VOLUME 66, NUMBER 23 PHYSICAL REVIEW LETTERS 10 JUNE 1991

Femtosecond Time-Resolved Measurement of Desorption

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(Received 26 December 1990)

Desorption of NO molecules from a Pd(111) surface induced by femtosecond visible laser pulses has been investigated in real time. The measurements, accomplished by means of a two-pulse correlation scheme, reveal a subpicosecond response time. The findings indicate that the desorption arises from coupling to the nonequilibrium electronic excitation in the substrate.

PACS numbers: 68.45.Da, 42.65.Re, 78.90.+t, 82.65.−i

The nature of coupling and the rate of energy flow between an adsorbate and a solid surface constitute key issues in surface dynamics.[1-7] Despite considerable experimental and theoretical effort, a complete understanding of these fundamental issues concerning the interaction between the localized excitation of the adsorbate and delocalized electronic and lattice excitation in the substrate remains elusive. For metal surfaces, strong coupling is generally present and typical relaxation rates lie in the picosecond to femtosecond range.[6,7] While these processes cannot be examined in real time using conventional surface science probes, laser-based techniques provide the possibility of time-domain studies.[8] Recently, real-time studies of relaxation of electronic[9] excitation at surfaces and of vibrational[7,10,11] excitation in adsorbates have been performed using pulsed laser excitation. In this Letter we report the results of the first direct time-resolved measurements of desorption from a surface under femtosecond excitation.[12]

The system of nitric oxide (NO) on Pd(111) was chosen as a model for desorption of a nondissociating chemisorbed molecule from a surface. In our laboratory we have previously characterized the yield and final-state energy distributions for NO molecules desorbed from Pd(111) by femtosecond laser pulses.[13] In contrast to the results obtained for desorption by nanosecond pulses,[14] the findings for desorption by femtosecond pulses could not be understood on the basis of equilibrium behavior, nor could the results be explained by a simple photochemical mechanism.[4,5] In the present work, we investigate the dynamics of desorption in the time domain. The time-resolved experiments are performed using a two-pulse correlation scheme in which the total desorption yield is measured as a function of temporal separation between a pair of excitation pulses. In this manner, we obtain femtosecond time resolution despite the time delay required before the desorbed molecules can be detected.[15] Examining correlation signals for both equal and unequal excitation pulses, we demonstrate that the excitation responsible for desorption has a finite lifetime not exceeding 1 ps. This result implies that nonequilibrium electronic excitation in the substrate is responsible for the desorption process, since mechanisms associated with coupling to substrate phonons would reflect the longer time scale required for cooling of the phonons to occur. We further show that the principal features of the time-resolved data can be understood through consideration of the substrate electronic temperature, which in the subpicosecond regime is largely decoupled from the lattice excitation.[16] Such time-domain measurements provide a new method of elucidating the mechanism of desorption and should aid in developing a complete understanding of this basic surface process.

The experiment was performed in an ultrahigh-vacuum system equipped for Auger-electron spectroscopy and low-energy electron diffraction.[17] The preparation and characterization of the single-crystal Pd(111) sample is outlined in Ref. 14. For the experiments reported here, the Pd sample was held at a base temperature of 400 K and maintained at saturation NO coverage through dosing with a pulsed molecular beam. Under these conditions the NO molecules are adsorbed nondissociatively in the γ state and occupy bridge sites.[18] Desorption was induced with the output of an amplified colliding-pulse mode-locked laser[19] operating at a repetition rate of 10 Hz and providing pulses at a wavelength of 620 nm with a 400-fs duration after propagation to the sample. The correlation measurements were performed using two orthogonally polarized pulses directed onto the sample with s and p polarization to minimize interference effects. The beam was incident on the surface at 60° from the normal and was lightly focused to produce a spot of ~ 1 mm diameter. It should be noted that the desorption yield was found to be independent of the polarization of the laser excitation after adjusting the fluence for the difference of s and p absorptivity. The desorbed NO molecules were detected above the surface by resonance-enhanced multiphoton ionization (REMPI) spectroscopy.[17] The REMPI technique permits detection of the desorbed NO molecules in a state-specific fashion. Here we report data for NO in the ground vibrational state ($v=0$) and rotational states forming the $Q_{11}+P_{21}$ bandhead. Typical desorption yields were $\sim 10^{-3}$ monolayer per pulse.

