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UV laser-induced desorption of CO from Cr₂O₃(111). A fully quantum state resolved mapping of the desorbing species

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Abstract

The laser-induced desorption of CO adsorbed on an epitaxially grown film of Cr₂O₃(111) has been studied using 193 nm (6.4 eV) laser light. The velocity flux distributions of the desorbing neutral CO in its ground electronic state were recorded quantum state specifically by making use of a (1+1') REMPI (resonance enhanced multiphoton ionization) technique. Single rovibrational states of the desorbing CO could be selected by using the (B¹Σ⁺ ← X¹Σ⁺) transition in the VUV at ≈ 115 nm for the first excitation step of the REMPI process. Excellent resolution was obtained in contrast to the most commonly used (2+1) REMPI process for the same intermediate state. The velocity flux distributions were bimodal for $v''=0$ and monomodal for $v''=1$. The high desorption cross section of $(3.5 \pm 1) \times 10^{-17}$ cm² is typical for the desorption from oxide surfaces.

1. Introduction

Photoinduced processes on surfaces, particularly processes in which lasers are involved, have found an increasing number of applications in industry and research and have been reviewed in a variety of papers [1–16]. However, there is still little knowledge of the elementary steps of these processes. As the excited states of the photoprocesses are short lived a direct access to the dynamics is difficult. The most detailed insight can be obtained by well characterizing adsorbate systems before and after the process and measuring final state distributions of the products [5,10,12,15,16].

From previous experiments it was suggested that the adsorbate geometry can have a direct impact on the photodesorption process [17–20]. Bimodal non-thermal velocity flux distributions of NO desorbing from epitaxially grown NiO(100)/Ni(100) and NiO(111)/Ni(111) were explained as being due to

the bent orientation of the adsorbed NO. The key for the dynamics is the bending vibration of the molecule and the momentum associated with the center of mass motion perpendicular to the surface. The latter has to be taken into account at the instant of excitation and thus is crucial for the development of the system after the excitation.

In order to test the model we chose an adsorbate system with a different geometrical orientation. In the case of CO adsorbed on a film of Cr₂O₃(111) epitaxially grown on Cr(110) the molecular axis of CO is oriented parallel to the surface plane [21]. In contrast to NO on NiO the excitation of the bending vibration of this system should not lead to a noticeable momentum perpendicular to the surface. Furthermore, the system chosen was studied with a variety of surface science techniques and is thus well characterized [21]. CO adsorbs without any sign of dissociation or reaction as a single species at chromium sites with an adsorption enthalpy of 44 kJ/mol.

The detection of the desorbing neutral CO in the molecular ground state is not easy as, in contrast to NO, the optically allowed electronic transitions for CO are situated in the VUV [22]. This wavelength region can only be reached with common laser spectroscopic methods by using multiphoton processes or generating the necessary VUV by making use of non-linear effects. For this reason only a few state selective experiments on CO in laser desorption experiments have been done so far [23–25]. Popular in scattering experiments as well as in gas phase experiments is the use of the (2+1) REMPI process via the B $^1\Sigma^+$ state. However, for this transition there is a lack of resolution in single rovibrational states [26]. In order to detect the desorbing CO state selectively we chose a REMPI (1+1') technique. We resolved single rovibrational states by using the (B $^1\Sigma^+ \leftarrow$ X $^1\Sigma^+$) transition in the VUV at ≈ 115 nm for the first excitation step of the REMPI process [27]. Data of the velocity flux distributions for single rovibrational states will be presented.

2. Experimental apparatus

Our experiments were carried out in an ultra-high vacuum chamber equipped with facilities for low-energy electron diffraction (LEED), Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS), quadrupole mass spectrometry for residual gas analysis and thermal desorption spectroscopy (TDS), and neon ion bombardment. Details of the system are given elsewhere [17]. The sample was spot welded to two tungsten wires which were connected to two tungsten rods mounted on a liquid nitrogen reservoir cooled to 100 K. Heating of the crystal was done via electron bombardment. The Cr(110) sample was cleaned via prolonged sputtering with Ne ions and oxidized by heating the crystal to 500 K in an atmosphere of 10^{-6} Torr oxygen for 3 min. Annealing to 1000 K removed excess oxygen leading to a well-defined oxide film with the hexagonal pattern of Cr₂O₃(111).

