Mechanism of the UV-laser-induced desorption of CO from Cr$_2$O$_3$(0001)

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Abstract

The UV-laser-induced desorption of CO from an epitaxially grown film of Cr$_2$O$_3$(0001) is reported using a (1+1') REMPI (resonance enhanced multiphoton ionisation) detection technique via the B$^1\Sigma^+$ electronic state for the desorbing molecules to obtain information on single rovibrational states. The final state distributions at three different wavelengths (6.4, 5.0 and 3.5 eV) were almost identical showing bimodal velocity flux distributions for $v''=0$ and monomodal distributions for $v''=1$. The desorption cross-sections varied between $(5.1 \pm 1) \times 10^{-18}$ cm$^2$ at 3.5 eV and $(3.5 \pm 1) \times 10^{-17}$ cm$^2$ at 6.4 eV. The overall behaviour indicates that the excitation mechanism is due to a primary electronic excitation step within the substrate. Possible mechanisms are discussed.

Keywords: Carbon monoxide; CO/Cr$_2$O$_3$(0001); Insulating films; Low index single crystal surfaces; Photon stimulated desorption (PSD)

1. Introduction

Progress in the understanding of photochemical reactions at solid surfaces has been made in recent years using well-characterised samples under ultra-high vacuum conditions [1-6]. The interests in these processes are multiple and range from heterogeneous photocatalysis, studies of photochemical processes in microstructuring of solid surfaces or photovoltaic, to name only a few examples [7-9]. In order to gain an insight into the dynamics of the photochemistry it has been shown that detailed studies of the most simple possible photochemical process, the bond breaking of the surface bond of a simple model molecule followed by desorption, have been quite instructive [1-6]. In particular, measurements concerning the detection of the final state distributions of desorbing molecules have contributed greatly to progress within the field.

In our group we have been concerned with quantum state resolved measurements on the UV-laser-induced desorption for some time [10-22]. We have concentrated our efforts on simple molecules adsorbed on transition metal oxides for which large desorption cross-sections allow detailed studies on final state distributions with high sensitivity. A further reason for choosing these systems was also that ab initio methods for such ionic surfaces with strongly localised metal d orbitals are very suitable [23,24]. Not only have they been applied to characterise the adsorption within the ground state but a first successful example of calculations on electronically excited states has been demonstrated [25]. From our experiments on NO/NiO(100) and NO/NiO(111) we

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suspected that the bent geometry in respect to the surface normal in the ground state and the bending vibration which implies a strong centre of gravity movement was important for the particular desorption dynamics [10–18]. Most recently we have focussed our interest on the system CO adsorbed on an epitaxially grown film of Cr$_2$O$_3$(0001) [19–22]. The particular interest in this system is the flat adsorption geometry and its impact on the desorption dynamics in comparison to other bent molecules. The flat bonding of CO on Cr$_2$O$_3$(0001) is quite unusual and the bonding mechanism for this special system is not yet completely understood from a theoretical point of view.

In analogy to the bonding of other molecules on transition metal oxides characterised by ab initio calculations [23,24], it is very likely that a strong Coulomb attraction caused by the electrostatic interaction of the electric multipole moments of the CO and the electrostatic field above the Cr$_2$O$_3$(0001) surface and the Pauli repulsion between the occupied $1\pi$ orbital and the $O^{2-}$ are the dominant components of the bonding. From measurements using a variety of different methods [26,27] it is clear that the molecule prefers a flat bonding to a bent one with the $4\sigma$ and $5\sigma$ orbitals of the CO molecule having an attractive interaction with two Cr atoms. Evidence for this interaction is given from strongly shifted binding energies of the $4\sigma$, $5\sigma$ and $1\pi$ orbitals of CO with respect to the free molecule by up to several electronvolts towards higher energies depending on the orbital, as observed by angular resolved ultra-violet photoemission spectroscopy (ARUPS) [26,27]. The overall binding energy of the molecule of 0.45 eV is rather weak. This makes the adsorption of molecules on transition metal oxide surfaces very different from the adsorption on metal surfaces. However, the nature of the bonding of molecules on oxide surfaces is still under investigation by ab initio methods [28].

