

Desorption Induced by Femtosecond Laser Pulses

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The yield and final-state distributions in translational and internal degrees of freedom have been established for NO molecules desorbed from a Pd(111) surface by 200-fs pulses of 2.0-eV photons. Among the significant characteristics of the desorption process are the large cross section and the high vibrational energy content ($T_v > 2000$ K) of the desorbed molecules. A comparison with the behavior for nanosecond laser pulses indicates that a new desorption mechanism, distinct from either conventional thermal or photochemical processes, is operative in this regime.

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The desorption of molecules from a solid surface, one of the most elementary surface processes, constitutes a subject of great fundamental and practical importance. Recently, considerable progress has been made in developing a detailed description of the desorption process in certain well-defined model systems through a complete characterization of the final-state distributions.¹ In these investigations, desorption has been induced by thermal means,¹ as well as through irradiation by energetic particles^{2,3} and photons.²⁻⁵ In all cases reported to date, the excitation has been of at least nanosecond duration, while energy flow between different degrees of freedom of the solid and the adsorbed molecules often occurs on the picosecond to femtosecond time scale.^{3,6} With subpicosecond excitation this natural time scale is approached and strong nonequilibrium conditions may be obtained. This leads to the possibility of novel desorption mechanisms, and, through analysis of the energy distributions of the desorbed molecules, to insight into the coupling between the solid and the adsorbed species.

In this Letter, we describe the first investigation of intact desorption of a molecular adsorbate induced by subpicosecond laser excitation.⁷ The system of NO/Pd(111) has been studied as a prototype of nondissociative chemisorption on a metal surface. We report here measurements of the desorption yield and its dependence on the laser intensity, as well as final-state energy distributions for translational, rotational, vibrational, and electronic (spin-orbit level) degrees of freedom of the desorbed NO molecules. These results cannot be explained in terms of a conventional thermal or photochemical process; rather, they reflect the highly nonequilibrium conditions that may be attained through excitation on a femtosecond time scale and the concomitant presence of new desorption mechanisms.

The ultrahigh-vacuum system and the technique for preparation of the single-crystal Pd(111) surface are discussed in Refs. 8 and 9. In these studies, the sample surface was maintained at a base temperature of 300 K with NO adsorbed at saturation coverage of $\sim \frac{1}{2}$ monolayer $= 6.5 \times 10^{14}$ cm⁻² in the β and γ states.¹⁰ Under

these conditions, the NO molecules are adsorbed at bridge sites with a binding energy of ~ 1 eV.¹⁰ In accordance with previous investigations of NO/Pd(111),¹⁰ we found no evidence for dissociation in either adsorption or desorption of NO under thermal conditions. Light pulses of 200-fs duration at 620 nm (2.0 eV) were produced by an amplified colliding-pulse mode-locked laser.¹¹ Each desorption event was induced by a single amplified laser pulse; the experimental data were obtained by repeating the process at a 10-Hz rate. In these measurements, the sample was illuminated with linearly polarized light containing both *s* and *p* components and the desorbed NO molecules were detected by means of resonance-enhanced multiphoton ionization (REMPI).⁸ The amount of NO desorbed was sufficiently low to render gas-phase collisions of the molecules negligible.¹² No emission of positive ions was observed and only weak electron emission was seen, with a yield several orders of magnitude below that of the desorbed NO molecules.

Figure 1 displays the observed NO desorption yield as a function of the absorbed fluence of the 200-fs laser pulses.¹³ In order to determine the absorbed fluence, the reflectivity of the sample was measured under the experimental conditions. No appreciable dependence of the reflectivity on laser fluence was detected. An important feature of the data in Fig. 1 is the nonlinear rise in the desorption yield with increasing absorbed fluence. We can represent this trend by a power-law relation with an exponent of $n=3.3$. The power-law form is introduced only to summarize the present results; it need not accurately describe the behavior outside the limited range of the present experimental data. The desorption process clearly cannot be characterized by a fixed quantum efficiency. For comparison, however, note that with an absorbed fluence of 3 mJ/cm², a quantum efficiency for desorption of 3×10^{-4} is obtained, corresponding to an average cross section of 4×10^{-19} cm².

