UV-laser induced desorption of NO from the pure and modified Cr$_2$O$_3$(0001) surfaces: Spin effects in surface state induced desorption

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ABSTRACT

We shall report the UV-laser induced desorption of NO/Cr$_2$O$_3$(0001) and the coadsorbate system NO/K/Cr$_2$O$_3$(0001). Resonance enhanced multiphoton ionisation (REMPI) was used for state selective detection of the desorbing NO after excitation with pulses of nanosecond duration and desorption laser energies between 3.5 eV and 6.4 eV. There are two adsorbate species of NO, a chemisorbed and a physisorbed species. We shall focus on data of the chemisorbed species. The main emphasis within this paper will be put on electron spin effects, particularly the preferential population of a fast translational desorption channel for the $^2\Pi_{3/2}$ state observed specifically in connection with surface state induced processes at desorption energies of 5.0 eV. For those processes changes within the final state distributions of desorbing NO are found when modifying the electronic surface structure via adsorption of small amounts of potassium.

Keywords: Laser induced desorption (LID), NO, K, Cr$_2$O$_3$(0001), surface states, spin effect, hyponitrate formation

1. INTRODUCTION

The dominant excitation process within photochemically induced surface reactions has been found to be an initial excitation of the substrate followed by a temporal interaction of the excited electrons with the adsorbate for a large number of adsorbate systems[1]. In such cases surface states are of particular interest as they may be modified via surface dopants and are interesting concerning molecule specific photochemistry at surfaces. However, only a few examples exist in which the photochemistry of such states have been studied[2+3]. While fcc oxide surfaces don't show pronounced optically allowed surface state transitions such states can be observed for the polar Cr$_2$O$_3$(0001) surface of the corundum-type chromium oxide[4]. It has been found that electronic transitions around 4.6 eV can be attributed to surface charge transfer states. These transitions are modified with adsorption of strongly interacting particles such as NO (exhibiting an intensity shift towards higher energies) and even more drastically with alkali adsorption. The rather large shift of the surface state with respect to the bulk charge transfer transitions (calculated[5] to start at around 6.2 eV) is connected to the specific surface structure of Cr$_2$O$_3$(0001). The stacking of layers along a direction perpendicular to the (0001) plane in the bulk consists of basically flat oxygen layers alternating with buckled metal ion layers. An electrostatically stable (0001) surface is obtained by cutting the stack of layers between the buckled metal ion layer[6], thus halvening the number of metal ions on the polar surface. Further strong relaxation of the first four layers leads to surface energies close to those found for non-polar oxide surfaces with non-divergent surface potentials[6]. Due to this particular surface structure the spins of the chromium ions very likely show a preferential orientation within the surface plane at 90 K as chromium oxide is antiferromagnetic. We shall show that this orientation is of importance for surface state induced photodesorption. As NO in the gas phase has an unpaired electron in the 2π* state the final population of the two related spin-orbit split (doublet) ground states can give an insight into possible coupling mechanisms between the adsorbate and the substrate during the excitation process. The dependence of the population on rotational and vibrational states is particularly useful for getting insight into the dynamics of the photodesorption process. Unusual populations of NO spin-orbit states have been reported in laser induced desorption (LID) experiments for oxidised Ni(100)[7], oxidised Ni(111)[8] and for Pt(111)[9,10] as well as in electron stimulated desorption (ESD) experiments NO/O/Pt(111)[11]. We shall report on the UV-laser induced desorption of NO when exciting bulk or surface states and compare the data to experiments on a surface with a surface electronic structure modified via coadsorption of potassium.