One of the important questions related to such a bonding geometry concerns the desorption mechanism itself. Which kind of influence does a change in the charge distribution induced from an electronic excitation within the surface have on the equilibrium of the bonding? For a system like NO/ NiO(100) it is known from ab initio calculations of the excited states that a charge transfer transition within the surface without a charge-transfer to the adsorbate does not lead to a repulsive state within the coordinate of the adsorbate-substrate bond distance [25]. The question is whether the same is true for CO/Cr$_2$O$_3$(0001). For the system NO/NiO(100) and NO/NiO(111) we have shown that an NO\(^{-}/\text{NiO}\(^{+}\) intermediate state is responsible for the desorption of NO [18,25]. The question is whether a negative ion can also be formed for CO/Cr$_2$O$_3$(0001). Furthermore, CO/Cr$_2$O$_3$(0001) shows a pronounced absorption in EEL spectra which can clearly be attributed to the adsorbate [29]. An important question is whether a direct excitation within the adsorbate is dominant, as has been observed for similar systems with strong adsorbate absorption [30] or whether a primary excitation within the substrate is more important.

We shall present quantum state resolved measurements of the CO desorption induced at three different wavelengths above the band gap of the surface, i.e. 3.5, 5.0 and 6.4 eV. The information that the primary excitation step is within the substrate can be obtained unambiguously. Suggestions about the mechanisms following this excitation will be discussed in detail.

2. Experimental setup

The experiments were carried out in a UHV chamber equipped with LEED (low energy electron diffraction), AES (Auger electron spectroscopy), XPS (X-ray photoelectron spectroscopy), XAES (X-ray Auger electron spectroscopy), a quadrupole mass spectrometer for residual gas analysis and TDS (thermal desorption spectroscopy) to characterise the adsorbate/substrate system before and after the laser experiments. Details of the machine are given elsewhere [17]. The epitaxial film of Cr$_2$O$_3$(0001) was grown on a Cr(110) single crystal surface by oxidising the cleaned crystal in an atmosphere of 10$^{-6}$ Torr of oxygen at 500 K. The well ordered film was obtained after the oxidation when annealing the film to 1000 K. The crystal was dosed with CO at 100 K during the experiments via a background
pressure of $2 \times 10^{-7}$ Torr to keep a steady-state coverage.

The experiments were of the pump-probe type where first the molecules were desorbed with a pump laser pulse impinging normal to the surface and then detected state selectively with REMPI in the gas phase after a well-defined time delay with a tunable probe laser. The desorption was induced with a broad band excimer laser (Lambda Physik EMG 200) with a pulse length of 15 ns and a fluence of mainly 1 mJ cm$^{-2}$ in most of the experiments. The excimer laser was run at three different wavelengths which were 6.4, 5.0 and 3.5 eV depending on the gas mixture used. At a distance of 29 mm the molecules were detected parallel to the surface with a detection laser beam generated by 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 molecules detected could be calculated. Laser light of 344.0–345.5 nm was focussed ($f=75$ mm) into a cell filled with 75 Torr xenon in order to produce VUV laser light at 114.6–115.2 nm via a non-linear process. The emerging VUV light was focussed together with the fundamental via a LiF lens into the centre of the chamber to excite the desorbing CO into the $B^1\Sigma^+$ intermediate state and to ionise the molecules by absorption of a second photon (the fundamental at $\lambda=345$ nm) as described by Rottke and Zacharias [31]. The ions were detected perpendicular to the desorption and detection laser beam via a detector consisting of a repeller, a flight tube, a microchannel plate and a phosphor screen. Our detector views a range of $\pm 30^\circ$ off the surface normal and is used in different experiments for 2D imaging [17]. The background signal was subtracted by running the detection laser at twice the frequency of the desorption laser with the help of a boxcar integrator run in toggle mode.

