

UV LASER-STIMULATED RESONANT DESORPTION FROM METAL SURFACES: NO/Ni(100)

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Received 5 January 1987; in final form 18 February 1987

NO chemisorbed on a Ni(100) surface at 170 K, has been desorbed with UV laser light (ArF, 193 nm = 6.42 eV) in the energy range of the most intense electronic absorption of the NO/Ni(100) system. The rotational and vibrational state distribution of the desorbing molecules is probed via laser-induced fluorescence. The desorbing molecules are vibrationally and rotationally excited. The rotational distribution is markedly non-Boltzmann. The velocity distributions are narrow and very different for various rotational states. They cannot be fitted to a Maxwell distribution. We believe that these results provide evidence for the resonant nature of the light-absorption-desorption process for NO on a Ni(100) surface.

1. Introduction

Light-induced gas-surface interactions have received considerable attention in recent years [1-3]. For UV photon-induced desorption studies the experiments and results have been critically reviewed and the general conclusion was that for prototype gas-metal systems such as CO on nickel or tungsten, the observed photodesorption was mainly thermal in nature [4,5]. A resonant effect, if present at all, was assumed to have a cross section of less than 10^{-22} cm², which is equivalent to less than 10^{-8} molecules desorbed per photon [1]. Only very few exceptions were noted where quantum yields above 10^{-8} have been measured at sufficiently high excitation energy, i.e. $E_{\text{exc}} = 5$ eV [6]. These higher yields were ascribed to resonance effects and have been interpreted within a model suggested by Menzel and Gomer [7] and Redhead [8] (the MGR model), originally proposed in the context of electron-stimulated desorption. Specifically, the MGR model consists of a two-step process: Desorption is initiated by an electronic

excitation from the ground state of the adsorbate-substrate complex to a repulsive excited state of the system. As a consequence, the adsorbed particle begins to move away from the surface, and, if deexcitation does not occur sufficiently rapidly, desorbs as a neutral species or an ion depending on the nature of the excitation process.

In the electron-stimulated desorption studies of Burns and co-workers [9], quantum state distributions measured via laser-induced fluorescence (LIF) indicated that NO desorbs from polycrystalline Ni by a resonant process which can be interpreted in terms of the MGR model. However, there have only been a few investigations in which lasers were used to induce the desorption process [1-3]. In most of these studies the desorbing neutrals were analyzed with a mass spectrometer, in some cases also by LIF. Laser detection has the pronounced advantage that time-of-flight distributions can be determined state selectively. In recent years a series of studies have been carried out on the collisional excitation of NO on various surfaces via laser-induced fluorescence

(LIF) [2,10]. Using this technique, considerable progress has been made towards a microscopic understanding of gas-surface reaction dynamics [11-14]. Most of these studies used infrared lasers [10,14-17], and there is some evidence that, even though the absorption process may be resonant, the absorbed energy is dissipated between neighbouring molecules and the substrate via phonon coupling, so that one finally observes a thermally induced desorption process [18,19]. King and co-workers [14] recently investigated the distribution of rotational states of NO by LIF after laser-induced thermal desorption (LITD) at 532 nm. In none of these studies have selective features been found in the distribution of the desorbed molecules.

The present work was based on the idea that by exciting electronic excitations in the adsorbate with UV light, a resonant desorption process may be induced. Some evidence for such an effect has recently been suggested in connection with the "Srinivasan effect" [20]. In this Letter we report the results of such an experiment: NO is adsorbed on a Ni(100) surface at 170 K, and desorbed with UV-laser light (ArF, 193 nm). This energy is in resonance with a strong electronic excitation of the adsorbate, as has been determined using electron energy loss spectroscopy [21]. The rotational and vibrational state distribution of the desorbing molecules is probed by LIF. We show that the state distribution of the desorbing molecules depends on the bonding state of the NO molecules on the surface. In particular, if NO is molecularly chemisorbed on the surface, the desorbing molecules are strongly vibrationally excited, even though the surface-induced temperature jump is less than 50 K. The rotational distributions are non-Boltzmann. Different rotational states exhibit different velocity distributions, the narrow shapes of which cannot be fitted to a Maxwell distribution [22], and are independent of the distance from the surface.

