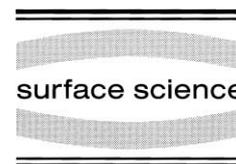




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Surface Science 427–428 (1999) 27–33



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Angular distributions of NO in laser-induced desorption from Pt(111)

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Abstract

The angular distributions of NO photodesorbed from a Pt(111) surface by UV-laser irradiation at 193 nm are investigated as a function of velocity using a quantum state specific detection method, which combines resonance enhanced multiphoton ionization (REMPI) and a two-dimensional-imaging technique. The angular distributions of NO in individual rovibrational states are observed to be strongly peaked in the surface normal direction and are consistently reproduced by gaussian functions in the desorption angle θ . The angular width of these distributions is found to decrease substantially with the velocity of the desorbing molecules. The identical velocity dependence of the angular distributions is observed independent of the rotational quantum states of the photodesorbed NO molecules. This is indicative of a de-coupling of the rotational motion of the molecular axis and the hindered parallel translation of the molecules in the adsorption ground state as well as in the excited states probed by the desorption process. The implications of a simple impulsive model, which relates the amplitude of the frustrated translational motion to the velocity dependence of the observed angular distributions, are discussed. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Chemisorption; Desorption induced by electronic transitions (DIET); Low index single crystal surfaces; Nitrogen oxides; Photon stimulated desorption; Platinum; Vibrations of adsorbed molecules

1. Introduction

To elucidate the dynamics of molecules interacting with a surface, the use of photons to initiate a dynamical process followed by the characterization of the final state by means of quantum state resolved methods has proven to be a particularly powerful approach [1–3]. Since the photoinduced dynamics reflect the nature of the chemical bonds

in both the ground and the excited states and include the fundamentally interesting aspect of energy conversion between the electronic system and nuclear motion, the photo-desorption of NO molecules from solid surfaces has been studied in some detail by state selective-detection techniques [4–15]. The adsorption of NO molecules on Pt(111) was characterized by various techniques of surface analysis, though there still seems to remain some ambiguity about the adsorption site assignment and geometry [16–20]. The angular distribution of molecules desorbing from or scattered at a surface contains important information

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on the dynamics of the molecule–surface interaction: While the angular distribution of molecules desorbing from thermal equilibrium with the surface often obeys a $\cos(\theta)$ law, distributions which are more sharply focussed in the preferred desorption direction are expected for molecules originating from direct elastic/inelastic scattering or from desorption induced by an electronic transition. In the latter case, two main factors may be considered to dominate the angular distribution: the frustrated translational motion of the molecules, which vibrate parallel to the surface in their adsorption potential on one hand, and directional dissociative forces on the other, acting along the molecule–surface bond in the desorption process. The former determines the electron stimulated desorption of CO from Cu(110) [21], while the latter has been shown to govern the photodesorption of CO from Si(100) surfaces [22].

In the present paper we report for the first time on *velocity and quantum state resolved* measurements of the angular distributions of NO molecules photodesorbed at 193 nm from a Pt(111) surface. The desorption is found to be strongly peaked in the surface normal direction, with a pronounced dependence of the angular distributions on the desorption velocity. Furthermore, an effective de-coupling from the rotational excitation of the desorbing molecules is observed. Within a simple dynamical model these results will be discussed in terms of their relation to the hindered translational motion of the NO molecule.

2. Experimental

The measurements were performed in an ultra-high vacuum chamber described previously [23]. The system was equipped with low-energy electron diffraction (LEED), X-ray photoelectron spectroscopy (XPS) and a quadrupole mass spectrometer. The Pt(111) sample was cleaned by Ar⁺ ion bombardment and repeated cycles of annealing in an O₂ atmosphere (2×10^{-7} mbar) at 1190 K and flashing to 1400 K. The sample cleanliness and order were checked by XPS and LEED. The sample was cooled to 90 K by liquid nitrogen and NO was adsorbed from a pulsed molecular beam