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2. EXPERIMENTAL SET-UP

The experiments were carried out in a UHV-chamber routinely used in our laser desorption experiments[12]. The chamber was equipped with low energy electron diffraction (LEED), Auger electron spectroscopy (AES), x-ray photoelectron spectroscopy (XPS), x-ray Auger electron spectroscopy (XAES) and a facility for thermal desorption spectroscopy (TDS). The work function was monitored by measuring the low energy cut off of the photo electron spectra. An epitaxial film of $Cr_2O_3(0001)$ was obtained by oxidising a $Cr(110)$ crystal cleaned prior to oxidation via prolonged sputtering. During oxidation the oxygen pressure was held at 10^{-6} Torr and the surface temperature at 500 K. Ordering of the film resulted after annealing the oxide to 1000 K. Potassium was dosed onto the surface at room temperature or at liquid nitrogen temperature from a thoroughly outgased standard SAES getter with a heating current kept maximally at 6.5 A.

The LID experiments were of pump-probe type. 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 eV, 5.0 eV 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 neutral 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). The neutral molecules were ionised state specifically using a (1+1) REMPI detection scheme via the $A^2\Sigma$-state[13]. 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. Time of flight spectra were obtained from a systematic variation of the time delay between the desorption and detection laser pulses. The velocity of the desorbing molecules could be calculated from these delay times and the known flight distance of the molecules to the detection laser beam. The time of flight spectra were then converted into velocity flux distributions in the usual way[1].

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) described elsewhere in more detail[14]. 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 $3 \cdot 10^{-10}$ Torr when the molecular beam was running with maximum output.

3. RESULTS AND DISCUSSION

NO on $Cr_2O_3(0001)$ exhibits a rich variety of molecular phases at liquid nitrogen temperature. Dosing with a molecular beam allows an exact control over the surface coverage. By choosing the coverage we have the opportunity to look at the photochemistry of isolated molecules interacting strongly with the surface (desorption temperature of (340 ± 20) K in TDS) or to study the high coverage regime in which dimer formation and collective phenomena can occur. We shall here focus on the low coverage regime and the chemisorbed species. Desorption from high coverages is reported elsewhere[14]. From wavelength dependant measurements of the desorption efficiency of the non thermal UV-laser induced desorption of NO from the $Cr_2O_3(0001)$ surface it was concluded that the initial excitation step is the interaction of hot electrons excited within the substrate with unoccupied levels within the adsorbate to initiate non thermal desorption[3]. The final state populations of the desorbing NO molecules are typical for such a process[3]. For example the desorbing molecules are quite highly vibrationally excited. The measured vibrational state population can be described by a Maxwell-Boltzmann distribution to which a vibrational temperature of (2900 ± 450) K can be attributed for a desorption energy of 6.4 eV. Independent of the vibrational state a rotational temperature of (700 ± 80) K is obtained for the same desorption energy from the integrated velocity distributions of single rovibronic states.
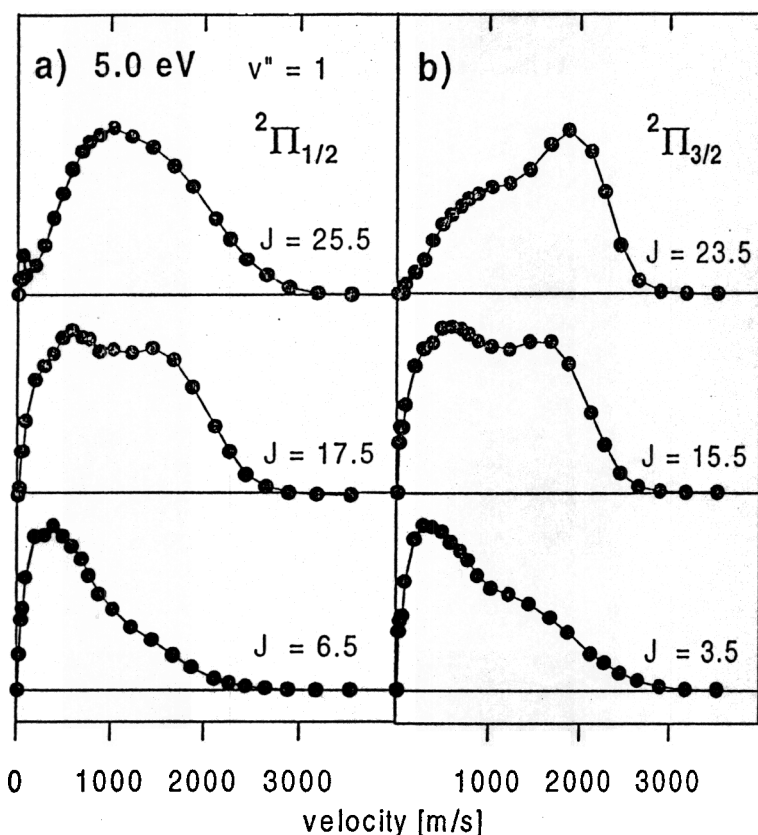
a) 5.0 eV v" = 1
$^2\Pi_{1/2}$
J = 25.5
J = 17.5
J = 6.5