The laser experiments were of the pump-probe type. The desorption was initiated normal to the surface by a pulsed broad band excimer laser (Lambda Physik EMG 200) run in ArF mode ($\lambda=193$ nm, $h\nu=6.4$ eV) with a pulse duration of 15 ns and a rep-

etition rate of 2 Hz. The typical laser fluence was 1 mJ/cm² per pulse. The desorbing molecules were probed parallel to the surface at a distance of 24 mm by making use of a (1+1') REMPI technique. We made use of the B $^1\Sigma^+(v'=0, 1) \leftarrow$ X $^1\Sigma^+(v''=0, 1)$ transitions of CO for the first excitation step by using tunable VUV light in the 114.5–115.5 nm range to excite the molecules state selectively. The absorption of a second photon, the fundamental of the laser light generating the VUV at 343.5–346.5 nm, led to the ionization of CO. This method for detecting gas phase CO is explained in more detail by Rottke and Zacharias [27]. Besides the sensitivity limit of about 4×10^5 molecules per cm³ and state the method has the advantage of being easy to use for deriving the rotational distribution of the X $^1\Sigma^+$ state. The reason for this is that the ionization probability does not vary with the rotational quantum number within the experimental resolution due to the saturation of the ionizing step [27]. 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 and a phosphor screen. The tunable VUV laser light was generated via frequency tripling in xenon [28]. The fundamental radiation at ≈ 345 nm was obtained from an excimer laser (XeCl, Lambda Physik LPX 205 i CC) pumped dye laser (Lambda Physik LPD 3002) operated with *p*-terphenyl dissolved in dioxane (pulse energy 10 mJ, 10–15 ns pulse length, repetition rate 4 Hz). The laser light was focused into the tripling cell by a planoconvex lens ($f=75$ mm). The optimum conversion was achieved at a xenon pressure of 75 Torr. The emerging VUV light together with the UV light was focused via a LiF lens ($f=50$ mm at $\lambda=248$ nm) into the center of the chamber.

Under the experimental conditions only a monolayer is formed. In order to keep a constant surface coverage prior to each of the pump excimer laser pulses the sample was redosed via a 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.

3. Results and discussion

Fig. 1 shows a rotationally resolved REMPI spectrum of desorbed CO. It was obtained by keeping the delay between the pump and the probe laser fixed and by scanning the VUV wavelength with a resolution of 0.001 nm. The spectrum was taken at a delay time corresponding to a velocity of 1330 m/s of the desorbing molecules. According to the selection rules for a ${}^1\Sigma^+ \leftarrow {}^1\Sigma^+$ single-photon transition the spectrum shows simple P and R rotational branches ($\Delta J = \pm 1$). The spacing of the lines is nearly equidistant as the molecular constants in both the upper and the lower electronic state are similar [29]. The desorption cross section was obtained by fixing the laser wavelength to the maximum of a rovibronic transition and monitoring the REMPI signal as a function of number of pulses impinging on the surface covered initially with a saturation coverage. For this particular experiment the ambient pressure was kept below 2×10^{-10} Torr. The data were analyzed by assuming first-order kinetics leading to a photodesorption cross section of $(3.5 \pm 1) \times 10^{-17}$ cm² for $v''=0$ independent of the rotational quantum number and velocity. This is a typical value for oxide surfaces when the excitation takes place in the charge transfer region of the substrate [17,18].

