

Photodesorption of NO from Ni(100)-O

F. Budde, A. V. Hamza, P. M. Ferm, and G. Ertl

Fritz-Haber-Institut der Max-Planck-Gesellschaft, D-1000 Berlin 33, Federal Republic of Germany

D. Weide and P. Andresen

Max-Planck-Institut für Strömungsforschung, D-3400 Göttingen 1, Federal Republic of Germany

and

H.-J. Freund

Ruhr-Universität Bochum, D-4630 Bochum 1, Federal Republic of Germany

(Received 6 November 1987)

Fully state-resolved analysis of NO molecules desorbed from an oxygen-covered Ni(100) surface by uv radiation ($\lambda=193$ nm) yields the operation of two desorption channels, thermal and nonthermal, via electronic excitation. The latter fraction exhibits as a particular feature pronounced spin-orbit selectivity at low rotational quantum numbers.

PACS numbers: 68.45.Da, 79.20.Ds

The investigation of the dynamics of gas-surface interactions by means of laser spectroscopic techniques has received much attention during recent years,¹ since in this way experimental determination of the energy partitioning between the various degrees of freedom becomes possible. So far these studies have been essentially concerned with scattering and thermal-desorption processes (including laser-induced thermal desorption), although desorption via electronic excitation through an electron beam was demonstrated also to be accessible by this strategy.² The present Letter reports on the first full state-resolved (i.e., with respect to translational, rotational, vibrational, and spin level distributions) results for molecules photochemically being desorbed from a well-defined surface, namely NO from oxygen-covered Ni(100). The nonthermal excitation of at least a fraction of desorbed molecules manifests itself in several effects among which the pronounced spin-orbit selectivity for low rotational quantum levels appears to be most remarkable. A preliminary report had been given elsewhere,³ but this previous work suffered from insufficient surface characterization.

Experimental details have been described elsewhere.^{3,4} Briefly, a NO molecular beam served as a gas doser and was directed at a Ni(100) surface centered in an UHV chamber. Auger spectroscopy and low-energy electron diffraction were used to determine surface cleanliness and order. A rotatable quadrupole mass spectrometer made possible measurement of temperature-programmed desorption (TPD) spectra. Cleaning of the Ni(100) surface was accomplished through standard techniques.⁵ NO adsorbed on an initially clean Ni(100) surface at 140 K was irradiated with uv-excimer laser light (ArF, 193 nm). The rotational and vibrational state distributions of the photodesorbed molecules were probed via laser-induced fluorescence. Frequency-doubled light

from a tunable excimer-pumped dye laser (around 226 nm) passed parallel to the surface typically at a distance of 25 mm to excite electronically the desorbed NO molecules. Fluorescence light from the excited molecules was focused on a photomultiplier and the resulting signal was digitally stored. Time-of-flight measurements were performed by variation of the delay between the desorption and the probe-laser pulses with the probe laser tuned to detect NO in a particular quantum state. The time-integrated populations in the various rotational states yielded internal energy distributions.

Starting with an initially clean Ni(100) surface which was continuously exposed to NO at 140 K (in order to establish stationary conditions by compensating for the loss of adsorbed particles by laser-induced desorption), the total flux of desorbed NO molecules was found to *increase* continuously with the duration of irradiation until after about 5000 shots (at ≈ 2 mJ/cm² laser power) a steady state was reached. Auger-electron-spectroscopy analyses performed afterwards exhibited the presence of considerable amounts of adsorbed oxygen which presumably resulted from the dissociation of adsorbed NO. (The surface concentration of N was always found to be much smaller, presumably because of secondary reactions causing release into the gas phase.) NO adsorbed on Ni(100) is known to partly dissociate thermally near 200 K.⁵ On the other hand, gaseous NO is known to dissociate by irradiation with light of 191-nm wavelength⁶ which is close to the energy of our desorption laser (193 nm). Dissociation of adsorbed NO in the present system might therefore be feasible through both channels, which has to be explored in further work.