2. Experimental details

Fig. 1 is a schematic of the experimental apparatus. The Ni(100) crystal is situated within a turbomolecular pumped ultra-high-vacuum system (base pressure 10^{-8} Pa), the details of which will be pub-

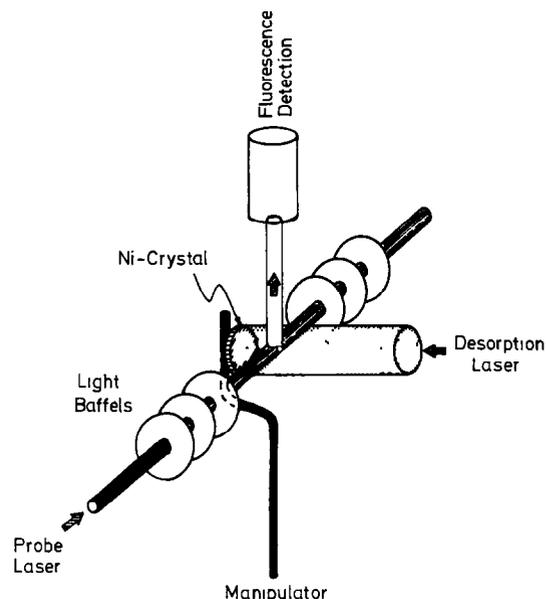


Fig. 1. Schematic representation of the experimental apparatus.

lished elsewhere [23]. The crystal, which can be resistively heated, is mounted on a sample manipulator. The sample can be cooled via copper braids connected to a liquid-nitrogen reservoir to about 170 K. The chamber is equipped with an Ar ion gun to clean the crystal by sputter-anneal cycles [21]. The residual gas can be analyzed with a mass spectrometer. The experiments were performed under a constant ambient pressure of NO, typically 10^{-5} Pa.

The desorption is initiated by an ArF excimer laser (Lambda Physik EMG 200) at 193 nm, which irradiates normal to the surface. Rather low energies of typically 3 mJ/cm^2 are used to desorb the NO which is detected state selectively by LIF via the ${}^2\Pi-{}^2\Sigma$ absorption band at 226 nm with a tunable UV probe laser [24]. CaF_2 windows are used to transmit laser light and fluorescence.

The probe laser is directed parallel to the surface at a variable distance of 10-20 mm. The relative laser-to-surface distance is adjusted with the manipulator. The fluorescence is measured with a photomultiplier (EMI 9813QB), and transmitted to a boxcar integrator. The diameter of the probe laser ($\approx 3 \text{ mm}$) determines the velocity resolution, and together with the imaging optics determines the detection volume. Efficient elimination of scattered light of both lasers

is crucial. The most severe problem is caused by fluorescence that originates from ArF laser scatter. This fluorescence is suppressed by a gating technique: The voltage between the cathode and the first dynode of the photomultiplier (PMT) is only turned on after the excimer laser has been fired. In addition, two UV reflection filters (Schott UV-R-250) are mounted in front of the PMT which transmit at 250 nm with a fwhm of 20 nm. Only a small part of the excimer fluorescence spans this frequency range. Scattered light from the probe laser is suppressed by highly reflective, conical light baffles and by the UV reflection filters which eliminate direct 226 nm scatter. In this way only the non-diagonal part of the fluorescence is sampled. The UV reflection filter causes problems in the comparison of the relative populations in different vibrational states. Because the Franck-Condon factors are different both in absorption and emission, the detection efficiency for the $v'' = 1$ state relative to the $v'' = 0$ state is approximately reduced by a factor of 3.5. The relative sensitivity of the detection for the different rotational states and branches was checked by a 300 K room temperature probe of NO molecules.

With this apparatus two types of experiments were carried out. Firstly, in the time-of-flight (TOF) experiments the probe laser is tuned to detect NO in one specific quantum state. The delay of the probe relative to the desorption laser is varied and the resulting fluorescence intensity monitored. This technique allows us to measure TOF distributions for single quantum states of the desorbed species. Secondly, the nascent quantum state distributions are recorded at a given delay in the usual way [24]. To discriminate between residual and desorbing NO the desorption laser is fired at 5 Hz, whereas the probe laser operates at 10 Hz. With every other pulse either the signal I_1 of the residual NO or the signal I_2 corresponding to both residual NO and laser-desorbed NO is measured. The boxcar is set such that the difference signal of two neighbouring pulses is formed automatically. In this way the boxcar signal corresponds to the difference intensity ($I_2 - I_1$), which is exclusively due to desorbed NO.

3. Results and discussion

Figs. 2–5 show quantum state and velocity distributions of desorbed NO, which we shall discuss consecutively.