b)
$^2\Pi_{3/2}$
J = 23.5
J = 15.5
J = 3.5

0 1000 2000 3000   1000 2000 3000
velocity [m/s]

Fig.   Velocity distributions of NO desorbing from $Cr_2O_3(0001)$
        for an excitation energy of 5.0 eV of some selected rotional
        states for v"=1
        a) $^2\Pi_{1/2}$ state of NO
        b) $^2\Pi_{3/2}$ state of NO

Fig.1 shows as an example the velocity distributions of three rotational states of NO desorbing from the $Cr_2O_3(0001)$ surface for a desorption energy of 5.0 eV for the two gas phase spin-orbit states of NO in the first vibrationally excited state. No remarkable dependence of the velocity distributions on the vibrational excitation has been observed for neither of the desorption energies nor spin states, i.e. the shape of the velocity distributions for a certain rotational excitation within a certain spin state is similar for different vibrationally excited states. All velocity distributions show clearly non Boltzmann shapes. There is a strong coupling between rotation and translation, i.e. the maxima of the velocity distributions are shifted towards higher velocities with increasing rotational excitation. While the velocity distributions of the $^2\Pi_{1/2}$ state resemble the velocity distributions of desorption energies of 3.5 eV and 6.4 eV the velocity distributions of the $^2\Pi_{3/2}$ state differ remarkably. Particularly for higher rotational excited states a pronounced maximum at fast desorption velocities is apparent. As the excitation energy of 5.0 eV is within the range of surface state transitions when NO is adsorbed this unusual spin dependence on the velocity distributions may be attributed to a surface state induced desorption channel[3].