TPD of NO adsorbed on Ni(100) exhibits two peaks, at 346 and 358 K.⁵ In the presence of adsorbed oxygen an additional peak at 240 K appears. If the Ni(100) surface is preexposed to O₂ up to saturation (which pro-

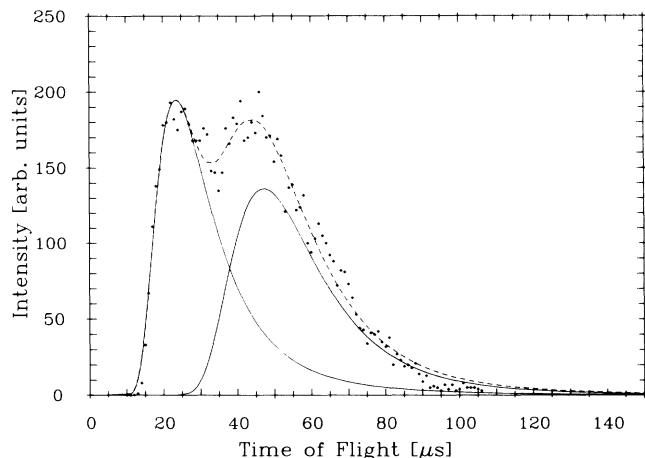


FIG. 1. Time-of-flight distribution for NO ($v''=0$, $J''=\frac{5}{2}$, $^2\Pi_{1/2}$) photodesorbed from Ni(100)-O. The peaks were fitted by velocity distributions of the form $f(v) = Av^3 \exp[-B(v - v_0)^2]$, where A , B , and v_0 are adjustable constants.

cedure is known to form a layer of NiO⁷), subsequent NO adsorption yields exclusively this weakly bound state which is therefore identified with NO adsorbed on an oxygen-covered surface, Ni(100)-O. Detailed experiments demonstrated that it is just the species which is desorbed by irradiation with the applied excimer laser pulses, while the small cross section for laser desorption of the more strongly held molecules adsorbed on the metallic surface prevents their detection. This explains why the signal increases with continuing irradiation, i.e., buildup of the surface oxide.

Figure 1 shows a typical time-of-flight distribution of NO molecules desorbed in specific vibrational ($v''=0$), rotational ($J''=\frac{5}{2}$), and electronic ($^2\Pi_{1/2}$) levels. Similar spectra were reported by Burgess *et al.*⁸ for laser-induced desorption ($\lambda=532$ nm) of NO from Pt-poly. The present data were analyzed in terms of superposition of two groups of molecules with high and low translational energies, in the present example exhibiting average values of $\langle E_{\text{trans}} \rangle / 2k = 1010$ and 250 K, respectively. The latter number should be compared with the TPD peak at 240 K for thermal desorption. The rotational-state population of the "slow" molecules was found to decrease more rapidly with increasing J'' than those of the "fast" particles, yielding a rotational temperature $T_{\text{rot}} = 170 \pm 20$ K. Their angular distribution was found to be cosine, while the flux of "fast" particles is peaked in the direction of the surface normal. These results strongly suggest that we identify the origin of the slow molecules with a thermal-desorption process caused by absorption of the laser pulse by the solid.

There are, on the other hand, a series of findings which demonstrate that the "fast" molecules arise from nonthermal desorption, i.e., from activation distinct from coupling to the heat bath of the solid.

(i) Their mean translational energy $\langle E_{\text{trans}} \rangle / 2k$ in-

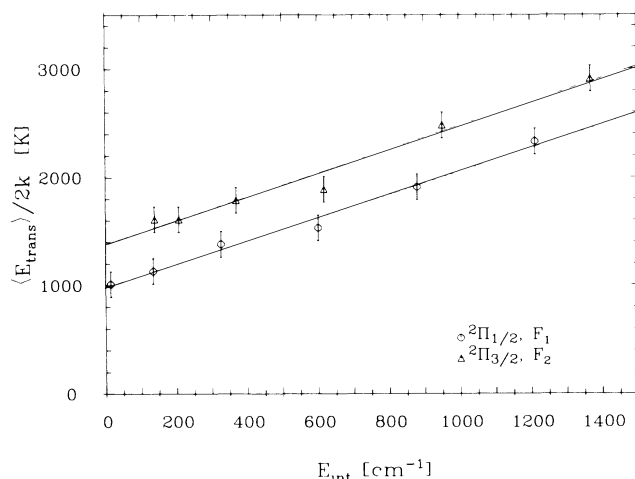


FIG. 2. Average translational energy of the "fast" particles as a function of their internal energy in the F_1 and F_2 branches.