doser up to saturation coverage. Photodesorption was induced by pulses of ultraviolet photons from an ArF excimer laser ($\lambda = 193$ nm, $h\nu = 6.4$ eV, pulse width: 15 ns) at normal incidence and a fluence of 1–2 mJ/cm². An increase of the surface temperature from 90 K due to the laser irradiation was not observed. The rovibrational quantum state selective detection of the desorbing NO molecules was achieved by (1+1)REMPI via the $A^2\Sigma^+ \leftarrow X^2\Pi$ transition. To compensate the depletion of the NO coverage during the photodesorption measurements, NO was redosed from the pulsed molecular beam source ($f = 2$ Hz) synchronized a few milliseconds after the detection laser firing, thus allowing evacuation of the unadsorbed and backscattered NO molecules between the laser pulses and reduction of the background signal due to atmospheric NO below the detection limit.

To obtain the angular distributions, a two-dimensional imaging set-up was employed in the present study [23]. By a telescope of cylindrical lenses, the detection dye laser beam was spread to a sheet of about 20 mm width in the plane perpendicular to the sample surface. The two-dimensional distribution of ions produced in this detection laser sheet was repeatedly imaged on a phosphor screen and accumulated by a CCD camera after directing the ions by a repelling electrode onto a microchannel plate for space resolved amplification. From these images, the angular distributions are derived as particle density profiles as a function of the desorption angle θ for a selected velocity, which is defined by the time delay between the excitation and detection laser pulses and the distance of a given position within the laser sheet from the sample surface. The desorption laser beam had a spot diameter of 2 mm on the sample, confining the angular resolution of the measurement to about $\Delta\theta = 2.5^\circ$.

3. Results and discussion

Fig. 1a shows a two-dimensional image of photodesorbed NO molecules ionized in the probe laser sheet 14 μ s after the pump laser pulse. The detection laser wavelength is tuned to probe the molecule in the rotational state of $J = 15.5$, its

