Photoinduced processes on alkali covered surfaces: NO desorption from $K/Cr_2O_3(0001)$

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Abstract

We have studied the ultraviolet laser induced desorption of $NO/Cr_2O_3(0001)$, $K/Cr_2O_3(0001)$ and the coadsorbate system $NO/K/Cr_2O_3(0001)$ using resonance enhanced multiphoton ionization spectroscopy for state selective detection of the desorbing species after excitation with nanosecond laser pulses. The goal of our experiments was to study the influence of surface electronic modifications via alkali adsorption on the photodynamics of a simple molecule. The photochemistry of the isolated and the coadsorbate systems is strongly dependent on the coverage of the diverse components. In this paper we shall mainly focus on data for the low coverage regime of potassium. From the two adsorbate species of NO, a chemisorbed and a physisorbed species, we present data of the chemisorbed species. The velocity distributions show a strong dependence on the excitation energy which we interpret on the basis of electron energy loss spectra as being due to surface charge transfer states. This is corroborated with our coadsorption experiments with low coverages of potassium which alter the velocity distributions. © 1997 Elsevier Science B.V.

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1. Introduction

The goal of fundamental investigations in surface photochemistry is to learn how one can tailor a system to obtain a desired photoreaction. Many examples are known for which the dominating step of the photoreaction is an initial excitation of the substrate [1,2]. We were therefore interested in how one can use surface dopants to modify the electronic surface structure for promoting a desired reactivity. Well known promoters in heterogenous catalysis are alkali metals adsorbed on metal surfaces [3–5]. The function of such promoters in

dark reactions is that alkali coadsorption can enhance charge transfer from the substrate into an antibonding orbital of a molecule adsorbed close to the alkali atom. Such a charge transfer may also have consequences for the photochemistry of coadsorbates. Though the photochemistry of alkali adsorbates has been studied on its own on a variety of metallic and non-metallic substrates [6–11] there is little knowledge about the photoactivity of coadsorbate systems [12]. Even less is known about the possibility of surface modification via metal deposition on oxide surfaces even though oxide surfaces play an important role in photocatalysis. We shall present the photochemistry of NO on $Cr_2O_3(0001)$ with coadsorption of low coverages of potassium and compare our results to the

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pure $NO/Cr_2O_3(0001)$ system. Of particular interest is the influence of surface charge transfer states of $Cr_2O_3(0001)$ which are known to be strongly modified with the adsorption of alkali metals. The very rich photochemistry of thicker potassium coverages will shortly be summarized but will be discussed elsewhere in more detail [13].

2. Experimental set-up

The experiments were carried out in an ultra-high vacuum chamber routinely used in our laser desorption experiments. Details of the machine are given elsewhere [14]. The chamber was equipped with LEED (low energy electron diffraction), AES (Auger electron spectroscopy), XPS [X-ray photoelectron (XP) spectroscopy], XAES (X-ray Auger electron spectroscopy) and a TDS facility [thermal desorption (TD) spectroscopy]. A Cr(110) single crystal surface was sputtered prior to each single experiment until contamination due to atomic nitrogen was below a few percent. An epitaxial film of $Cr_2O_3(0001)$ was obtained by oxidizing the cleaned crystal in an atmosphere of 10^{-6} Torr of oxygen at 500 K and annealing the oxide to 1000 K. Potassium was dosed onto the surface at room temperature or onto the surface cooled with liquid nitrogen from a thoroughly outgased standard SAES getter. The heating current was held at maximally 6.5 A. The change in work function was monitored by measuring the low energy cut off of the photo electron spectra.