creases markedly with internal energy for the $^2\Pi_{1/2}$ as well as the $^2\Pi_{3/2}$ branch as shown in Fig. 2 up to values of almost 3000 K. Remarkably $\langle E_{\text{trans}} \rangle$ is systematically higher for the molecules in the $^2\Pi_{3/2}$ electronic configuration. Translational energies of the observed order of magnitude are completely incompatible with thermal origin, even if a barrier should exist in the exit channel: Remember that thermal desorption of the particles under consideration takes place with maximum probability at a surface temperature of 240 K. The surface temperature under the present conditions of laser irradiation will never exceed about 300 K, as otherwise one would observe also desorption of those other species which show up with a peak around 350 K in TPD. The possible existence of a substantial barrier in the ground-state exit channel could, in addition, not be reconciled with the high sticking coefficient for adsorption with a gas temperature of 300 K. For particles thermally desorbing from a surface temperature at T_s , one observes $\langle E_{\text{trans}} \rangle / 2k \leq T_s$, independent of their internal energy, while a decrease of $\langle E_{\text{trans}} \rangle$ with E_{int} may occur in direct-inelastic scattering.⁹

(ii) Figure 3 shows "Boltzmann plots" for the rotational-state population of the "fast" particles in the $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ levels. While the data for the former yield approximately a straight line to which formally a rotational temperature of about 300 K can be assigned, this is certainly not the case for the $^2\Pi_{3/2}$ species where a marked underpopulation of the rotational levels with J'' up to $J'' = \frac{11}{2}$ is present. This is considered as being the most remarkable result of the present study and will therefore be discussed further below.

(iii) The total yield of molecules desorbed in the first vibrationally excited state was of the order of about 1% with respect to the flux of $v''=0$ particles, which is less than observed in the preliminary study³ but still about 2

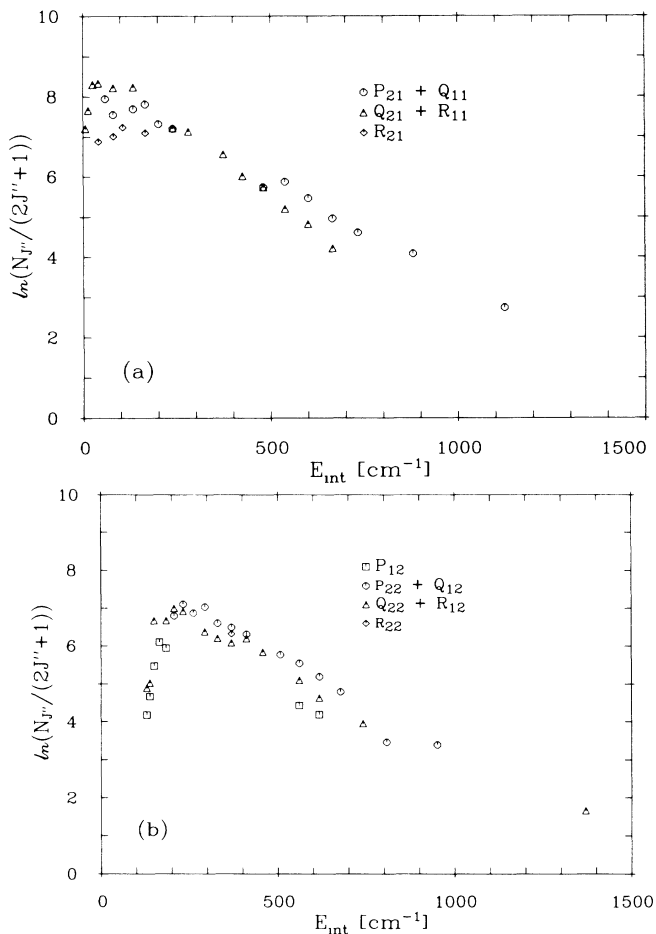


FIG. 3. Boltzmann plots of the internal energy populations for the (a) ${}^2\Pi_{1/2}$ and (b) ${}^2\Pi_{3/2}$ branches.

orders of magnitude more than corresponding to thermal equilibrium at 300 K. Although not investigated in great detail, the qualitative features of these particles were similar to those with $v''=0$: high kinetic energies (e.g., $\langle E_{\text{trans}} \rangle / 2k = 1300$ K for $J'' = \frac{23}{2}$, ${}^2\Pi_{1/2}$), approximately Boltzmann-type internal energy distribution for the ${}^2\Pi_{1/2}$ branch (yielding $T_{\text{rot}} = 625 \pm 50$ K), while the ${}^2\Pi_{3/2}$ particles again exhibit underpopulation for low J'' . Only "fast" particles were found with $v''=1$, which is further confirmation for the origin of the "slow" molecules by a thermal process.