Fig. 2 shows a collection of spectra taken under two different conditions. The spectra in the upper panel are taken after the cold (170 K) Ni(100) surface has been exposed for a long period to the residual NO gas, i.e. the surface is covered with undefined reaction products. We denote this surface “dirty” in the following. The spectra in the lower panel are taken immediately after heating the crystal for a short time up to approximately 400 K and cooling to 170 K. We call this surface “clean”. We have used conditions under which it can be assumed that the surface is impurity free and well ordered [21]. However, our present apparatus does not allow for an independent check of the cleanliness and order of the surface. On the left- and right-hand sides of fig. 2 different sections of the LIF spectrum of NO [25] are shown. In the spectrum on the right-hand side only low-lying rotational states of the vibrational ground state $v'' = 0$ are probed. In contrast, the section on the left side contains contributions from both high rotational states of $v'' = 0$ and some lower rotational states of $v'' = 1$. The wiggly lines above and below the spectra represent the variations of the laser power for comparison. The spectra are well resolved and show a good signal-to-noise ratio. To estimate the number of desorbed species, we can compare directly the LIF signals from the residual NO with those from the desorbed NO. The signal induced by the desorption laser is of the same order of magnitude as the signal from the residual gas. This implies that the density of desorbed NO is approximately 10^{-5} Pa. At this pressure collisions among the desorbed species can be excluded. The most striking feature in fig. 2 is the large difference between the NO desorbed from the “dirty” and the “clean” Ni surface. This difference is most pronounced on the left-hand spectrum, where the high rotationally and vibrationally excited NO is formed almost exclusively from the “clean” surface. As mentioned in section 2, the vibrationally excited NO is detected with much less efficiency than vibrational ground state NO. However, even taking into account this factor there is hardly any noticeable population of vibrationally excited states of NO desorbed