Fig. 2 shows the P branch of the spectrum in more detail for two different delay times corresponding to velocities of 1330 and 270 m/s of the desorbing molecules. Besides the strong ($v'=0 \leftarrow v''=0$) transitions one observes further lines. These can be assigned to ($v'=1 \leftarrow v''=1$) rotational transitions of vibrationally excited CO. A sudden intensity change can be noticed between $J'=37$ and 38 for $v''=0$ and $J'=17$ and 18 for $v''=1$. This is due to the predissociation

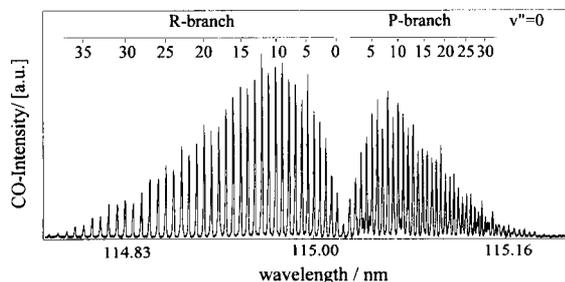


Fig. 1. Rotation–vibration spectrum of CO desorbing from $\text{Cr}_2\text{O}_3(111)$ for molecules with a velocity of 1330 m/s.

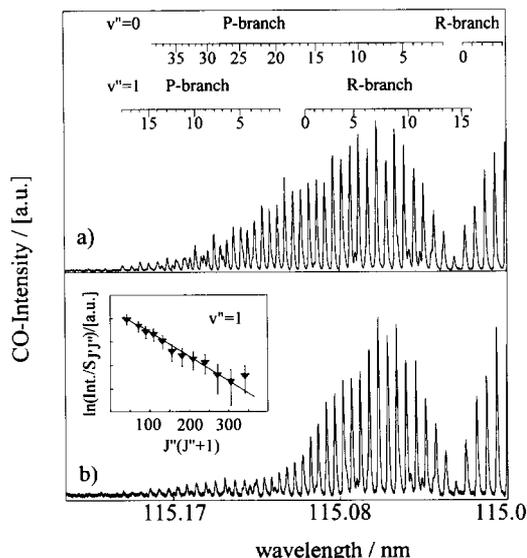


Fig. 2. P-branch of the rotation–vibration spectrum of CO desorbing from $\text{Cr}_2\text{O}_3(111)$ showing vibrationally excited CO. (a) Velocity 1330 m/s; (b) velocity 270 m/s; the inset shows a rotational Boltzmann plot for $v''=1$.

limit of the B ${}^1\Sigma^+$ state. As one can see from Fig. 2 the rotational distribution is strongly dependent on the velocity of the desorbing species particularly in $v''=0$. In order to get the proper rotational temperature the velocity flux distribution has to be recorded for each rotational transition. For this purpose the VUV probe laser was fixed to the maximum of a specific rovibronic transition. The probe laser pulses were electronically delayed by 0–800 μs relative to the pump laser pulses. For each single delay the signal was averaged over 150 shots. The intensity of the pump and the VUV probe light were recorded in order to correct for intensity fluctuations. As such a time of flight (TOF) spectrum is dependent on the distance from the sample to the probe volume we transform the TOF spectrum into a velocity flux distribution. Fig. 3 shows velocity flux distributions for several rotational states in $v''=0$ and $v''=1$.

In $v''=0$ we observe bimodal distributions with the slow channel being rotationally cold and the fast channel being rotationally hot. In $v''=1$ we find monomodal velocity flux distributions. There is only little coupling between rotation and translation for this case as the maximum of the distribution changes little with increasing rotational excitation. There-

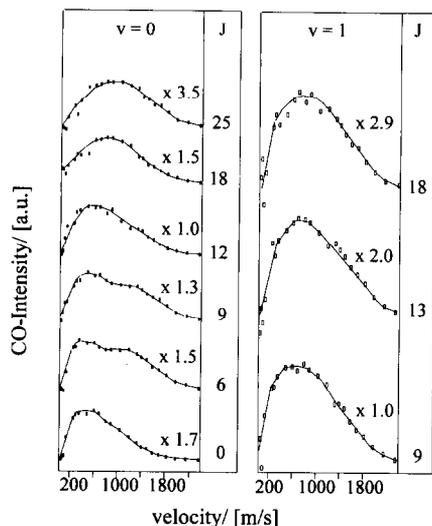


Fig. 3. Velocity flux distributions for CO/Cr₂O₃(111) for varying rotational quantum numbers in $v=0$ and $v=1$.