The LID (laser induced desorption) experiments were of pump-probe type. Desorbing potassium as well as desorbing NO were detected using REMPI (resonance enhanced multi photon ionization). The adsorbates were desorbed normal to the surface with a pump laser pulse, a broad band excimer laser (Lambda Physik EMG 200) run at three different wavelengths (6.4, 5.0 and 3.5 eV). The laser fluence was typically 1 mJ cm^{-2} in most of the experiments and the pulse length was 15 ns. The desorbing atoms and molecules were then detected in the gas phase after a well defined time delay at a distance of 32 mm parallel to the surface with a tunable probe laser, an excimer laser (XeCl, Lambda Physik LPX 205 i cc) pumped dye laser

(Lambda Physik LPD 3002). From the known distance and flight time the velocity of the detected atoms and molecules could be calculated. Laser light of 344.637 and 344.738 nm was used to excite the desorbing potassium atoms from the 4s $^2S_{1/2}$ into the 6p $^2P_{1/2}$ and the 6p $^2P_{3/2}$ intermediate state [15]. By absorbing a second photon the excited atoms were then ionized. For the NO-detection the well known $(1+1)$ REMPI scheme via the $A^2\Sigma$-state was chosen [16]. The ions were detected perpendicular to the desorption and detection laser beam direction via a detector consisting of a repeller, a flight tube, microchannel plates and a phosphor screen.

The NO molecules were redosed after each laser desorption pulse using a pulsed molecular beam apparatus (pulse width 701 μs, pressure behind nozzle = 2 bar). This allowed an exact control of the surface coverage and a back ground free monitoring of the desorbing molecules. In all experiments including the coadsorbate experiments dosing of NO was done at 90 K. The base pressure did not exceed 3×10^{-10} Torr when the molecular beam was running with maximum output.

3. Results

3.1. Pure potassium on $Cr_2O_3(0001)$

The dosing of the potassium was performed at two different surface temperatures, namely 90–100 K and 280–300 K. For low coverages a mainly linear decrease of the work function is observed until a very shallow minimum is reached [13]. In XP spectra mainly the Cr 2p emission becomes less intensive with potassium adsorption while the O 2p emission remains constant. For both XPS signals a shift towards higher binding energies of up to 0.4 eV due to band bending effects can be observed. When dosing at room temperature only a saturation coverage could be obtained corresponding to the minimum of the work function. When dosing the potassium at 90–100 K the work function changes are very similar to the room temperature behaviour. However, thicker layers showing the characteristics of pure potassium metal can be obtained. In the

K 2p XP spectra plasmonic features show up as side bands. The workfunction approaches the value of potassium metal. Potassium coverages are given in relative numbers as multiples of the saturation coverage at room temperature. It was not possible to obtain absolute values as only a damping of the $Cr_2O_3(0001)$-LEED pattern but no defined super structure patterns could be found after potassium dosage. Details of the characterization will be given elsewhere [13]. We shall here report results concerning small coverages below the work function minimum.

Fig. 1 shows the velocity distribution of desorbing potassium atoms measured along the surface normal for a very small potassium coverage (10^{-5}–10^{-4} monolayers) (Fig. 1a), a coverage around half of the saturation coverage (Fig. 1b) and a saturation coverage for a room temperature dosing for an excitation energy of 6.4 eV. The maximum at 1800 m s^{-1} for the low coverage of potassium corresponds to a mean kinetic energy

of 0.66 eV ($\langle KE \rangle / 2k_B = 3800$ K). This indicates that the desorption process is nonthermal in origin. The distribution cannot be fitted with a Boltzmann distribution. Around the workfunction minimum plasmonic features appear in the K 2p XP spectrum. The velocity distribution becomes slimmer and the maximum shifts towards slower velocities. Coadsorption of NO does not influence the velocity distribution of potassium in the low coverage regime.

The desorption cross-sections are $(2 \pm 1) \times 10^{-20}$ cm^2 for desorption energies of 3.5 and 5.0 eV and $(2 \pm 1) \times 10^{-19}$ cm^2 for 6.4 eV, respectively (subsaturation coverage). These cross-sections are one to two orders of magnitude smaller than the corresponding cross-sections for NO desorption. Therefore we can treat the potassium concentration as being approximately constant during the coadsorption experiments.