3. Results

The use of the ($1+1'$) REMPI detection scheme via the $B^1\Sigma^+$ intermediate electronic state is advantageous in order to obtain a good resolution of single rovibrational states [19–22,31]. This is demonstrated by the desorption spectrum shown in Fig. 1, which was recorded at a desorption energy of 5.0 eV with a fixed time delay between desorption and detection corresponding to a velocity of $v=1450$ m s$^{-1}$ and by varying the detection laser wavelength. The selection rules for $\Sigma-\Sigma$-type transitions in the first excitation step allow $\Delta J=\pm 1$ transitions. These P- and R-branch transitions are well separated due to the similarity of the rotational constants in the ground and excited state [32]. Such a good separation is not obtained for the ($2+1'$) REMPI via the same state used in other groups which only allows $\Delta J=\pm 0$ transitions [33]. As CO predissociates at excitation energies above $J'=37$ in $v'=0$, $J'=17$ in $v'=1$ and for all higher vibrational states of the $B^1\Sigma^+$ intermediate electronic state, a drastic drop in intensity of two orders of magnitude is observed within the REMPI spectrum when the threshold for predissociation is reached. For this reason, vibrational transitions of $v''=2\leftarrow v''=0$ and higher cannot be observed although the molecules desorb with a high degree of vibrational excitation as can be seen from smaller extra features due to vibrational excitation of $v''=1$ within the P-branch of $v''=0$.

Examples of velocity flux distributions for single rotational states for the vibrational ground state at three different desorption wavelengths are given in Fig. 2. They were calculated from the time-of-flight distributions which were measured at the maximum of a single rovibrational transition by varying the time between desorption and detection and averaging over up to 300 laser pulses for every single time delay. The distributions shown in the figure were normalised to the same height in order to make the main features better visible. The line drawn through the measured points is a guide for the eye and not a fitted curve. For all three desorption wavelengths the differences in shape are only marginal. For low rotational excitation the distributions show two, though not very pronounced, maxima. The maxima at 300 m s$^{-1}$ and 1000 m s$^{-1}$ do not shift with rotational excitation as becomes clear from fits with two Gaussian distributions. Trying to fit the curves with two Maxwell–Boltzmann distributions or with two superimposed stream velocity distributions is not successful. At a rotational excitation with $J''>18$
only one channel is visible. As there is no coupling between rotation and translation, the rotational temperature for this channel can be obtained from a Boltzmann fit of the intensities extracted from a desorption spectrum taken for a velocity close to the intensity maximum of this channel and only taking $J''>18$ into account. The results for the three different wavelengths were very similar and are listed in Table 1. We obtained rotational temperatures for the fast channel between $900 \pm 100$ K for 6.4 eV and $1100 \pm 250$ K for 3.5 eV. The rotational temperature of the slow channel of $300 \pm 100$ K was calculated from a Boltzmann fit of the integral intensities of the Gaussian fitted to this channel. Similarly to $v''=0$, the velocity flux distributions in $v''=1$ did not change with desorption wavelength, as can be seen in Fig. 3 for one example. The maximum of the monomodal nearly
Table 1  
Desorption cross-sections and rotational temperatures ($v = 1160$ m/s) for CO/Cr$_2$O$_3$(0001)

<table>
<thead>
<tr>
<th>$h\nu$ (eV)</th>
<th>3.5</th>
<th>5.0</th>
<th>6.4</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_{rot}$ (K)</td>
<td>1100±250</td>
<td>900±100</td>
<td>900±100</td>
</tr>
<tr>
<td>$\sigma$ (cm$^2$)</td>
<td>$(5.1±1) \times 10^{-18}$</td>
<td>$(2.3±1) \times 10^{-17}$</td>
<td>$(3.5±1) \times 10^{-17}$</td>
</tr>
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Fig. 3. Velocity flux distributions for $J''=5$, $v''=1$, $E_{des}=3.5$ eV, 5.0 eV, 6.4 eV.

Gaussian distribution with 800 m s$^{-1}$ is in between the two channels in $v''=0$ and does not shift with rotational excitation. We obtained a rotational temperature of 270±100 K from a Boltzmann fit of the desorption spectrum. Further details of the data for a desorption energy of 6.4 eV are given elsewhere [19–22].