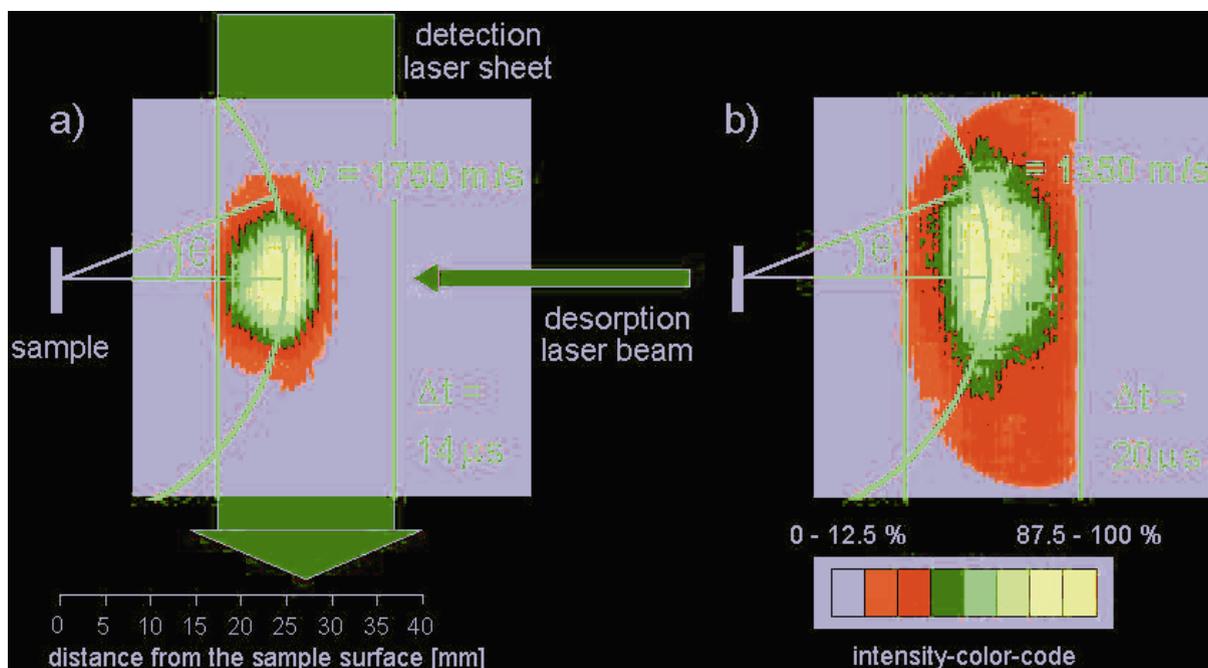


Fig. 1. The two-dimensional images of NO molecules desorbed from Pt(111) in the quantum state ($v''=0$, $\Omega=1/2$, $J=15.5$) at different time delays after the photoexcitation at 193 nm, as viewed by a horizontal REMPI laser sheet in front of the surface. For clarity, the maximum intensity in each image has been normalized to use the 8-step color-intensity code.

vibrational ground state $v''=0$ and the spin-orbit state of $\Omega=1/2$. For clarity, the detection geometry is indicated in Fig. 1 and the intensity-normalized images are displayed in an eight-step color code. The delay times Δt labeled to the images denote the time differences between the firings of the pump and the probe laser. As evident from comparing Fig. 1 a and b, a shallower shape of the desorption cloud in the vertical direction, which corresponds to the coordinate parallel to the Pt(111) surface, can be noticed for the faster desorbing molecules detected after 14 μs . An analysis of the digital images is shown in Fig. 2, where the desorption intensity is plotted as a function of the desorption angle θ for a variety of molecule velocities. Solid curves represent least square fits of the data to gaussian functions of the type $A \cdot \exp\{[-(1/2) \cdot (\theta - \theta_0)^2 / b^2]\}$, where A , θ_0 and b are fit parameters. Since θ_0 , the center of the distributions, ranges within limits of $\pm 2.5^\circ$, the desorption is concluded to be peaked in the surface normal direction within experimental accuracy.

The angular width b of the distributions is found to decrease substantially with increasing velocity of the desorbing molecules, reflecting the increasingly peaked shape of the desorption cloud for faster molecules (ref. Figs. 1 and 2). To ease comparison with the angular distribution of $\cos(\theta)$ encountered in thermal desorption, angular distributions of molecules desorbing or scattering from surfaces have frequently been expressed by functions of the type $\cos^N(\theta)$, which are equivalent to gaussian functions for angles $\leq 30^\circ$, with N corresponding to $1/b^2$ (rad). Using this notification, our angular distribution data are well reproduced by $\cos^N(\theta)$ functions with $N=(4-5)$ for velocities ≤ 1100 m/s, increasing rapidly at higher velocities to reach $N > 18$ at 1700 m/s. These results compare well with the values of $N=4$ at 1330 m/s reported by Schwarzwald et al. [9] and $N=(11 \pm 4)$ found by Buntin et al. after time-integrating TOF spectra recorded at different desorption angles [6,7]. In agreement with these earlier studies, the strongly peaked angular distributions ($N \gg 1$) obtained in