Nonthermal desorption of particles from surfaces caused by absorption of uv or visible photons has already been reported for a number of systems.¹⁰⁻¹⁴ The desorption may be either directly or indirectly induced by light. In the former case, localized photon absorption within the substrate-adsorbate bond would be responsible for this effect. Indirect photochemical desorption would comprise electronic excitation within either the adsorbate or the substrate (creation of hot carriers) as primary step and subsequent conversion into activation of the substrate-adsorbate bond.¹⁰ No distinction between

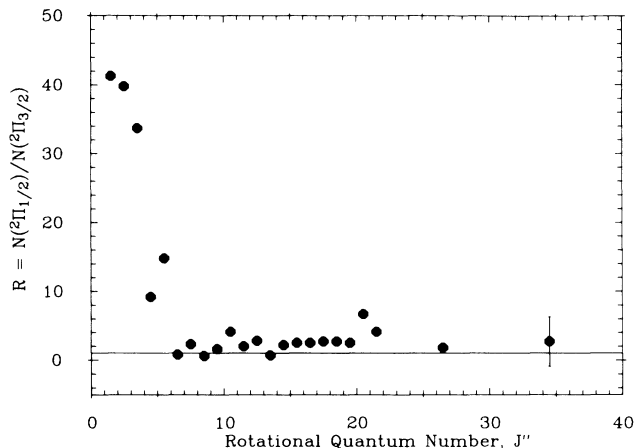


FIG. 4. The ratio $R = N({}^2\Pi_{1/2})/N({}^2\Pi_{3/2})$ of the populations of the two spin-orbit branches as a function of rotational quantum number. The solid line represents equal populations of both spin-orbit manifolds.

these possibilities can be made on the basis of the available data, but in any case the system will reach a situation characterized by a potential which is *repulsive* with respect to the molecule-substrate interaction from where the particle starts to leave the surface. Electronic relaxation into the ground state is very efficient—especially with metal surfaces—and as a consequence the cross sections for such processes may be very small and also strongly dependent on the specific adsorption state.¹³ This is presumably the reason why, with the present system, photodesorption is only observed from the nonmetallic Ni(100)-O surface. (Likewise, Domen and Chuang¹² observed photodissociation and photodesorption of CH_2I_2 only from nonmetallic substrates, but not from Ag.)

The energy distributions in the various degrees of freedom of molecules desorbed as a result of electronic excitation and passage over repulsive potential curves are, of course, expected to be quite different from those resulting from thermal excitation from the ground state, and it is therefore not surprising that also different types of energy partitioning are observed. We shall concentrate our further discussion, however, only on the novel effect of spin-orbit selectivity in desorption. Figure 4 shows a plot of the ratio R of the populations of the F_1 ($={}^2\Pi_{1/2}$) over that of the F_2 ($={}^2\Pi_{3/2}$) species as a function of the rotational quantum number J'' . In the present case, R goes up to a value of 40! This can be compared with $R \approx 1.5$ (also at low J'') reported for direct-inelastic scattering of NO at an Ag(111) surface (where the incident molecules were predominantly in the F_1 level),¹⁵ if we remember that desorption is essentially a scattering process.