The strong dependence of the final state distributions on the spin state of the desorbing NO is also visible from the population of the rotational states. Fig. 2 shows the ratio of the rotational population within the two spin states ($^2\Pi_{3/2}$ / $^2\Pi_{1/2}$) as a function of rotational excitation. This ratio was extracted from velocity-specific excitation spectra, recorded by scanning the probe laser frequency with a fixed time delay between the desorption and probe lasers for different desorption velocities for a desorption energy of 5.0 eV (fig. 2a) for the vibrational ground state of NO. Fig. 2b shows the corresponding ratio for a desorption energy of 6.4 eV. The splitting of the two spin-orbit states is 121.1 cm^{-1} with the $^2\Pi_{3/2}$ state being the upper state[15]. As both states have the same degeneracy factor of two the ratio of the population of the electronic two level system can maximally be one at elevated temperatures in case there is thermal equilibration following Maxwell-Boltzmann statistics. The ratio of the thermal equilibrated population at 100 K (the surface temperature) would be 0.17. However, from fig. 2 it is apparent that there is a clear population inversion of the $^2\Pi_{3/2}$ state for low rotational excitations at a desorption excitation energy of 5.0 eV. The population inversion decreases linearly with rotational excitation. For moderate rotational excitation and a desorption velocity of 450 m/s the population ratio runs through a minimum and then approaches a constant value. In other words the difference between the population ratio is more pronounced for the fast desorption velocity for which also a stronger coupling between translation and rotation is observed within the velocity distributions. The observed loss in propensity for higher rotational excitation is considerably greater than that expected because of mixing of the wavefunctions for the $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ levels due to the spin-uncoupling operator at high J[15]. Our observations of the spin-orbit propensity at 5.0 eV is very reminiscent of a similar observation in LID of NO from Pt(111) for which differing translational energy distributions for the two spin-orbit states, the hotter being the $^2\Pi_{3/2}$ state have been found as well as a preferential population of the $^2\Pi_{3/2}$ state at low quantum numbers[9,10] as well as
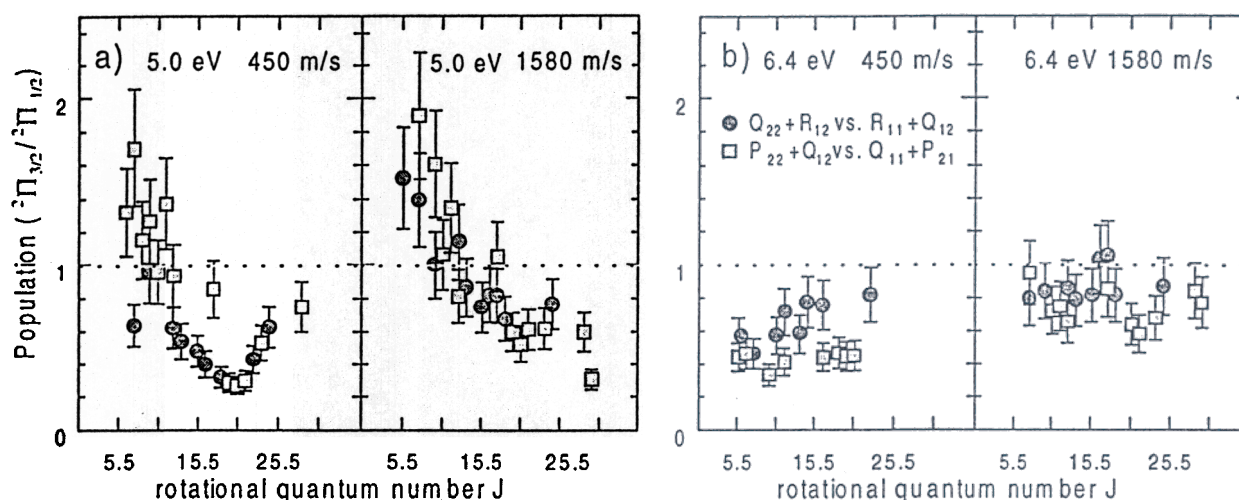
Fig.2: Ratio of the population ($^2\Pi_{3/2}$ / $^2\Pi_{1/2}$) as a function of rotational excitation extracted from velocity-specific excitation spectra, recorded by scanning the probe laser frequency with a fixed time delay between the desorption and probe lasers for a desorption velocity of 450 m/s and 1580 m/s
a) for an excitation energy of 5.0 eV
b) for an excitation energy of 6.4 eV

ESD experiments on the coadsorbate system NO/O/Pt(111)[11]. The spin-orbit states for a desorption energy of 6.4 eV are populated independent of the rotational excitation. The population scales roughly with the amount of translational excitation. Assuming a Maxwell-Boltzmann distribution one can calculate an electronic temperature of $T_{el} \approx 300$ K (population ratio: 0.55±0.2) for 450 m/s ($E_{kin}/2k = 180$ K) and $T_{el} \approx 1500$ K (population ratio: 0.89±0.15) for 1580 m/s ($E_{kin}/2k = 2250$ K).