While the fast channel and the vibrationally excited molecules origin clearly form a non-thermal process, this is not evident for the slow channel in $v''=0$ in the first place. We assigned the slow channel in an earlier publication to a thermal channel in a preliminary way [19]. Thermal desorption spectroscopy of CO from Cr$_2$O$_3$(0001) shows a desorption maximum around 160±15 K with the desorption starting around 125 K. As the working temperature during the laser experiments was 100 K one could think that in principle a minor amount of desorption due to the temperature jump within the surface could be possible. As we now extended our measurements to 5.0 eV where the excimer laser has more power we could study the intensity dependence of the slow with respect to the fast channel with a better signal-to-noise ratio in a well-defined way. We did not detect any noticeable differences when changing the laser fluence over two orders of magnitude. This is a strong indication that this desorption channel is also non-thermal, though this is not a fully exclusive criterion as thermal desorption induced in the raising part of the temperature jump cannot be fully excluded [34]. Unfortunately, we could not work at lower temperatures due to experimental constraints.

A major information on the desorption mechanism is obtained from the desorption cross-sections, $\sigma$. For such measurements the surface was covered with a saturation coverage of CO and then the background dosing was switched off. Fig. 4 shows a semilogarithmic plot of the REMPI intensities of the desorbed molecules as a function of the number of photons impinged on the surface for the three desorption wavelengths investigated. Assuming a first order desorption kinetics the desorption cross-sections can be obtained from the

Fig. 4. A semilogarithmic plot of the REMPI intensities of the desorbed molecules as a function of photons impinged on the surface ($J''=5$, $v''=0$, $v=1160$ m/s). $E_{des}=3.5$ eV (triangles), 5.0 eV (squares), 6.4 eV (circles).
slopes. The results are given in Table 1. The cross-sections obtained for a single detection wavelength were independent of the translational, rotational and vibrational excitation. The error bars given in Table 1 result from the averaging of up to 25 independent measurements. In order to decide whether the desorption is due to the majority species, a comparison of a gas phase spectrum taken at a well-defined pressure was done with the intensities measured in the desorption spectra. The measured intensities were in the same range as intensities estimated from the desorption cross-sections for saturation coverage [20]. Therefore, minority desorption could be ruled out.

Fig. 5 shows the desorption cross-sections together with an electron energy loss spectrum (EELS) for the clean and the CO-covered Cr$_2$O$_3$(0001) [29]. The strong change of absorption around 4.6 eV, a diminishing of a peak during adsorption of CO, is speculated to be a possible charge transfer surface state of the substrate, as discussed by Ehrlich [29]. Further changes at lower energies are changes of localised surface d–d band transitions [35]. The inset shows the EEL spectrum of the physisorbed system CO/Al$_2$O$_3$(0001) for comparison, in which the CO spectrum can be distinguished from the substrate spectrum in a straightforward way [36]. From the CO/Al$_2$O$_3$(0001) spectrum one can see that the lowest observable transition starts at 5.9 eV peaking at 6.2 eV. It is the a$^3\\Pi$ state, a triplet state which is optically forbidden in the gas phase. For the system of CO/Cr$_2$O$_3$(0001) the adsorbate transitions are much broader without any clearly distinguishable vibrational states and shifted towards higher energies. So it is very unlikely that any absorption of the adsorbate occurs at energies lower than 5.0 eV. For this reason we can conclude that the first excitation step takes place within the substrate.

4. Discussion

With the assumption that the initial excitation takes place within the substrate, as the wavelength dependence of the desorption cross-sections indicates, there are still several possibilities concerning the desorption mechanism which we now want to discuss in more detail. It is also clear from the final state distributions that both channels in $v''=0$ have to be attributed to the same initial electronic excitation as the intensities of the two channels with respect to each other do not change with desorption wavelength.