fore, we can obtain the rotational temperature of $v''=1$ from a semi-logarithmic plot of the line intensities of non-overlapped transitions divided by the Hönl–London factor $S_{J',J''}$ versus the rotational energy as is shown in the inset in Fig. 2b. The rotational temperature of $v''=1$ is 270 K. The maxima of the velocity flux distributions in $v''=1$ are shifted by 200 m/s to slower velocities when comparing the fast channel in $v''=0$ to $v''=1$. In order to obtain the rotational temperature and vibrational population for $v''=0$ we fitted the curves of the velocity flux distributions with Student-t distributions. Fits using simple or modified Maxwell–Boltzmann distributions could not fit our data well. From Boltzmann plots of the integrals of the curves obtained thus, we obtained rotational temperatures of 300 K for the slow and 900 K for the fast channel in $v''=0$.

The monomodal velocity flux distribution in $v''=1$ is consistent with the model proposed in refs. [19,20]. The origin of the bimodality in $v''=0$ is not clear at the moment. As there is only one species at the surface there must be two different channels for the desorption process. The most likely explanation is that there is one thermal and one non-thermal channel as was found in systems such as NO₂/NO/Pt(111) or NO/Pt(100) [30,31]. From thermal desorption spectroscopy it is known that thermal desorption of CO already starts at 25 K and peaks at 60 K above

the actual working temperature of 100 K [21]. Such a temperature rise can be achieved by a temperature jump at the surface induced by the laser. The ratio between slow and fast channel is sensitive to the laser fluence supporting the interpretation of one channel being thermal. Thermalization with the surface via a trapping desorption process could also lead to a thermal desorption channel [30]. Expressing the translational energy in terms of $\langle E_{\text{trans}} \rangle / 2k$ [32] we obtain for the slow channel with a velocity of 300 m/s a temperature of 100 K close to the surface temperature. However, the rotational temperature of 300 K is higher. This may be due to the difficulty of fitting the data. The slow channel only occurs at low rotational quantum numbers and is strongly overlapped for higher quantum numbers by the fast channel. So only few data can be used in order to extract the rotational temperature.

We found indication of a minor amount of ion desorption. The wavelength independent ion signal led to a non-linear background in the TOF spectra and was only noticeable and, therefore, had to be subtracted for weak signals. The actual experimental arrangement does not allow us to identify the nature of the ions. From gas phase experiments it is known that two-photon absorption of 6.4 eV of CO via the a³Π state can lead to subnanosecond photolysis of CO [33,34]. Such a two-photon absorption is even more likely at the surface as the antiferromagnetic Cr₂O₃(111) can modify the strict selection rules concerning spin conservation in an optically allowed transition. In electron energy loss spectra (EELS) a noticeable absorption band, though rather broad and peaking at 9 eV, can be observed around 6.4 eV [35]. However, due to the broadness of the band the amount of dipole as opposed to electron impact excitation also allowed in EELS is not easy to extract at this wavelength. The two-photon dissociation of CO in the gas phase is interpreted as being due to an interaction between an a³Π Rydberg state and a ³Π valence state at 12.8 eV. This interaction leads to the dissociation and impedes multiphoton ionization. On the other hand, no remarkable atomic carbon formation at the surface is observed in our laser experiments. The ionization potential of CO is 14.0139 eV in the gas phase [36]. In principle, ions can already be formed in photoinduced processes on surfaces at energies that are up to the amount of the work func-

tion of the substrate lower than the vacuum value for the ionization [4]. This leads to the preliminary interpretation that the observed ions are possibly CO^+ .