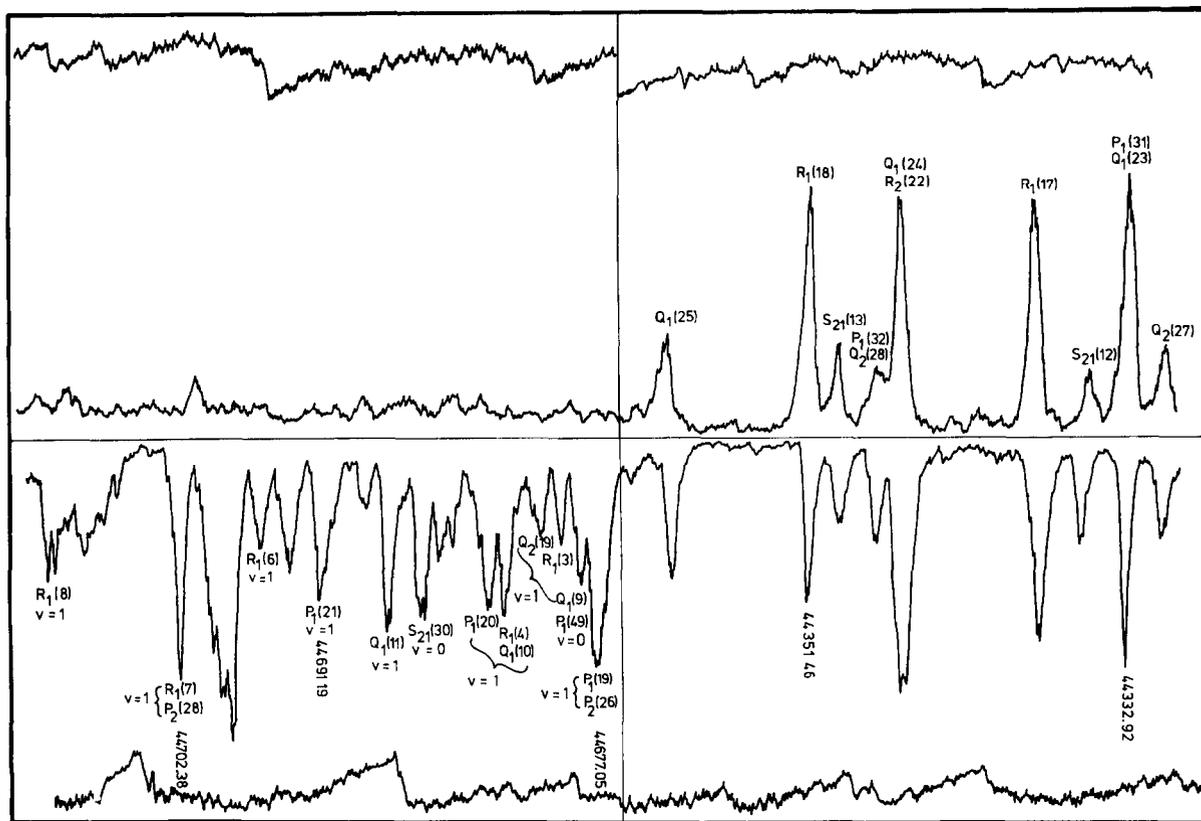


Fig. 2. LIF spectra of desorbing NO molecules. On the left a spectral region within the vibrational band $v=1$ of the probed ${}^2\Pi-{}^2\Sigma$ excitation is plotted; on the right a spectral region within the vibrational band $v=0$ is shown. For some lines the excitation frequencies are given in cm^{-1} (e.g. 44351.46). Upper panel: "dirty" Ni(100) surface. Lower panel: "clean" Ni(100) surface.

from the "dirty" surface. Clearly, the important observation is that the situations dramatically changes as soon as we change the preparation conditions of the metal surface. Obviously, under the present conditions the $v=0$ region changes only moderately as far as relative populations of rotational levels are concerned. However, the $v=1$ region now shows much higher population, and taking the abovementioned considerations regarding relative intensity distributions into account, it is estimated that approximately the same amount of NO is formed in $v=0$ and $v=1$ for the "clean" crystal. Without any further experimental evidence, it is obvious that such an observation cannot be explained by a thermal process: it suggests a resonant excitation-desorption process. This will be confirmed both by the TOF results and the rotational state distributions.

Fig. 3a shows a series of TOF spectra of the "clean" surface for the quantum state ${}^2\Pi_{1/2}, N=17$ as a function of distance from the crystal surface. The rise in intensity at short times is an experimental artefact resulting from the fluorescence of the ArF laser. The inset of fig. 3a shows the linear shift of the peak maximum with increasing distance. Indeed, if we extrapolate the d versus TOF dependence we reach the origin of the plot, corroborating the above statement. Fig. 3b allows a direct comparison of the velocity distributions. The velocity distributions coincide, which indicates that desorption takes place within the time period of the laser pulse. Their widths are compatible with a "thin sheet" of molecules leaving the surface. As mentioned above, the present width is determined by the diameter of the probe laser. This explains the slightly larger width at smaller distances from the surface. For comparison a Maxwellian

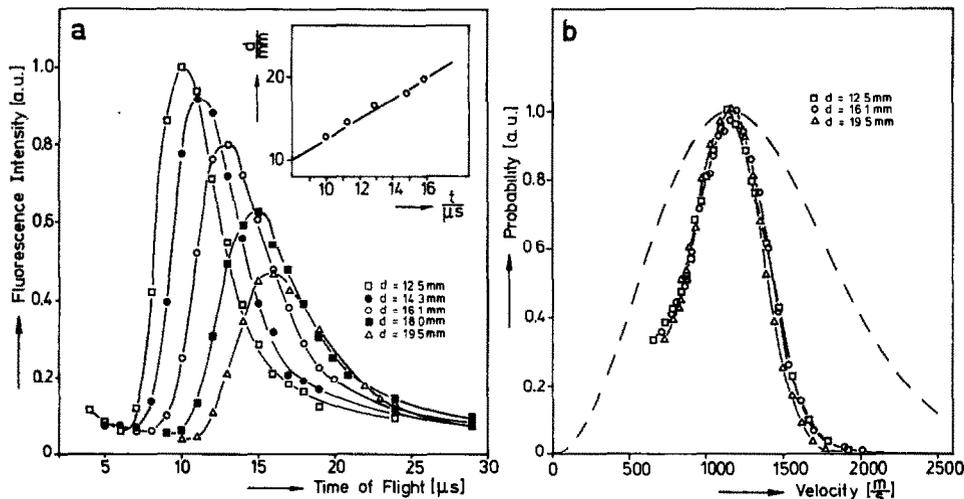


Fig. 3. (a) TOF spectra of the rotational state ${}^2\Pi_{1/2}$, $N=17$ for various distances (d) between the metal surface and the probe laser. (b) Velocity distribution calculated from the TOF spectra in (a) in comparison with a Maxwell distribution.

velocity distribution for a temperature of 2800 K is plotted. It has been calculated so as to fit the position of the maximum of the observed distributions. Clearly, the observed distributions are much too narrow to be represented by a Maxwell distribution. The true width of the distributions may be even smaller if the finite width of the probe laser were eliminated.