The actual status of knowledge concerning Cr$_2$O$_3$(0001) is that this transition metal oxide with d$^3$ in Cr$^{3+}$, i.e. only occupied t$_{2g}$ parts of the d band, is a Mott–Hubbard insulator. An excitation above the band gap of 3.3 eV includes an excitonic transition between the d electrons of two neighbouring Cr ions which produces a Cr$^{+2}$ and a Cr$^{+4}$ state [37]. The Cr d bands show little dispersion and thus are strongly localised. We already pointed out that the bonding of the CO molecule to the surface with a resulting flat bonding geometry can be explained by a balance between strong attractive interactions between the 4e and 5o orbitals of the CO with two neighbouring Cr ions and a strong repulsive interaction.
between the 1π and the oxygen bands. However, a change in the electronic structure of the substrate could disturb this balance and might even produce a repulsive excited state. A Menzel–Gomer–Redhead-type of desorption could take place [38,39]. The Pauli repulsion of the oxygen atoms would push the CO into a bent configuration as soon as the interaction of one of the σ orbitals with the d band of one Cr ion is weakened while the molecule moves away from the surface because of the repulsive nature of the electronic state. As soon as the exciton diffuses away from this surface location the adsorbate–substrate system turns back to the electronic ground state. However, the molecule is now far off its equilibrium position and also has gained kinetic energy while moving along the repulsive potential energy surface. As a result, the molecule can desorb with a high degree of angular excitation. The possibility that this channel can occur will be strongly dependent on the time while the exciton is located in the direct surrounding of the adsorbate to affect the bonding. The question of localisation of excitons will be discussed further below.

It is interesting to note that a change in the LEED pattern of Cr₂O₃(0001) from a (1×1) pattern to a (√3×√3)R30° superstructure at 150±15 K has recently been attributed to an order-to-order transition which changes to a disordered phase above 150 K [35]. The (1×1) pattern itself is discussed to be due to a surface reconstruction in which every second Cr atom is missing in respect to the bulk configuration in order to stabilise the polar surface. It is still under investigation whether the observed phase transition destabilises the bonding of CO or even whether the reverse is true: that CO stabilises the (√3×√3)R30° superstructure as for certain CO coverages such a superstructure can also be observed [27] at 100 K. A question, therefore, is whether there might be a laser-induced phase transition which then leads to a destabilisation and thus to desorption of CO.

In both possible mechanisms suggested so far, the main point is that the CO molecule remains neutral during the excitation process. However, the high degree of vibrational excitation can only be explained if a strong change in CO bond length has taken place in an intermediate state. In the gas phase the bond length of CO does not change significantly in the case of the formation of a CO⁺ [32]. On the other hand a strong change is expected for a CO in a triplet electronic excited state or a CO⁻. From the wavelength dependence of the desorption we could rule out a direct excitation of the adsorbate itself, so we strongly favour a CO⁻ intermediate formation to be the origin of the CO excitation. Closely related ²Π negative ion resonances have been observed in a couple of experiments including CO adsorption for systems such as CO/graphite (1.6 eV above the vacuum level [40]) or condensed CO (2.5 eV above the vacuum level [41]). As the work function of oxides is in the order of 4.5 eV and the band gap of Cr₂O₃(0001) is 3.3 eV it might be surprising that the desorption at 3.5 eV should also be due to a CO⁻ intermediate, as has to be concluded from the similarity of desorption behaviour compared to excitation at higher energies. This could only mean that the unoccupied 2π* state into which the electron has to tunnel from the substrate is strongly shifted below the vacuum level. This is not as unlikely as one might think in the first place as the occupied 4σ, 5σ and 1π states are known to shift by up to several electronvolts towards higher binding energies, as already discussed. It is very likely and supported by measurements concerning the rotational alignment [21,22] that the extra electron in the 2π* state of the CO⁻ will have a strong impact on the bonding geometry. The molecule is like NO which is known to have a bent geometry with an angle of 50° in respect to the surface normal [42]. The strong Pauli repulsion between the 2π* electron of the CO⁻ and the oxygen band will push the molecule towards an upright position. At the same time the molecule will be strongly accelerated towards the surface as there is a strong Coulomb attraction between the CO⁻ and the positively charged substrate ions. In the related system, NO/NaO(100), it is known from ab initio calculations that the well depth of such an excited state can be up to a factor of ten deeper in the coordinate of the molecule–surface bond distance. Thus we have to deal with an Antoniewicz type of desorption [43].

So within the model which assumes a CO⁻ formation, the observation of the high degree of
vibrational as well as rotational excitation can be explained. An open question is still the origin of the occurrence of the second desorption channel in \( \nu'' = 0 \). One possibility is that we observe desorption due to an Antoniewicz and the Menzel–Gomer–Redhead mechanism described before. In other words, the initial step in both cases will be an excitonic transition within the surface, however, a certain percentage of the excited electrons can temporarily scatter in a second step into the unoccupied \( 2\pi^* \) state. The intensity distribution in the two channels would therefore reflect the tunnelling probability into the adsorbate state.