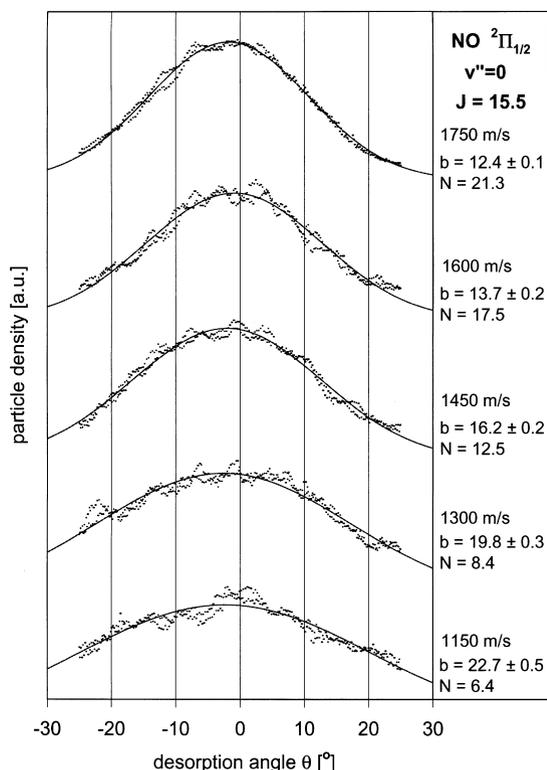


Fig. 2. Velocity dependence of the angular distributions of NO photodesorbed from Pt(111) at 193 nm, detected in the quantum state ($v''=0$, $\Omega=1/2$, $J=15.5$). Solid curves are fits to gaussian functions, the gaussian widths b (°) of which are listed in the right-hand panel. For comparison, N values for $\cos^N(\theta)$ functions calculated according to $1/b^2 \approx N$ are included.

the present investigation clearly reflect the non-thermal character of a desorption induced by an electronic transition (DIET), being well established for the photodesorption of NO/Pt(111) [4–15,24–26]. As an interesting observation, the angular width b of the distributions decreases markedly with the velocity ($N=1/b^2$ increases) only for fast molecules ($v \geq 1100$ m/s), while it appears to remain almost constant below this velocity. As reported previously [12], the velocity distribution of desorbing NO consists of two components, a fast and a slow channel. Since we are mainly probing the fast channel in the present study, the very limited number of data in the velocity range of $v \leq 1100$ m/s will be excluded from our further analysis.

Desorption of molecules induced by an

electronic transition has been successfully discussed on the basis of a simple impulse model [22,24–26]. For an NO molecule adsorbed on-top of a Pt surface atom [16–18], the rotational excitation is considered to be the product of the linear momentum transferred along the Pt–N bond and the bending angle ϕ of the molecular axis with respect to this bond direction, caused by the frustrated *rotational* motion of the adsorbed molecule. The frustrated *translation*, on the other hand, resembles a low frequent vibration of the NO parallel to the surface. The two modes of hindered molecular motion at the surface differ considerably in energy: While a value of $(\hbar\omega) \approx 60$ cm⁻¹ for the ground state of the hindered translational mode is reported for on-top NO on Pt(111) [27], 465 cm⁻¹ have been determined for the hindered rotation [28], justifying treating these two degrees of freedom independently within the model. It should be noticed in this context, that within experimental accuracy *no* significant dependence of the angular distributions on the rotational excitation of the desorbing NO molecules could be observed. This is evident from the fact that the gaussian width b of the angular distributions of NO detected in different rotational quantum states ($J=6.5$ and $J=15.5$) exhibits comparable values and the same dependence on the desorption velocity (Fig. 3). This observation strongly suggests that during the course of the desorption event, the frustrated rotation of the NO molecule, which gives rise to the rotational excitation of the desorbing particles [25,26], is obviously de-coupled from the motion which determines the angular distributions, consistent with the impulsive model assumptions.

We tentatively apply this classical picture to derive information about the frequency of the hindered translational motion from the velocity dependence of the angular distributions. The frustrated translation generates a periodically fluctuating deviation of the Pt–N bond direction from the surface normal. The dissociative force on the desorbing molecule is assumed to act in the Pt–N direction and therefore includes an angle of liberation θ_{lib} with the surface normal in the moment of bond rupture. If the potential for the hindered translation is harmonic, this liberation angle θ_{lib}