One difficulty in getting the vibrational temperature is the large overlap of $v''=1$ transitions with transitions of the P branch of $v''=0$. We obtained the temperature by integrating the velocity flux distributions of non-overlapped states normalizing them by the rotational weight factor. Assuming that the fast component of $v''=0$ belongs to the same channel as $v''=1$ we obtain a vibrational temperature of 2000 K using the Franck–Condon factors of ref. [37]. The noticeable population of $v''=1$ can be explained by a temporal change of the C–O distance prior to desorption. In the case of NO on NiO(100) and NiO(111) this could only be explained by a change in the NO bond in the excited state of the photoprocess. In our case the vibrational excitation may just be due to the release from the surface. On the other hand, as indicated by the appearance of ionic desorption the a $^3\Pi$ state may play a role in the excitation process. In the gas phase the bond length of this state is 7% longer than that of the ground state value. If the situation is similar at the surface both effects may sum and lead to the observed vibrational excitation.

In principle, a substrate mediated process could also be possible. In Cr_2O_3 there are several optically allowed Cr d–d transitions below 5 eV [38]. The first of the charge transfer transitions is calculated to be at 6.2 eV [39]. In the case of NiO the latter dominate the desorption process while the Ni d–d transitions are not as efficient [18]. However, the formation of an intermediate CO^- similar to NO/NiO is much more difficult than for NO. The $^2\Pi$ negative ion resonance of CO for weakly bound systems can have values such as 1.6 eV (on graphite [40]) or 2.5 eV (condensed CO [41]) above the vacuum level. Assuming a similar value for CO/ Cr_2O_3 the formation of CO^- would just be feasible but is probably not efficient. Whether the desorption is substrate mediated or influenced by the a $^3\Pi$ state of the adsorbate will be seen from further experiments carried out at different wavelengths.

4. Conclusions

The UV laser-induced desorption of CO from an epitaxially grown film of $\text{Cr}_2\text{O}_3(111)$ was studied using 193 nm (6.4 eV) laser light. Neutral CO was detected in its ground electronic state fully quantum state resolved by making use of a $(1+1')$ REMPI technique. In contrast to the most commonly used $(2+1)$ REMPI process resolution of single rovibrational states was obtained by using the $\text{B } ^1\Sigma^+(v'=0, 1) \leftarrow \text{X } ^1\Sigma^+(v''=0, 1)$ transitions in the VUV at ≈ 115 nm for the first excitation step of the REMPI process. The cross section of $(3.5 \pm 1) \times 10^{-17} \text{ cm}^2$ is quite high for laser processes at surfaces and typical for the desorption from oxide surfaces. The system was chosen in order to test a model for laser-induced desorption developed to explain bimodal non-thermal velocity flux distributions of NO desorbing from NiO(100) and NiO(111) [17–20]. The model suggests that the adsorbate geometry, particularly the momentum associated with the center of mass motion perpendicular to the surface, is responsible for the bimodality. As the molecular axis of CO on $\text{Cr}_2\text{O}_3(111)$ is oriented parallel to the surface plane [21] the momentum perpendicular to the surface should be small. Consistent with the model we observe monomodal velocity flux distributions for vibrationally excited CO in $v''=1$. The velocity flux distributions for $v''=0$ were bimodal. In the case of CO/ $\text{Cr}_2\text{O}_3(111)$ the temperature jump at the surface induced by the laser can already lead to some thermal desorption. The translational temperature of the slow channel of 100 K is close to the actual working temperature and, therefore, supports the preliminary interpretation of this channel being thermal. However, the desorption process itself may be different, i.e. adsorbate mediated in contrast to the substrate mediated process in NO/NiO(100) and NiO(111). This interpretation is supported by the minor amount of ion desorption for CO/ $\text{Cr}_2\text{O}_3(111)$ observed which we interpret as being due to a two-photon process via the a $^3\Pi$ state of adsorbed CO. Whether this interpretation holds will be seen from further experiments carried out at different wavelengths.

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