3.2. NO on $Cr_2O_3(0001)$

Fig. 2 shows thermal desorption spectra (TDS) of NO from $Cr_2O_3(0001)$ for increasing dosing times using our molecular beam apparatus and a linear temperature ramp of 4 K s^{-1}. As well as a chemisorbed species desorbing at (340 ± 20)K a physisorbed species at high NO coverages can be observed. LID is found to be sensitive to the coverage. Two different desorption mechanisms are present for low and high coverages. We shall discuss here the low coverage regime for which only the chemisorbed species is present. A typical TDS for the steady state concentration of the LID experiments is shown as the lowest trace. The chemisorbed species is known to be adsorbed with a tilt angle of 30–50° on top of the chromium ions [17].

The desorption cross-sections for NO desorption are $(2 \pm 0.5) \times 10^{-17}$ cm^2 for 6.4 eV, $(6 \pm 2) \times 10^{-18}$ cm^2 for 5.0 eV and $(2 \pm 1) \times 10^{-18}$ cm^2 for 3.5 eV. These are typical values for desorption from oxide surfaces [18].

3.3. LID experiments of the coadsorbate system $NO/K/Cr_2O_3(0001)$

Fig. 3a shows the velocity distributions as a function of rotational excitation for the first vibra-
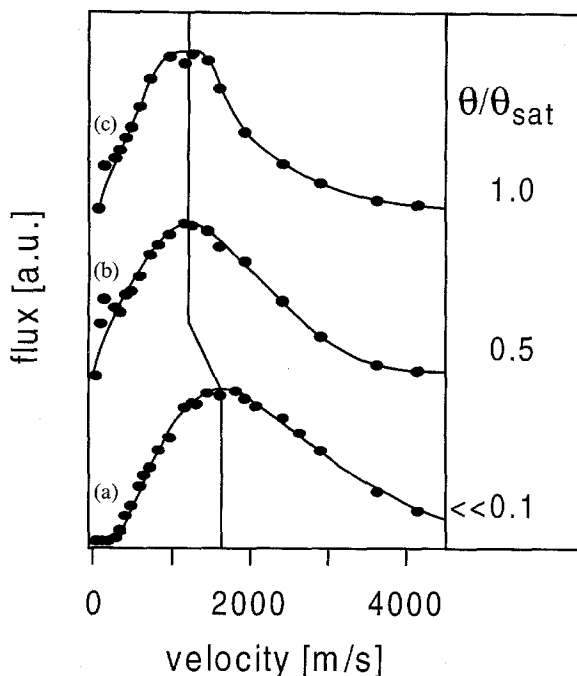

Fig. 1. Velocity distribution of desorbing potassium atoms measured along the surface normal, potassium dosed at room temperature; $E_{des} = 6.4$ eV (a) Very small potassium coverage (10^{-5}–10^{-4} monolayers); (b) $\Theta/\Theta_{sat} = 0.5$; (c) $\Theta/\Theta_{sat} = 1$.
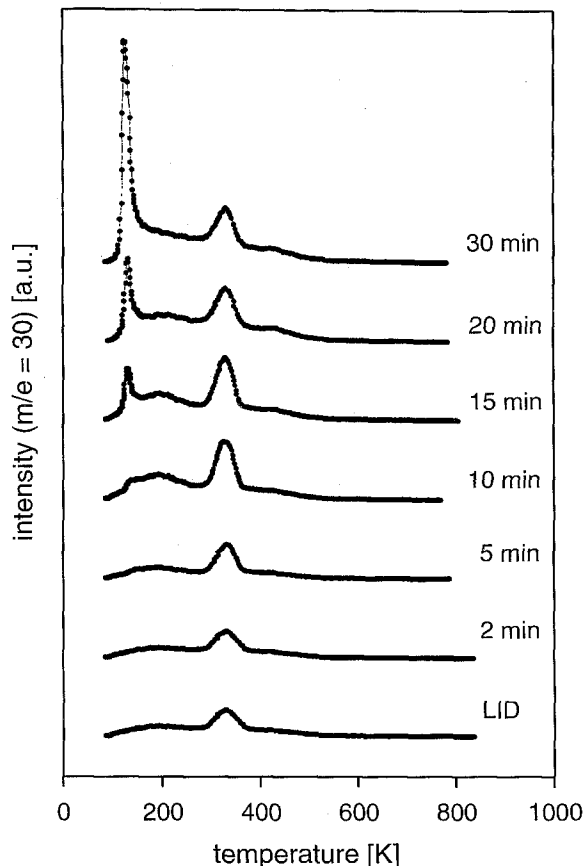
Fig. 2. TDS of NO from $Cr_2O_3(0001)$ for increasing dosing times at 90 K (dosing with a molecular beam: 4 Hz, pulse width 701 μs, pressure behind nozzle = 2 bar; lowest trace, equilibrium concentration at surface during LID experiments; linear temperature ramp: 4.0 K s^{-1}.