The inverted spin-orbit propensity for low rotational quantum numbers can be attributed to mainly four factors: a) an open shell diatomic desorbate which has temporarily been negatively ionised before desorption, b) the quantisation axis of the desorbate being preferentially oriented along the surface normal, c) a strong spin-orbit coupled substrate with d) a surface state being particularly relevant. We want to discuss these points in more detail now. The NO molecules are known to adsorb on top of the chromium ions[16]. No theoretical calculations exist so far about the NO-chromium oxide bond so that there is not a detailed knowledge about the exact interaction between the adsorbate and the substrate. For a large number of molecules it is known that the interaction of adsorbates with ionic oxide surfaces is dominated by electrostatic interactions. However, the binding energy of the chemisorbed NO species of 1.01 eV (97.5 kJ/mol) (desorption peak at (340±20)K) on Cr_2O_3(0001) is unusually large for an ordinary molecule-oxide surface interaction[14,16]. This suggests that beside electrostatic interactions there must be a fair amount of mixing of the molecular states with substrate states. Experimentally it has been found that NO is bound tilted to the surface with a bonding angle of 20°-40° [16]. Therefore the $2\pi_x^*$ and $2\pi_y^*$ orbitals of the NO, degenerate by symmetry in the gas phase and in upright adsorption geometries, are not equivalent any more due to the interaction with the surface. The bent configuration implies that the principal axis of the electronic configuration of the adsorbate is not parallel to the molecular axis. The observation of high propensity of one spin state for low rotational quanta may be connected to a vertical geometry of the molecule at the time of breaking the molecule surface bond. At this geometry the linear axis is a quantization axis for the spin states[9-11]. The interpretation is also supported by the fact that the rotation and translation are strongly coupled. Such a coupling also has been observed for the LID of NO from NiO(100)/Ni(100)[8]. Ab initio calculations and three dimensional wavepacket calculations for the latter system within ab initio excited states revealed that for this system a change of a 45° bending angle to a 0° angle with respect to the surface normal is occuring within the excited state when the molecule is accelarated towards the surface[17-20]. The reason for this geometry change is a strong Pauli repulsion of the O2p bands of NiO and the occupied $2\pi^*$ orbitals within NO[17]. This process is rather similar to the system NO/Cr_2O_3(0001). The change in propensity is due to the involvement of the hindered rotation within the desorption process and a related dependence on the tilt angel. However, the binding geometry is only one part of the story.

During the excitation process an electron interacts with the adsorbate and is backtransferred to the surface before the molecule desorbs. In view of the excitation-deexcitation process the spin effect is likely to be connected to a specific magnetic structure of the surface which can lead to strong electronic symmetry constrains during the charge transfer process. The propensity thus reflects the density of states within a specific spin-orbit state of the surface. For this reason we want to shortly stretch out some aspects of the electronic and magnetic properties of chromium oxide and then discuss the interaction of NO with the surface. The ground state of the Cr^{3+} ion (d^3 configuration) is a spin-quartet state according to Hund's rule. The symmetry of the ground-state wavefunction is $^4A_{2g}$ within the crystal field (t_{2g}^3 configuration). Chromium oxide is antiferromagnetic with a Néel temperature at 307 K[21]. Along the direction perpendicular to the (0001) plane the spins of the Cr^{3+} are oriented pairwise in opposite directions within the bulk. The antiferromagnetic coupling of neighbour chromium ions is strongest within the (0001) direction with a coupling parameter of $J_1 \approx 90$ cm^{-1} due to a superexchange via connecting oxygen ions[22]. The second strongest interaction is the interaction of chromium ions within the basal plane with a coupling parameter of $J_2 \approx 40$ cm^{-1}. All other coupling constants are much smaller and in the order of 1 cm^{-1}. When cutting the basal plane of the chromium ions between the buckled metal ion layers to obtain a stable polar surface the J_2 coupling parameter is missing within the upper most layer. Due to the discussed stabilisation of the polar surface the spins within the surface plane are believed to exhibit the same orientation at 90 K[23]. The surface Néel temperature is probably below the bulk value as LEED experiments indicate[23] due to a reduced coupling and a lower coordination. In LEED experiments an order to order transition is observed at 150 K followed by an order to disorder transition at temperatures above 150 K[24]. During the interaction of the adsorbed NO with the surface the local magnetic properties are perturbed. The order to order transition observed at 150 K, visible in LEED as a ($\sqrt{3} \times \sqrt{3}$)R30° superstructure and interpreted as being due to a partial change of spin orientation within the surface, disappears during the interaction of strongly chemisorbed species such as NO[23]. In the moment of desorption the long range magnetic order is recovered. For the photochemical process involving an electron transfer only a certain spin orientation is energetically favoured for the backtransfer due to the strong coupling with the chromium ion underneath the surface chromium ion. The barrier for a different spin orientation is evident from the surface Néel temperature. As the interaction of NO with the surface is strong the propensity would then reflect the local density of spin-orbit states of the surface and explain the preferential population of one spin-orbit state of the desorbing NO. As the propensity is also related to molecules in the upright position molecules with low angular momentum will show a stronger propensity then molecules with large angular momentum[10]. Remarkable in this context is the fact that a fast desorption channel seems to be constrained to the $^2\Pi_{3/2}$ state reflecting a possible large energy separation between different spin-orbit states of the surface. Our arguments follow similar arguments of Burns et al. to explain spin-orbit propensities observed for NO from Pt(111)-O[11] and Zimmermann and Ho[1]. As the occurence of the propensity is only observed for a desorption energy of 5.0 eV we suspect that it is confined to surface state transitions. In this context it would be interesting to perform spin-polarised experiments to get further details about the surface electronic structure.