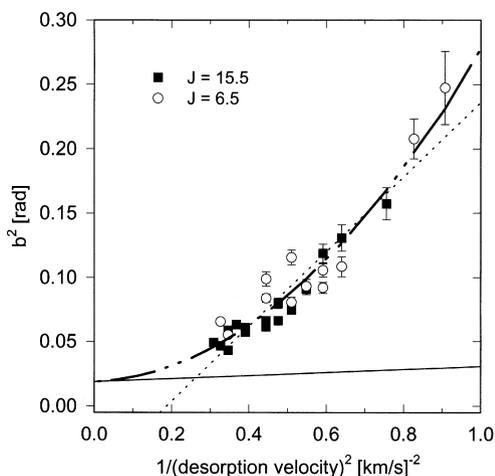


Fig. 3. Angular width b of the gaussian angular distributions of NO photodesorbing from Pt(111) in different rotational states $J=6.5$ and $J=15.5$ ($v''=0$, $\Omega=1/2$) as a function of velocity v , presented in a b^2 versus $1/v^2$ diagram. Refer to the text for the function assignments.

will be gaussian distributed around the surface normal. Furthermore, the hindered translation imposes a velocity component v_{\parallel}^0 parallel to the surface to the molecule's center of mass: $v_{\parallel}^0 \approx l \cdot d(\theta_{\text{lib}})/dt$ ($l \approx$ distance between the Pt-atom and the NO center of mass). If this lateral momentum is conserved in the transitions between the ground and the short-lived excited state and the impulse in the Pt–N direction yields the molecule's desorption velocity v , the parallel (v_{\parallel}) and the perpendicular (v_{\perp}) velocity components are to be described as $v_{\parallel} = v \cdot \sin \theta_{\text{lib}} + v_{\parallel}^0$ and $v_{\perp} = v \cdot \cos \theta_{\text{lib}}$. Since the liberation angle θ_{lib} is likely to be small, these can be approximated by $v_{\parallel} \approx v \cdot \theta_{\text{lib}} + v_{\parallel}^0$ and $v_{\perp} \approx v$, finally defining the desorption angle θ by $\tan(\theta) = v_{\parallel}/v_{\perp} = (v \cdot \theta_{\text{lib}} + v_{\parallel}^0)/v$. Since the cross term $\langle (\theta_{\text{lib}} v_{\parallel}^0) \rangle$ vanishes for a harmonic oscillation, the squared width b^2 of the observed angular distributions contains two contributions: $b^2 = \langle \theta^2 \rangle = \langle \theta_{\text{lib}}^2 \rangle + \langle (v_{\parallel}^0)^2 \rangle / v^2$, where the latter term introduces a dependence on the measured velocity v . The uncertainty of the parallel velocity $\langle (v_{\parallel}^0)^2 \rangle$ is given by the mean square amplitude of the gaussian wavefunction $u_0(p)$ for the harmonic hindered translation in momentum space, assuming that only the vibrational ground state has to be considered: $u_0(p) =$

$N_0 \cdot \exp\{-\frac{1}{2} \alpha^2 p^2\} = N_0 \cdot \exp\{-\frac{1}{2} \alpha^2 m^2 (v_{\parallel}^0)^2\}$, with the momentum $p = m \cdot v_{\parallel}^0$ and $\alpha^2 = 1/(m\hbar\omega)$. The mass of the NO molecule is represented by m and ω is the frequency of the parallel vibration. Thus, $\langle (v_{\parallel}^0)^2 \rangle$ writes as $1/(\alpha^2 m^2) = (\hbar\omega)/m$, and a linear dependence of b^2 on $1/v^2$ is expected:

$$b^2 = \langle \theta^2 \rangle = \langle \theta_{\text{lib}}^2 \rangle + \{\hbar\omega/m\}/v^2. \quad (1)$$