tional excited state of NO for pure NO (steady state concentration during LID: approximately half of the saturation coverage of the chemisorbed species) and NO postdosed at 90 K after covering the surface with a small coverage of potassium ($\Theta/\Theta_{sat} = 0.25$) at room temperature. A desorption energy of 5.0 eV was used. Each point is an average of 150 laser pulses. Fig. 3b shows the changes of the velocity distributions of NO desorption for one rovibronic state ($v'' = 0$) as a function of laser desorption energy. All velocity distributions shown have neither a clear Boltzmann nor a single Gaussian form. Apparently there are two channels which show a strong wavelength dependence with

respect to the relative intensities and are influenced by the coadsorption of potassium.

For the pure $NO/Cr_2O_3(0001)$ system enhancement of the intensity of the fast channel can be observed for a desorption energy of 5.0 eV. When coadsorbing potassium this enhancement is strongly modified. At 5.0 eV the fast channel is quenched. At a desorption energy of 3.5 eV the fast channel is more intense than for the pure NO system. This may be interpreted and will be discussed further below in more details as being due to changes in the surface electronic structure of the substrate. The intensity changes are independent of the vibrational state.

Related to the modification of the electronic properties of the substrate are also changes in the desorption efficiency of NO. We obtained $(5.5 \pm 2.5) \times 10^{-18}$ cm^2 for 6.4 eV, $(12 \pm 7) \times 10^{-18}$ cm^2 for 5.0 eV and $(2 \pm 1.8) \times 10^{-18}$ cm^2 for 3.5 eV.