The translational energy in the desorbed molecules is too high to be explained by laser heating of the substrate. The desorbing laser pulse can cause a

maximum temperature rise of less than 50 K[†], i.e. from 170 K to less than 220 K, in the metal surface under our experimental conditions. This result is obtained assuming that all energy is dumped into the surface. Because the TDS results show that NO starts

[†] This value (exact: 38 K) has been calculated by the method of Bechtel [26] to solve the heat diffusion equation, using a program written by Schäff [27]. As input we have used optical constants from ref. [28].

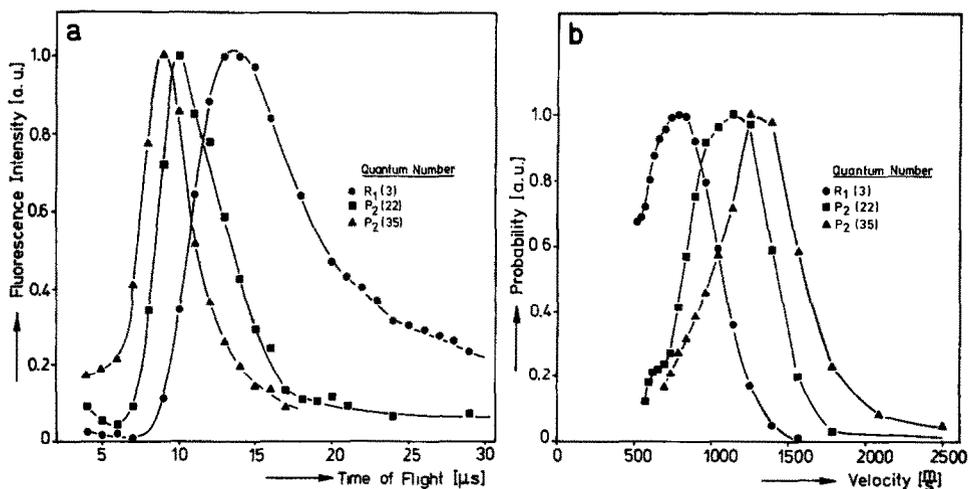


Fig. 4. (a) TOF spectra for various rotational states. (b) Velocity distributions corresponding to (a).

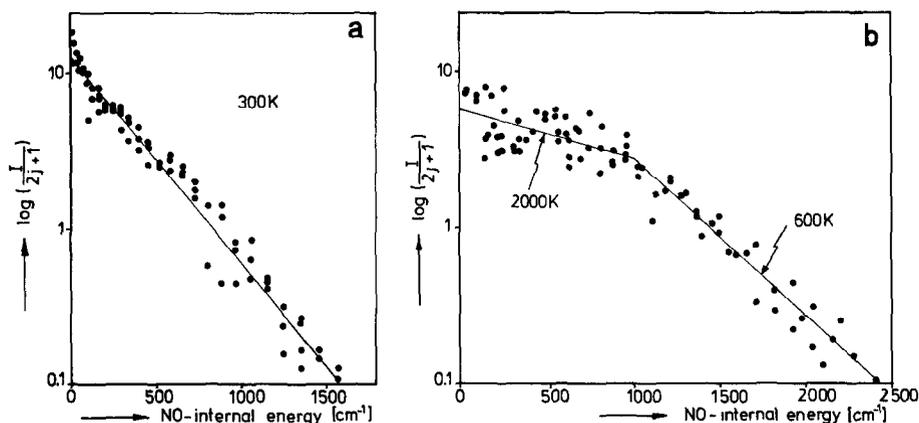


Fig. 5. Rotational state distributions: (a) for 300 K NO from a reference cell; (b) for desorbed NO with a delay of 9 μ s at a distance of 12.5 cm from the surface. The slopes of the two lines indicate a Boltzmann temperature of 2800 K (lower states) and 600 K (higher states). The same symbol has been used for all different rotational branches.

to desorb only above 300 K from Ni(100) [23], a thermal induced desorption mechanism can be definitely excluded.