As we attributed the unusual velocity distributions and propensity of the spin-orbit states of desorbing NO after excitation at 5.0 eV to a surface state induced process we wanted to confirm this interpretation by studies in which the surface electronic structure is modified via coadsorption. For this purpose we investigated the laser induced desorption of the coadsorbate system NO/K/Cr_2O_3(0001). Potassium exhibits two different phases on Cr_2O_3(0001) depending on the growth conditions[25]. Potassium can be obtained either as partially ionised dispersive species or as aggregates of metallic character. The metal aggregates are highly reactive towards NO even without irradiation while no dark reactions are observed for the ionic phase. We therefore want to restrict our discussion to the coadsorption of a partially ionised potassium species. The desorption efficiency of potassium is at least one order of magnitude smaller then the corresponding desorption efficiency of NO so that we can treat the potassium concentration as being constant during the coadsorption measurements of final state distributions. Fig. 3 shows the velocity distributions of desorbing NO from the clean surface (black circles) and the potassium covered surface (grey squares) as a function of rotational excitation for NO in the vibrational ground state for a desorption energy of 5.0 eV (fig. 3a) and 6.4 eV (fig. 3b). While the velocity distributions are barely effected for a desorption energy of 6.4 eV they are modified for a desorption energy of 5.0 eV. Particularly the fast channel is strongly suppressed. This confirms our interpretation of the involvement of surface electronic states for the desorption at 5.0 eV in contrast of excitation energies at 6.4 eV where bulk transitions are dominant.