X-ray photoelectron spectra show differences for coadsorption of potassium and NO with respect to the single adsorbate systems. A strongly coverage depending shift of the maximum of the K 2p emission is observed up to (0.9 ± 0.3) eV towards lower binding energies with coadsorption of NO relative to the pure potassium coverage. At the same time the strong band bending observed for the $Cr_2O_3(0001)$ substrate is partially removed as the maxima of the photo emission spectra shift back by 0.2–0.3 eV with coadsorption of NO with respect to the potassium covered surface. Related to the changes in the XP spectra is the formation of a reaction product. In NO TD spectra we observe a strongly chemisorbed species with a desorption temperature of (600 ± 30) K. This reaction dominates at high coverages of potassium. Plasmonic features in the K 2p XP spectrum at these coverages disappear with coadsorption of NO. From TD spectra and the N 1s XP spectra we preliminary assign the species to a $K_2N_2O_2$ alike product. For the very similar $NO/Na/Cr_2O_3(0001)$ system infrared data indicate a similar $Na_2N_2O_2$ product formation [19]. It is most likely that small clusters of potassium exist even at low coverages which are too small to show plasmonic features in the K 2p XP spectra but
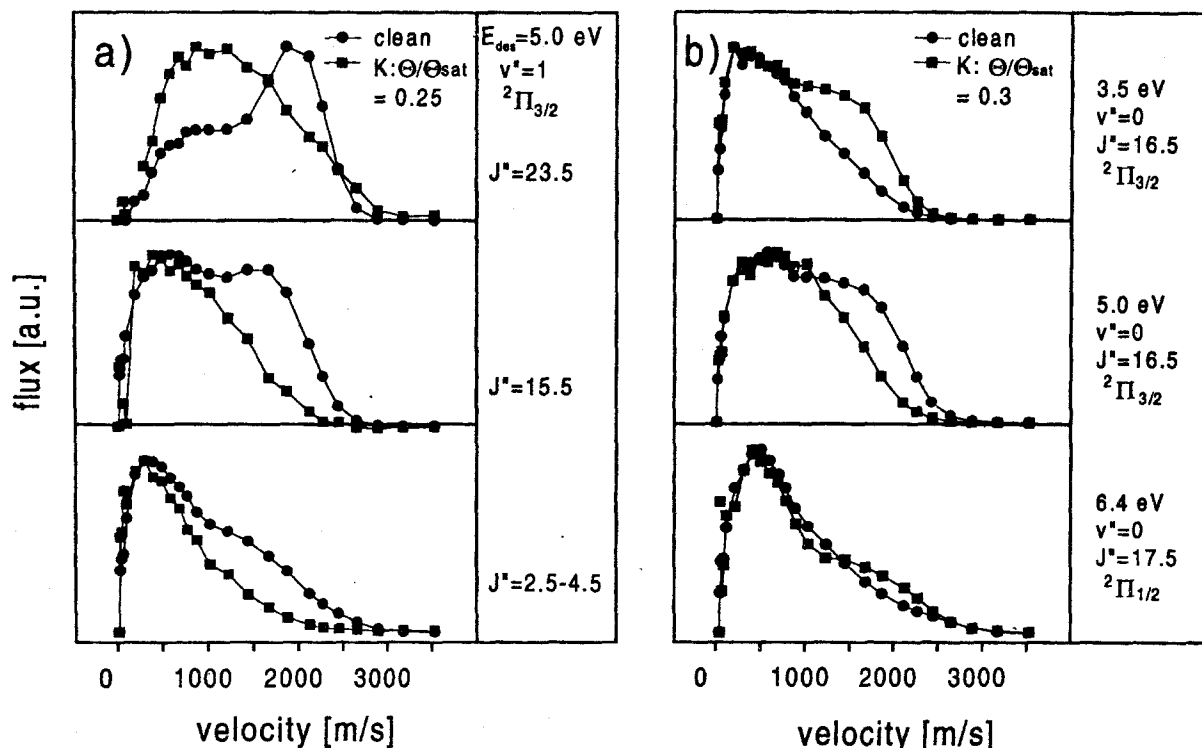
Fig. 3. (a) Velocity distributions for selected rotational states ($v' = 1$, $^2\Pi_{3/2}$) of desorbing NO of the pure surface (●) and a surface predosed with a small coverage of potassium (■, $\Theta/\Theta_{sat} = 0.25$), $E_{des} = 5.0$ eV (intensities normalized to the maximum of the velocity distribution). (b) Velocity distributions for one rovibronic state of desorbing NO from the pure surface (●) and a surface predosed with a small coverage of potassium (■, $\Theta/\Theta_{sat} = 0.3$) as a function of laser desorption energy (6.4 eV: $v'' = 0$, $J'' = 17.5$, $^2\Pi_{1/2}$; 3.5 eV/5.0 eV: $v'' = 0$, $J'' = 16.5$, $^2\Pi_{3/2}$). Potassium dosed at room temperature, NO redosed at 90 K with molecular beam after each laser pulse (equilibrium concentration on surface like lowest trace in Fig. 2 corresponding to approximately half of the saturation coverage of the chemisorbed species).

could be responsible for the formation of small amounts of hyponitrate.