Fig. 4a shows velocity distributions obtained for the "clean" surface for three rotational states, i.e. for a low (${}^2\Pi_{1/2}$, $N=3$), an intermediate (${}^2\Pi_{3/2}$, $N=22$), and a high (${}^2\Pi_{3/2}$, $N=35$) rotational state. Fig. 4b shows the corresponding velocity distributions. For low rotational states we find a low translational energy content, and for high rotational states a high content. This behaviour suggests that more energy is transferred to the surface for low than for high rotational quanta.

Finally, fig. 5 shows two rotational state distributions as Boltzmann plots for the "clean" surface. The distribution on the left has been taken on a reference cell of NO at 300 K, the other on desorbing NO molecules at a delay of 9 μ s and a distance of 12.5 mm. Clearly, while the Boltzmann plot of the rotational distribution of 300 K NO in the reference cell can be fitted by a straight line of corresponding temperature, the rotational distribution of the desorbing molecules exhibits strong deviations from the behaviour observed in the reference cell. Therefore, as with the vibrational and velocity distributions, the rotational distributions exhibit selective features for the desorbing molecules corroborating a resonant absorption-desorption mechanism.

After having discussed and characterized the quantum state and velocity distributions of the

desorbed particles, a comment concerning the chosen wavelength of the desorption laser is appropriate: 193 nm is equivalent to 6.42 eV and is thus in the neighbourhood of the most intense electronic transition of the NO/Ni(100) system as observed via electron energy loss spectroscopy (EELS) by Peebles et al. [21] at 5.6 eV loss energy. Due to the large width of this transition centered at 5.6 eV, the cross section at 6.42 eV is still between 80 and 90% of the maximum value. *Therefore our desorption laser frequency is in resonance with an intense electronic excitation of the adsorbate system.* The nature of the adsorbate transition, or transitions (it is not yet clear how many electronic transitions contribute to the observed band) is not known at present. Considering, however, what is known about electronic transitions in CO adsorbate systems, charge-transfer transitions between the substrate and the molecule as well as intramolecular NO transitions are expected to occur in this energy range [29]. Even if the desorption laser light has been resonantly absorbed by the adsorbate, there is still a chance that the absorbed energy is dissipated between the substrate and neighbouring molecules finally causing thermal desorption to occur. This, however, can be excluded on the basis of the measured vibrational, rotational and TOF distributions. We have carried out preliminary experiments at a second desorption wavelength, i.e. at 248 nm (=5.0 eV). Even though this energy is still within the range of the broad excitation band observed in

EELS, the shape of the velocity distributions of desorbed molecules are more similar to Maxwell distributions than those in figs. 3 and 4. A detailed account of these results will be published elsewhere.

4. Summary

We have presented in this study conclusive evidence for the occurrence of selective features in the quantum state and velocity distributions of molecules desorbed by a laser-induced process. The selectivity is probably due to the fact that resonant light absorption takes place at 193 nm for the NO/Ni(100) system. The desorption may then occur via a true photodissociation process. Four main experimental observations have been made via the LIF technique after exposing the NO/Ni(100) adsorbate system to UV laser light:

(i) Vibrationally excited NO molecules desorb from the surface only if the metal surface has been cleaned so that the NO molecules are chemically bound to the surface before desorption is initiated.

(ii) The velocity distribution of the desorbing molecules is extremely narrow and is compatible with a "thin sheet" of desorbing particles. It cannot be fitted to a Maxwell distribution.

(iii) The velocity distributions are different for different rotational states, indicating that the energy take-up of the surface depends on the rotational level.

(iv) The rotational state distribution of desorbed molecules is markedly non-Boltzmann.

These experimental observations directly contradict the assumption of a thermally induced desorption mechanism. Clearly, further experimental studies are necessary to characterize the desorption process. Experiments with *in situ* characterized adsorbates, other wavelengths and polarization techniques are currently in progress.

Acknowledgement

We thank the "Deutsche Forschungsgemeinschaft" (SFB 93, "Photochemie mit Lasern") and the "Fonds der Chemischen Industrie" for financial support, and Professors G. Wedler, G. Ertl and E.W. Plummer for useful discussions. For help in the early

stages of this work we thank U. Wellhausen, and for help in data evaluation U. Schüller. We are obliged to Dr. H. Gonska for loaning the Ar ion sputter gun, and to K. Witan for his help in calculating the surface temperature. HJF thanks the Fritz-Haber-Institut der Max-Planck-Gesellschaft for providing the Ni(100) single crystal.

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