A second possibility could be that molecules desorbing in the slow channel might have undergone a single collision via an equivalent second adsorbate position or several collisions with the surface before desorption.

Our discussion was based on the assumption that the band gap transition is Mott–Hubbard-like. Ehrlich [29] has discussed the possibility that a peak in EEL spectra of \( \text{Cr}_2\text{O}_3(0001) \) with a maximum around 4.6 eV might be attributed to a two-dimensional charge-transfer state within the surface. The origin of a reduction of the energy of charge-transfer transitions, which include a transition between \( \text{O}_2\text{p} \) and \( \text{Cr} \) bands and which are calculated to be at 6.2 eV for bulk states [44], might be the recently observed surface reconstruction. So we cannot rule out such a transition as the primary excitation step and the occurrence of the two channels might be attributed to two different band gap transitions. As complex surfaces such as polar surfaces can form domains of different reconstructions (see for example \( \text{NiO}(111) \) [45]) this would mean that in the future we might find examples of surfaces which show strongly domain-independent photochemistry. A similar reconstruction-dependent photochemistry involving surface states has been found for the system \( \text{NO}/\text{Si}(111) \) \( 7 \times 7 \) [46]. We plan to extend our investigations to wavelengths around 4.6 eV in order to test this explanation.

A further possibility which we cannot rule out at the moment is that the two channels are due to different mediate life-times which are connected to different relaxation probabilities into different states [25]. As could be seen in Fig. 5, \( \text{Cr}_2\text{O}_3(0001) \) shows pronounced structures in electron energy loss spectra within the band gap due to local bulk and surface d–d transitions within the same Cr atom which are typical for transition metal oxides [35]. The important question is which role these transitions, also known as localised Frenkel excitons [37], play in relaxation processes of electronically excited states and lifetimes in contrast to oxides of the main group. In spin polarised EELS experiments on the related system, \( \text{NiO}(100) \), it has been shown that a strong spin exchange interaction between different electronic excited states particularly of a triplet–triplet type of interaction in local surface states could be observed [47]. A strong spin flip has also been observed for \( \text{Cr}_2\text{O}_3(0001) \) [48]. On the other hand, the Frenkel excitons, particularly those belonging to surface states, could also lead to a strong localisation of the excited state within the substrate in states which have a very low interaction with the ground state, similar to transitions in ruby. We want to emphasise further investigations of the experimental as well as of the theoretical type which help to illuminate the electron dynamics of transition metal oxides.

5. Summary

From quantum state resolved measurements of the UV-laser-induced desorption of CO from \( \text{Cr}_2\text{O}_3(0001) \) at three different excitation energies above the band gap of the substrate (3.5 eV, 5.0 eV and 6.4 eV) we conclude that the initial excitation of the desorption process takes place within the substrate. Whether the substrate excitation is Mott–Hubbard-like or a charge-transfer transition is still open. At all three wavelengths the final state distributions are almost identical except for the overall desorption cross-sections. They show bimodal velocity flux distributions with high rotational excitation in the fast channel and low rotational excitation in the slow channel for the vibrational ground state. vibrationally excited CO in \( \nu'' = 1 \) has a monomodal velocity flux distribution with a maximum in between the two of the vibrational ground state and a low rotational excitation indicating a coupling of this coordinate
to the centre of gravity movement along the surface normal. The high degree of vibrational excitation indicates a strong change in bond length during the desorption process. Whether this is due to a CO\(^-\) formation is not clear as the flat bonding of CO to the surface is not yet fully understood. A CO\(^-\) formation as an intermediate state at 3.5 eV implies a strong shift of the 2\(\pi^*\) orbital in respect to the gas phase. This is not so unusual compared to the strong shifts of the 4\(\sigma\), 5\(\sigma\) and 1\(\pi\) orbitals of the CO to higher binding energies. A destabilisation of the CO bond by a substrate excitation resulting in a repulsive intermediate state without a charge transfer to the adsorbate cannot be fully excluded as a further possible desorption channel, which might even be present simultaneously with the others discussed.

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