The translational energy distribution of the desorbed NO molecules, obtained from state-specific time-of-flight measurements, could be fitted by a Boltzmann form within our experimental accuracy. For an absorbed laser

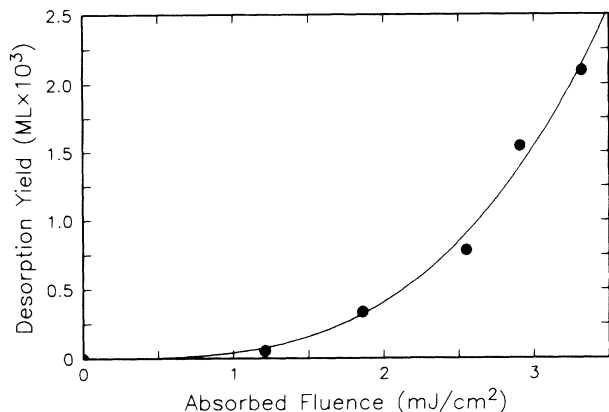


FIG. 1. Desorption yield of NO in monolayers as a function of the adsorbed laser fluence. The fluence is measured in the broad region of maximal intensity of the laser beam. The solid line is a power-law fit to the data.

fluence of 3 mJ/cm^2 , the translational energy distribution was described by a temperature of $\sim 600 \text{ K}$. Only a modest dependence on the internal quantum state of the desorbed NO was observed in the velocity distribution.

Internal-state distributions were measured over a wide range of rotational states J in the ground ($v=0$) and first excited vibrational states ($v=1$) for molecules in both the ${}^2\Pi_{1/2}$ and ${}^2\Pi_{3/2}$ spin-orbit states. Results obtained for an absorbed fluence of 3 mJ/cm^2 are displayed in Fig. 2. The rotational-state distributions clearly cannot be characterized by a single temperature, which would correspond to a straight line in the figure. The rotational distributions in either vibrational state can, however, be adequately represented by two temperatures, $T_{r1}=400 \text{ K}$ and $T_{r2}=2600 \text{ K}$, for the regions of the low and high rotational energy. As depicted in Fig. 2, for most J the two spin-orbit states have similar populations, corresponding to a very high spin-orbit temperature; for low J in the $v=0$ level, however, there appears to be an enhanced population in the ${}^2\Pi_{1/2}$ state, i.e., a finite spin-orbit temperature (comparable to T_{r1}). One of the prominent features of Fig. 2 is the high degree of vibrational excitation in the desorbed NO molecules. We have characterized the vibrational excitation by summing the population in the $v=0,1$ levels over all rotational states between $J=0.5$ and $J=30.5$. The resulting ratio of populations is $N(v=1)/N(v=0) \approx 0.3$. This implies a vibrational temperature of $T_v \approx 2200 \text{ K}$ for a thermal distribution.

It is instructive to compare these findings with the results of previous investigations of the thermal desorption of NO/Pd(111) induced by laser pulses of nanosecond duration.⁹ We find that the desorption process associated with 200-fs pulses is qualitatively different. The most obvious discrepancy concerns the desorption yield. For example, with an absorbed fluence of 3 mJ/cm^2 in a

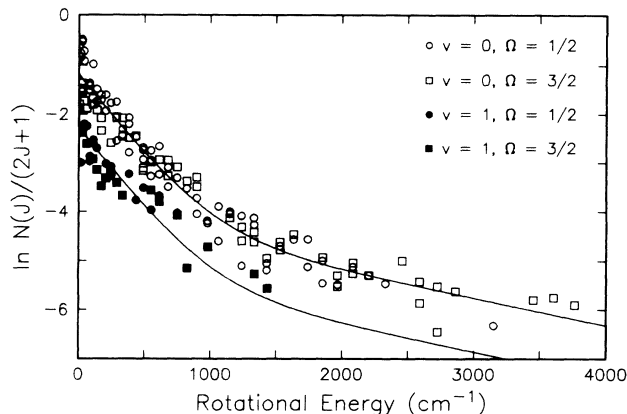


FIG. 2. Quantum-state distribution of desorbed NO molecules plotted as a function of rotational energy for $v=0,1$ vibrational and ${}^2\Pi_{1/2,3/2}$ spin-orbit levels. The data were obtained from REMPI spectroscopy using $A^2\Sigma^+(v'=v) \leftarrow X^2\Pi(v)$ transitions and taking the ionization cross section of the $A^2\Sigma^+$ state as independent of rotational and vibrational level.