The experimental data are shown in a b^2 versus $1/v^2$ diagram in Fig. 3. It is obvious that a linear function (dotted line) fitted to the data can roughly reproduce the high velocity regime ($v \geq 1100$ m/s). However, the slope of this straight line yields a value of $(\hbar\omega) \approx 730 \text{ cm}^{-1}$ for the frustrated translational quanta, which is considerably larger than the value of 60 cm^{-1} derived from scattering experiments [27]. Even in view of possible hollow site adsorption, which is still under discussion as the ground state geometry [19,20] and would probably account for a higher frequency of the lateral vibration, the obtained value appears to be unusually large. As a possible origin of this discrepancy, strong directing forces acting on the molecule parallel to the surface in the excited state of the photodesorption process might be discussed. This interpretation would be equivalent to a considerably higher frequency of the lateral vibration in the excited state as compared to the ground state, which is, of course, neglected completely in the naive model outlined above. However, such a 'hardening' of the parallel vibration in the excited state appears to be unlikely, since the excited state potential involved has been suggested to be repulsive [29].

Assuming a wavenumber for the hindered translation of 60 cm^{-1} [27] and estimating a maximum liberation angle θ_{lib} of 7.9° from this value, Eq. (1) predicts a much smaller slope in the b^2 versus $1/v^2$ plot and a small positive intersect with the ordinate (solid straight line in Fig. 3). According to this function, the angular distributions should possess even much smaller angular widths (lower b^2 values) than observed experimentally. It therefore has to be concluded that compared to the assumptions of the dynamical model, a considerable amount of additional lateral

momentum is transferred to the molecules in the photodesorption process. This surprising result implies that probing the potential energy surfaces of electronically excited states in the desorption process may not only induce substantial translational energy gain and internal excitation of the desorbing particles, but may also have a strong impact on nuclear dynamics occurring parallel to the surface. Since the experimental approach as well as the theoretical treatment of these topics still remain rather delicate tasks, this has scarcely been investigated so far.

The thermal excitation of the lateral vibration due to laser heating may be ruled out as the cause for the unexpectedly large lateral translational energy, since the picosecond surface temperature rise induced by the laser pulses can be estimated to amount only a few Kelvin.

Fig. 3 further shows that the data are not satisfactorily reproduced by a straight line, since the constant desorption angle contribution due to $\langle \theta_{\text{lib}}^2 \rangle$ is predicted to be negative by the straight line fit, which is surely in conflict with the underlying physics. Obviously some qualitative improvements of the employed model are necessary. One alternative explanation accounting for wider angular distributions would be a post-acceleration of the desorbing molecules induced by an adsorption barrier, leading to desorption velocities which are effectively higher than those determining the photodesorption angle. It can be shown that this introduces an additional term into Eq. (1): $b^2 = \langle \theta_{\text{lib}}^2 \rangle + \{ \hbar\omega/m \} / v^2 + C/v^4$. The bold dash-dotted line in Fig. 3 indicates a single parameter fit to such a function, assuming again $\theta_{\text{lib}} = 7.9^\circ$ and $\hbar\omega = 60 \text{ cm}^{-1}$. Much closer agreement with the data is achieved; however, the parameter C conveys an unreasonably high post-acceleration velocity in this case, and its relevance is in fact questionable since NO adsorption on Pt(111) is known to be a non-activated process [30]. The impulsive model therefore obviously fails to quantitatively describe the velocity dependence of the angular distributions in this photodesorption process, even though the observed trend of an angular width decreasing with increasing velocity is qualitatively in line with its predictions.

Acknowledgements

The work was supported by Japanese–German Corporation Science Promotion Program of the Japan Society for the Promotion of Science, by an Grant-in-Aid for Creative Basic Research and by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports and Culture, Japan. The authors are grateful for indispensable help during the experimental work by A. Braun and T. Hellwig.