Before we discuss the electronic properties of the surface in more detail we have to address the problem whether the intensity changes within the velocity distributions of desorbing NO could be the result of the photodissociation of this nitroso-compounds present at the surface. In such a case we would expect a change of the relative intensities of the two channels as a function of the amount of reaction products being formed. However, this is not the case. We conclude that the desorbing NO is not a reaction product of photodissociated hyponitrate but results from the NO species showing up in the TDS at (340 ± 20) K which coexists to the hyponitrate-like species.

4. Discussion

To summarize we found two new effects in the LID of the NO/Cr$_2$O$_3$(0001) system and the coadsorbate system NO/K/Cr$_2$O$_3$(0001) which have not been reported before. First of all there is the resonance enhancement of the fast velocity component within the velocity distributions of single rovibronic states of NO desorbing from the pure NO/Cr$_2$O$_3$(0001) system at 5.0 eV compared to desorption at 3.5 and 6.4 eV. This enhancement shows a strong dependence on the amount of rotational excitation. Second we found a strong change of the final state distributions when potassium is coadsorbed to NO. We now want to discuss how these findings can be understood when taking

the particular electronic structure of the $NO/Cr_2O_3(0001)$ system into account and which impact coadsorption of potassium has on NO desorption.

Fig. 4 shows an electron energy loss spectrum of the pure substrate, the NO covered substrate and a sodium covered substrate taken from Ref. [20]. The most interesting feature in the spectrum is a band peaking at 4.6 eV. This peak was attributed by Ehrlich [20] to optically allowed
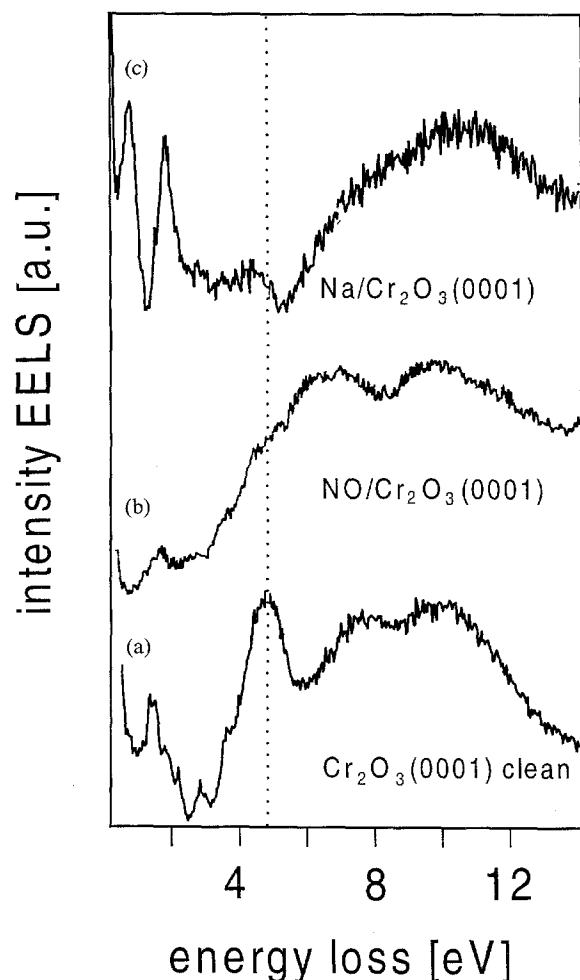
surface charge transfer transitions of $Cr_2O_3(0001)$. The corresponding bulk charge transfer excitations are calculated to be at 6.2 eV [21]. Adsorption of NO leads to a strong shift of the surface states towards higher energies into the rising edge of the bulk charge transfer states. Enhancement of the fast channel in the velocity distributions of NO desorbing from the pure chromium oxide surface can be understood as being due to a channel originating from these surface state transitions.