200-fs pulse, we predict for conditions of equilibrium heat flow¹⁴ that the surface attains a peak temperature of 900 K for a few picoseconds. The observed desorption yield under these conditions is, however, similar to that found by heating the surface to the same temperature with nanosecond laser pulses.⁹ Thus the desorption rate for a conventional thermal mechanism is orders of magnitude too low to explain the results for the 200-fs pulses. The internal energy distributions of the desorbed NO molecules are also difficult to reconcile with a conventional thermal process. In particular, the measured vibrational temperature is far higher than the peak surface temperature assuming equilibrium behavior, whereas for desorption induced by nanosecond laser pulses, the NO vibrational temperature was comparable to the surface temperature.^{9,15} The rotational energy distribution for the femtosecond desorption process differs as well from the distributions characterized by a single temperature obtained for thermal desorption with nanosecond pulses.

Another valuable point of comparison for understanding our results is an examination of *nonthermal* desorption processes occurring under irradiation of nanosecond (or longer) duration. Recently, such photodesorption processes have been reported for molecules on metal surfaces by several groups.¹⁶⁻²³ In our case, an upper bound of $\sigma < 10^{-21} \text{ cm}^2$ for the photodesorption cross section was established for nanosecond laser pulses, in line with the results of Buntin *et al.*¹⁷ for desorption of NO/Pt(111) induced by visible light. Clearly a different desorption mechanism must be operative for femtosecond laser pulses, for which $\sigma \gtrsim 10^{-19} \text{ cm}^2$. The nonlinear dependence of the desorption yield on absorbed fluence for femtosecond laser pulses is also incompatible with the usual picture of photodesorption from a metal

surface.

Broadly speaking, the presence of a distinctive desorption mechanism for excitation on a subpicosecond time scale can be understood as a consequence of the existence of highly nonequilibrium conditions in the solid and adsorbed molecule on this time scale. Here we introduce a description of the excitation in the Pd substrate based on existing models of the response of metals to extremely short pulses.²⁴ It is assumed that the electronic and lattice excitation can each be characterized by a temperature. The flow of energy is governed by a diffusion equation for each system linked through an electron-phonon coupling term. While this simple model cannot provide a detailed description of the electron and phonon energy distributions, it should provide an adequate framework for examining possible desorption mechanisms. It should be noted that we treat only laser excitation of the substrate and neglect direct electronic excitation of the adsorbed NO molecules. This approximation can be justified by the strong coupling between excitation in the adsorbate complex and the bulk,³ where the vast majority of the adsorbed energy resides. In solving the coupled diffusion equations, we use an electron-phonon coupling strength $g = 5 \times 10^{11}$ W/cm³K, obtained from the relation given by Allen.²⁵ For an adsorbed fluence of 3 mJ/cm² in a 200-fs pulse, a peak electronic temperature of $T_e \approx 3000$ K is reached. The electronic temperature falls because of diffusion and energy transfer to the lattice. After approximately 1 ps, the electronic excitation comes into equilibrium with the lattice, which reaches a peak temperature of $T_l \approx 650$ K. The common electronic and lattice temperature then decays in ~ 10 ps as the equilibrated excitation diffuses into the bulk. We now reexamine possible desorption mechanisms using this more realistic treatment of excitation in the substrate.