References

- [1] H.-L. Dai, W. Ho (Eds.), in: *Laser Spectroscopy and Photochemistry on Metal Surfaces*, World Scientific, Singapore, 1995.
- [2] X.-L. Zhou, X.-Y. Zhu, J.M. White, *Surf. Sci. Rep.* 13 (1991) 73.
- [3] P. Avouris, R.E. Walkup, *Annu. Rev. Phys. Chem.* 40 (1989) 173.
- [4] F. Budde, A.V. Hamza, P.M. Ferm, G. Ertl, D. Weide, P. Andresen, H.-J. Freund, *Phys. Rev. Lett.* 60 (1988) 1518.
- [5] P.M. Ferm, F. Budde, A.V. Hamza, S. Jakubith, G. Ertl, D. Weide, P. Andresen, H.-J. Freund, *Surf. Sci.* 218 (1989) 467.
- [6] S.A. Buntin, L.J. Richter, R.R. Cavanagh, D.S. King, *Phys. Rev. Lett.* 61 (1988) 1321.
- [7] S.A. Buntin, L.J. Richter, D.S. King, R.R. Cavanagh, *J. Chem. Phys.* 91 (1989) 6429.
- [8] J.A. Prybyla, T.F. Heinz, J.A. Misewich, M.M.T. Loy, J.H. Glowina, *Phys. Rev. Lett.* 64 (1990) 1537.
- [9] R. Schwarzwald, A. Mödl, T.J. Chuang, *Surf. Sci.* 242 (1991) 437.
- [10] K. Fukutani, A. Peremans, K. Mase, Y. Murata, *Phys. Rev. B* 47 (1993) 4007.
- [11] K. Fukutani, A. Peremans, K. Mase, Y. Murata, *Surf. Sci.* 283 (1993) 158.
- [12] K. Fukutani, Y. Murata, R. Schwarzwald, T.J. Chuang, *Surf. Sci.* 311 (1994) 247.
- [13] K. Fukutani, M.-B. Song, Y. Murata, *Faraday Discuss. Chem. Soc.* 96 (1993) 105.
- [14] M. Menges, B. Baumeister, K. Al-Shamery, H.-J. Freund, C. Fischer, P. Andresen, *J. Chem. Phys.* 101 (1994) 3318.
- [15] K. Fukutani, Y. Murata, *Surf. Sci.* 390 (1997) 164.
- [16] H. Ibach, S. Lehwald, *Surf. Sci.* 76 (1978) 1.
- [17] B.E. Hayden, *Surf. Sci.* 131 (1983) 419.
- [18] M. Kiskinova, G. Pirug, H.P. Bonzel, *Surf. Sci.* 136 (1984) 285.
- [19] N. Materer, A. Barbieri, D. Gardin, U. Starke, J.D. Batteas, M.A. Van Hove, G.A. Somorjai, *Phys. Rev. B* 48 (1993) 2859.

- [20] Q. Ge, D.A. King, *Chem. Phys. Lett.* 285 (1998) 15.
- [21] J. Ahner, D. Mocuta, R.D. Ramsier, J.T. Yates, *Phys. Rev. Lett.* 79 (1997) 1889.
- [22] F.M. Zimmermann, W. Ho, *Surf. Sci. Rep.* 22 (1995) 127.
- [23] M. Menges, B. Baumeister, K. Al-Shamery, H.-J. Freund, C. Fischer, P. Andresen, *Surf. Sci.* 316 (1994) 103.
- [24] Y. Murata, K. Fukutani, in: A. Okiji, H. Kasai, K. Makoshi (Eds.), *Elementary Processes in Excitations and Reactions on Solid Surfaces*, Springer Series in Solid-State Science, vol. 121, Springer, Berlin, 1996, p. 56.
- [25] Y. Murata, K. Fukutani, *J. Mol. Structure* 352/353 (1995) 519.
- [26] Y. Murata, K. Fukutani, *J. Electron Spectrosc. Relat. Phenom* 64/65 (1993) 533.
- [27] C.W. Muhlhausen, L.R. Williams, J.C. Tully, *J. Chem. Phys.* 83 (1985) 2594.
- [28] A.R. Burns, E.B. Stechel, D.R. Jennison, *Phys. Rev. Lett.* 58 (1987) 250.
- [29] H. Aizawa, S. Tsuneyuki, *Surf. Sci.* 363 (1996) 223.
- [30] W. Ranke, *Surf. Sci.* 209 (1989) 57.