Although desorption and scattering are, of course, fundamentally different processes, the experimental findings will be tentatively interpreted on the basis of an elemen-

tary step of scattering. In view of the mechanism of non-thermal desorption discussed above, we may consider this process—in which molecules are created on a repulsive potential from where they start to come off the surface—as a kind of half collision, so that qualitative comparison with information on direct-scattering processes is considered to be justified. Theoretical treatment of *scattering* of open-shell 2Π molecules at flat surfaces revealed that in fact *two* sets of interaction potentials, V_+ and V_- , have to be taken into account.^{16,17} These potentials are degenerate when the molecule is oriented perpendicular to the surface, but differ because of the two possible orientations of the singly occupied 2Π orbital if the orientation of the molecular axis has a component parallel to the surface. Interaction of F_1 molecules with a surface will exhibit small transition probability into the F_2 spin-orbit manifold at low J'' , which, however, increases with increasing J'' so that finally both manifolds reach equal population, i.e., $R=1$. This effect is due to quantum-mechanical interference between scattering on the V_+ and V_- surfaces which becomes stronger with increasing J'' . The data of Fig. 4 follow exactly this trend, which suggests that the photo-excitation process indeed predominantly creates molecules of the F_1 manifold. Recent close-coupling calculations for scattering at varying sets of potentials¹⁸ demonstrated further that $R(J'')$ may oscillate. The available experimental data of Fig. 4 allow, however, no clear conclusion in this respect.

The qualitative agreement of the experimental observations (pronounced spin-orbit selectivity at low J'' and its decay with increasing rotational excitation) with the main predictions of the quoted theoretical treatments of direct scattering is considered as additional support for the proposed mechanism of nonthermal desorption via a repulsive exit channel.

In conclusion, the present work demonstrates the operation of two desorption channels by irradiation of a surface with uv photons. The nonthermal part exhibits very strong spin-orbit selectivity at low rotational quan-

tum numbers.

Support by the Deutsche Forschungsgemeinschaft, the Alexander von Humboldt-Stiftung for one of us (A.V.H.), and the Studienstiftung des deutschen Volkes for another (F.B.) is gratefully acknowledged.

¹M. C. Lin and G. Ertl, *Annu. Rev. Phys. Chem.* **37**, 587 (1986).

²A. R. Burns, E. B. Stechel, and D. R. Jennison, *Phys. Rev. Lett.* **58**, 250 (1987).

³D. Weide, P. Andresen, and H.-J. Freund, *Chem. Phys. Lett.* **136**, 106 (1987).

⁴A. Mödl, H. Robota, J. Segner, W. Vielhaber, M. C. Lin, and G. Ertl, *J. Chem. Phys.* **83**, 4800 (1985).

⁵D. E. Peebles, E. L. Hardegree, and J. M. White, *Surf. Sci.* **148**, 635 (1984).

⁶A. G. Gaydon, *Dissociation Energies and Spectra of Diatomic Molecules* (Chapman and Hall, London, 1968).

⁷P. F. A. Alkemade, S. Deckers, F. H. P. M. Habraken, and W. F. van der Weg, *Surf. Sci.* **189/190**, 161 (1987).

⁸D. Burgess, D. A. Mantell, R. R. Cavanagh, and D. S. King, *J. Chem. Phys.* **85**, 3123 (1986).

⁹A. Mödl, T. Gritsch, F. Budde, T. J. Chuang, and G. Ertl, *Phys. Rev. Lett.* **57**, 384 (1986).

¹⁰T. J. Chuang, *Surf. Sci. Rep.* **3**, 1 (1983), and *Surf. Sci.* **178**, 763 (1986).

¹¹E. B. D. Bourdon, P. Das, I. Harrison, J. C. Polanyi, J. Segner, C. D. Stanners, R. J. Williams, and P. A. Young, *Faraday Discuss. Chem. Soc.* **82**, 343 (1986).

¹²K. Domen and T. J. Chuang, *Phys. Rev. Lett.* **59**, 1484 (1987).

¹³See *Desorption Induced by Electronic Transitions—DIET II*, edited by W. Brenig and D. Menzel (Springer-Verlag, Berlin, 1985).

¹⁴R. R. Cavanagh, private communication.

¹⁵A. C. Luntz, A. W. Kleyn, and D. J. Auerbach, *J. Chem. Phys.* **76**, 737 (1982).

¹⁶M. H. Alexander, *J. Chem. Phys.* **80**, 3485 (1984).

¹⁷G. C. Corey and W.-K. Liu, *Surf. Sci.* **148**, 675 (1984).

¹⁸J. E. Smedley, G. C. Corey, and M. H. Alexander, *J. Chem. Phys.* **87**, 3218 (1987).