulsive electrostatic potential. The molecule in the excited state was then treated as being a free rotor. The present model is considerably modified including explicit treatment of the rotational quantum states within the angle dependent potential (Fig. 6), but we shall show that most of the conclusions drawn before remain valid.

The bending motion introduces a momentum $k$ associated with the center of mass motion of the molecule in the ground state which is conserved during the electronic excitation thus effectively coupling bending and translational motion. In the most simplified case we can describe the motion, i.e., the wave function in the excited and the ground states by a product of angular (rigid rotor) motion and translational (plane wave) motion. The angular part of the motion is, of course, not included in the schematic representation of Fig. 5 but is shown in Fig. 6. An excitation process may be viewed as follows:

The molecule is suddenly excited from the lower into the upper hypersurface. Due to the changes in equilibrium bond length, i.e., the positions of the minima, the molecule will experience a net force towards the surface. However, the trajectory of the center of gravity of the molecule in the excited state will depend on its trajectory in the ground state and the particular moment when it was “kicked” onto the upper hypersurface. For example, the bending motion could be moving the molecule in the ground state either towards or away from the surface along the $z$ direction. This motion will be characterized by a component $k_z$ or $-k_z$ in the translational (plane wave) part of the motion. Since $k$ is conserved the translational motion on the excited state will depend on the motion in the ground state. Deactivation occurs after a given lifetime, and there will be a distribution of life times in the excited state. The point on the hypersurface of the excited state where deactivation occurs is therefore dependent on the starting conditions.

We have modeled the dynamics on the two hypersurfaces by quasiclassical trajectory calculations, in which rotational motion and electronic excitation were treated quantum mechanically and translational motion classically. It turns out, and this will be shown in detail elsewhere, that for a given distribution of lifetimes, bimodal distributions may be obtained. The two constituent distributions may be traced back to originate from two factors. On one hand the sign of $k_z$, and on the other hand the position of deactivation relative to the surface and the position of the minima in the hypersurfaces are important. Those trajectories belonging to longer lifetimes allow the molecule to reach the strongly repulsive part of the potential thus leading to high translational energies upon deactivation.

The increase of linear momentum with increasing angular momentum or, in other words, the coupling of translation to rotation is connected with the angular dependence of the potentials involved. The very fast molecules have gained their translational energy from a particularly long interaction with the angle dependent potential. Thus, molecules with large linear momentum will show a strong population of high rotational quanta.

Comparing the (100) and (111) state we observe changes in the relative populations of the two channels. If we assume the same excited state potentials for both surfaces, we can explain the relative population by different life time distributions in the excited state. This fact is supported by the different vibrational temperatures as discussed earlier. In addition, the steepness of the potential energy surface will have an impact on the final translational energy distribution. The shape of the potential surface, however, is influenced by the actual surface properties. Thus, the different intensity distributions and behaviors as a function of rotation of the velocity flux distributions also reflect the steepness of the potential curve in the excited state due to a different interaction of the adsorbate with the surroundings.

We also did more sophisticated calculations assuming an attractive Morse potential of the excited state with the distance of the negatively charged molecule towards the posi-
tively charged surface being shorter than in the ground state. The relaxation probability was assumed to be variable and to depend on the position within the potential energy surface in the excited state. These calculations confirm our findings that the bimodality is due to the translational motion of the center of gravity of the molecule in the moment of excitation and to the distance relative to the surface where relaxation occurs. Details of these calculations will be discussed elsewhere.\(^7\)

**V. CONCLUSIONS**

We have discussed the similarities and differences of the laser induced desorption of NO from an epitaxial film of NiO(100) grown on Ni(100) and an epitaxial film of NiO(111) grown on Ni(111). For both surfaces we observe bimodal nonthermal velocity flux distributions independent of the rovibrational states but showing different intensity distributions. We interpret the bimodality as being due to the desorption mechanism itself. The key leading to the two channels is the bent geometry of the molecule. The momentum associated with the center of mass motion of NO due to the bending vibration is conserved in the moment of excitation and is therefore crucial for the development of the system after the excitation. The wavelength dependence of the desorption cross sections measured for NiO(111) indicates that the desorption is induced by hot carriers formed in charge transfer transitions in the substrate. The final state distribution of the desorbing NO is interpreted as being due to a NO\(^{-}\) intermediate state. Desorption from both surfaces showed similar rotational (400 K) temperatures. For the desorption from NiO(100) we observed an increased rotational excitation coupled to increased translational energy. In both cases there is no coupling between vibration and translation. While the vibrational temperature for NO desorption from NiO(100) is 1890 K we observe a spin dependence of the vibrational temperature for NiO(111) giving 2050 K for the \(^1\)P\(_{1/2}\) state and 1600 K for the \(^1\)P\(_{3/2}\) state. This can be explained by the different magnetic properties of the two surfaces. The antiferromagnetic NiO consists of two different spin lattices with antiparallel spin orientations of the Ni\(^{2+}\) ions. Along the (100) surface the lattice spin orientation has no overall spin orientation. However, in the case of the (111) surface the spins show a preferential orientation. The result is a dependence on the electron spin for the recombination probability of the NO\(^{-}\) intermediate state.

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