Electron energy loss (EEL) spectra for potassium adsorption on $Cr_2O_3(0001)$ are not known. However, sodium adsorption shown in Fig. 4 is very similar in its adsorption behaviour as known from XPS, XAES and LEED [22]. From Fig. 4 it can be seen that adsorption of sodium quenches the surface states. A remaining weak band is broader with an asymmetric maximum shifted by up to 0.2 eV to lower energies with respect to the uncovered surface. The sodium electron is partially transferred to the surface followed by the formation of a Cr^{2+} ion in a low coverage regime (see discussion in [22]). With reservations we assume that potassium most likely has the same effect on the surface state of $Cr_2O_3(0001)$. The linear decrease of the workfunction with increasing potassium coverage and the band bending effects in the XP spectra of $Cr_2O_3(0001)$ support the assumption that a partial electron transfer from potassium to the chromium oxide takes place. Further evidence is obtained from the desorption cross-sections of the pure potassium desorption. The cross-sections are similar and rather small at 3.5 and 5.0 eV and increase by one order of magnitude for 6.4 eV. Compared to the EEL spectrum of the sodium covered surface this can be interpreted as being due to a substrate induced excitation with a quenched surface charge transfer state.

For the coadsorbate system our XPS data clearly indicate principal changes of the electronic structure with respect to the pure systems. In the high potassium coverage regime we observe a clear disappearance of plasmonic features in the K 2p XP spectra due to a dark reaction with NO. As the potassium clusters react with NO we can rule out that the initial electronic excitation is due to

Fig. 4. EEL spectrum of (a) the clean $Cr_2O_3(0001)$, (b) the NO covered substrate (saturation coverage of chemisorbed species at 90 K) and (c) a sodium covered substrate (submonolayer obtained by heating a multilayer to 520 K) taken from Ref. [20]; $E_p = 100$ eV, specular.

an excitation within possible potassium clusters. Therefore we can rule out that the intensity enhancement in the fast desorption channel of NO of the coadsorbate system at 3.5 eV is due to metallic particles and a related plasmon resonance (3.8 eV for potassium, bulk value) [23]. This is consistent with findings on potassium desorption from graphite. In these experiments the ionic two-dimensional K-phase was found to be the only photoactive species for photodesorption of potassium at $\lambda = 217$–280 nm though a condensed "metallic" phase is coexisting at higher coverages [10,11]. The results on graphite are different to results on the desorption of sodium atoms from adsorbed clusters on LiF which were attributed to a plasmon resonance [7].

Details of the adsorption behaviour of our coadsorbate system are similar to the coadsorbate system $CO_2/Na/Cr_2O_3(0001)$ which has intensively been studied with a variety of surface spectroscopical methods [24]. For this system it has been observed that sodium loses any metallic character with CO_2-adsorption due to carbonate formation. The character of the surface overlayer was found to be dielectric.

The relative intensity distributions in the two desorption channels are not dependent on the amount of hyponitrite being formed. This rules out that surface modifications due to this product formation are important. Xu et al. pointed out that the Cr 3d bands are strongly localized [17]. Dillmann et al. discussed that the electronic excitations for the submonolayer $Na/Cr_2O_3(0001)$ system show local character [22]. Furthermore for the coadsorbate system $C_2H_4/Na/Cr_2O_3(0001)$ the same authors discuss the pronounced influence of sodium on ethene adsorption because of charge transfer from sodium to the surface. Assuming the analogy to the potassium system we therefore preliminary assign the changes in photodesorption to be related to a $K^{\delta+}NO^{\delta-}$ pair of closely adsorbed potassium and NO and related modified charge transfer states.

To summarize our data we have shown that within the NO desorption from $NO/Cr_2O_3(0001)$ and $NO/K/Cr_2O_3(0001)$ desorption wavelength dependent changes within translational energy distributions of single rovibronic states can be related

to surface charge transfer states. There are only very few other examples within the literature for which a clear influence of surface states onto photoreaction processes have been demonstrated [25]. However, for the system $NO/Si(111)$ (7×7) only impact on the desorption cross-sections in coadsorption experiments have been reported but no related changes in the final state distributions. Surface states are of particular interest as they may be steered via surface dopants and are interesting concerning molecule specific photochemistry at surfaces.

For more details about the separate systems we refer to further publications [13,26].

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