Clearly desorption associated with excitation of the molecule-surface vibration by phonons in the substrate can still be ruled out in the two-temperature model, since the inferred lattice temperature is even lower than that found for complete equilibrium. We conclude that desorption induced by lattice vibrations could occur only in the presence of a significantly *nonthermal* distribution of phonons. On the other hand, if the molecule-surface vibration is most strongly coupled to the electronic excitation in the substrate, we can understand the principal experimental results. Indeed, by simply applying an Arrhenius expression for the rate of thermal desorption at temperature of $T_e = 3000$ K, we predict a yield comparable with experiment. The elevated vibrational temperature of the desorbed NO molecules would reflect the high electronic temperature, whereas the lower average energy in the rotational and translational degrees of freedom could be explained in terms of dynamical effects seen in conventional thermal desorption.¹ Two criteria must be satisfied for such an "electronic" desorption mechanism to be significant. First, the molecule-surface

vibration must couple to the electronic excitation of the solid more strongly than to the phonons; and, second, the *absolute* coupling strength of the molecule-surface vibration to the electronic excitation of the solid must be large enough to permit desorption before electronic cooling occurs. Model calculations of thermal desorption by Korzeniewski, Hood, and Metiu²⁶ suggest that the first criterion is not satisfied, at least not under conditions approximating equilibrium. Recent studies by Persson and Ryberg²⁷ for weak excitation of the molecule-surface vibration of CO/Pt indicate, however, that the first criterion is indeed met, although the second may not be.

We now consider the important class of mechanisms involving desorption via *electronic* excitation²⁻⁵ of the NO-Pd complex. Such a process may occur through motion on a purely repulsive excited-state potential following the Menzel-Gomer-Redhead (MGR) scheme,³ an attractive potential with a minimum at a smaller separation may also lead to desorption after deactivation to the ground state.³ For NO/Pd(111), the relevant electronic excitations presumably involve the $2\pi_{a,b}$ valence levels, either through the capture of an electron^{17,28} or a hole. Note that the general character of the energy distribution of NO molecules is compatible with desorption through an excited electronic state. In particular, the high vibrational energy content of the NO molecules can be attributed to changes in the equilibrium bond length of the adsorbed NO upon making an electronic transition.³ The high desorption cross section and its dependence on laser fluence must still be explained.

We can identify two factors contributing to the high desorption cross section for subpicosecond excitation. First, on this time scale, there may be an enhanced flux of energetic electrons (or holes) at the surface for each adsorbed photon. This may be described most naturally in terms of the model of thermalized hot electrons. The flux of hot carriers above the energy threshold required for the relevant electronic transition in the adsorbate complex will depend strongly on the electronic temperature and, hence, on the laser fluence. The second factor is the possibility of multiple excitation of the adsorbed NO molecules. For an electronic temperature of 3000 K, the flux of energetic electrons (or holes) is sufficiently high so that more than one carrier may arrive at each adsorbed NO molecule while nonequilibrium carrier excitation is present. The following may then occur. Upon capturing a hot carrier, an adsorbed NO molecule begins to desorb. Owing to the short lifetime of electronic excitation,³ the adsorbed molecule will generally be electronically deactivated without having obtained enough energy to escape from the surface. Another hot carrier may, however, excite the adsorbed molecule again before the energy in the molecule-surface vibration has dissipated. For rapid successive interactions, this process increases the effective lifetime of the excited state, which may enhance the desorption rate significantly.

In summary, intact desorption of NO from a Pd(111)

surface has been induced by 200-fs laser pulses of 2-eV photon energy. The yield and energy distribution of the desorbed NO molecules have been established. Among the important features of the desorption process is the strong dependence of the yield on adsorbed laser fluence. The internal energy distribution of the desorbed molecules exhibits a markedly nonthermal rotational population and a high degree of vibrational excitation. A comparison with desorption induced by nanosecond laser pulses reveals that a new desorption mechanism must be operative, one differing from conventional thermal and photochemical processes. A distinctive aspect of femtosecond excitation is the substantial decoupling of electronic and vibrational excitation. The ensuing high density of electronic excitation leads to the possibility of several novel schemes for desorption, involving both the ground and excited electronic states of the adsorbate complex. Further experimental and theoretical investigations should yield a more complete picture of desorption in this regime and additional insight into the nature of energy flow between surfaces and adsorbates.

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