We want to now discuss the implications of the potassium adsorption onto the surface electronic structure. Our discussion will focus on the coadsorption of a partially ionised potassium species as it appears to be relevant for the NO desorption
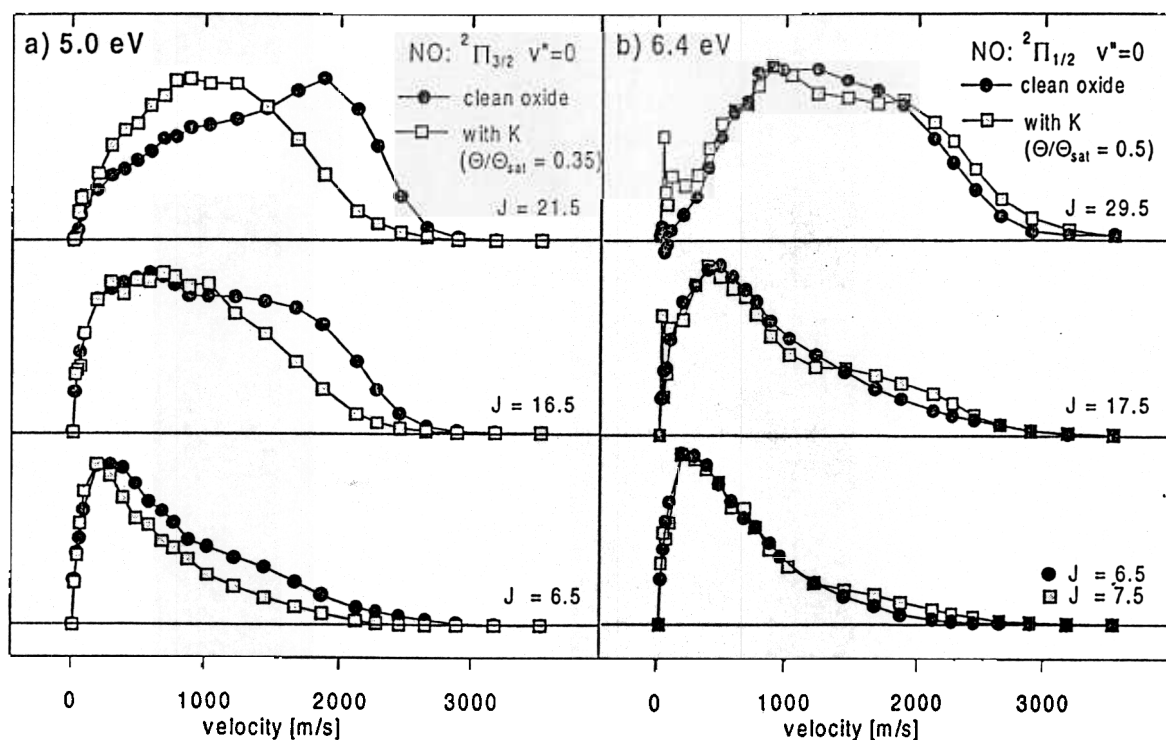
Fig. 3: Velocity distributions of NO desorbing from Cr₂O₃(0001) of some selected rotional states for v"=0 for a clean surface (black circles) and for NO coadsorbed to potassium (grey squares); the potassium coverage is given as multiples of a saturation coverage at room temperature
a) for an excitation energy of 5.0 eV
b) for an excitation energy of 6.4 eV

process in the coadsorbate system. The ionic potassium species is believed to adsorb in a threefold hollow position on the oxygen atoms[25]. In this position the potassium atoms are quasi completing the missing chromium ions in the topmost layer to meet a situation closer to the bulk. Furthermore it partially transfers an electron to the underlying chromium ion. This might be the reason why the surface charge transfer state is strongly modified with respect to the clean surface. An ionic potassium atom in the neighbourhood of the chromium ion would not only modify the local electronic property but also the local magnetic property in the first and second chromium ion layer and thus influence the surface state induced effects.

4. CONCLUSIONS

Quantum state selective experiments on the UV-laser induced desorption from low coverages of NO on the Cr₂O₃(0001) surface have been reported for excitation energies of 3.5 eV, 5.0 eV and 6.4 eV. Particular emphasis has been put on spin-orbit state populations within different rovibrational states of the desorbing NO molecules as a function of the desorption energy. We observe an unusual spin-orbit state population after excitation of surface charge transfer states at 5.0 eV of the Cr₂O₃(0001) surface. This is apparent as a maximum in the velocity distributions at high translational excitation which specifically occurs for the upper $^2\Pi_{3/2}$ spin-orbit state and is particularly pronounced at high rotational excitation. Parallel to this observation a population inversion is observed for low rotational excitation linearly decreasing with increasing rotational excitation. Changes of the photochemistry of the NO/Cr₂O₃(0001) system have been observed when NO is coadsorbed to potassium. A partially ionised atomic potassium species in the neighbourhood of NO modifies the surface electronic structure in such a way that the fast desorption channel for NO desorption at a desorption energy of 5.0 eV is surpressed while no changes are observed for a desorption energy of 6.4 eV.

5. ACKNOWLEDGEMENTS

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