Figure 1(a) displays the results of a correlation measurement performed with pump pulses of approximately the same absorbed fluence[20] (1.7 and 1.8 mJ/cm^2). The

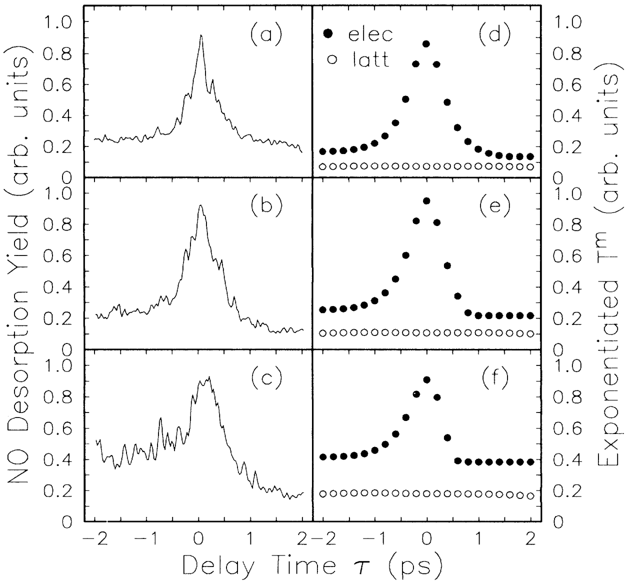

FIG. 1. Two-pulse correlation data as a function of pulse delay τ of the weak excitation pulse with respect to the strong pulse. (a)-(c) The experimental desorption yields of NO for different pulse-pair fluences: (a) 1.7 and 1.8 mJ/cm^2, (b) 1.6 and 2.2 mJ/cm^2, and (c) 1.3 and 3.0 mJ/cm^2. (d)-(f) Calculations of the exponentiated peak electronic (solid symbols) and lattice temperatures (open symbols), as discussed in the text, for the conditions corresponding to (a)-(c), respectively. The results for the exponentiated lattice temperature have been multiplied by a factor of 5000.

strong symmetrical correlation peak rises to a value of ~4 times the base line for two pulses separated by a few picoseconds. In addition to this feature appearing at short delays, the base-line signal drops further for long time delays (> 10 ps) to reach a small value corresponding to the yield of two fully separated pulses. The enhancement of the NO yield above the base line seen in the figure is somewhat less than that anticipated from the previously measured dependence of the desorption yield on the laser fluence to the 3.3 power.[13] This reflects the fact that the two pulses still remain somewhat correlated for a time delay of tens of picoseconds. The width of the correlation trace is determined to be $\Delta t = 600$ fs (FWHM) from a fit of the data by a sech^2 form. This value can be considered as the characteristic response time of the system under excitation by pulses of finite duration. We see immediately that a conventional thermal-desorption process cannot be operative since cooling of the surface by equilibrium heat flow would require $\gtrsim 10$ ps and would lead to a much broader correlation feature. We may also ask whether the data can be described by an instantaneous response to the laser excitation. Such a model might be appropriate for a multiphoton desorption mechanism, for example. In this case, we would expect the correlation signal to follow the form of the total adsorbed laser intensity $I(t)$ raised to the appropriate power to reproduce the fluence dependence, namely, $[I(t)]^{3.3}$. This results in a feature with a width (FWHM) of 450 fs. Since this width falls below the experimental value, it is clear that a finite response time for desorption is present.[21]

In Figs 1(b) and 1(c) data are presented for excitation with pulse pairs with unequal adsorbed fluences. For such conditions, the correlation trace exhibits a strongly asymmetric form. The desorption yield is observed to be higher when the weak pulse precedes the strong one than for the reverse ordering of the pulses. We discuss below how this behavior can be understood in terms of the electronic temperature of the substrate. Let us only observe here that this finding demonstrates the inadequacy of treating the desorption process as instantaneous: In the limit of a vanishing response time, the correlation trace must necessarily be symmetrical for excitation with symmetrical laser pulses.

In order to analyze the results further, we introduce a description of the lattice and electronic excitations of the substrate[22] on the subpicosecond time scale. As remarked above, a treatment based on full thermal equilibration is not appropriate. Instead we consider a model in which the electronic and lattice excitations are treated as being thermalized individually, but are linked by a finite electron-phonon coupling constant and may attain different temperatures.[16] The spatial and temporal flow of energy is governed by a set of coupled diffusion equations with the laser excitation providing the initial electronic excitation. This approach, which has been applied extensively in the literature,[16] should provide an adequate qualitative picture of the substrate excitation. In solving these equations numerically, we use temperature-dependent thermal conductivity and heat capacities and an electron-phonon coupling of $g = 5\times10^{11}$ W/cm^{3}K based on a relation given by Allen.[23] For the electronic heat capacity the usual form of $C_e(T_e) \sim T_e$ is assumed for all temperatures. Since the density of states of Pd is sharply peaked about the Fermi level,[24] this relation overstates the heat capacity at sufficiently high electronic temperatures where the effective density of states will decrease.

Figure 2 displays selected profiles for the electronic and lattice temperatures at the surface of the Pd sample calculated using the above approach. The results in the figure represent irradiation with unequal laser pulses corresponding to the conditions of the data in Fig. 1(c) for pulse separations of $\tau = -1$, 0, and 1 ps. Consider first the case of coincident laser excitation ($\tau = 0$) shown in Fig. 2(b). Initially the electronic temperature is seen to be decoupled from that of the lattice and the low heat capacity of the electrons permits a peak temperature T_e^m ~3500 K to be reached. On the time scale of 1 ps, the electronic excitation begins to cool as energy is transferred to the lattice. The subsequent diffusive cool-

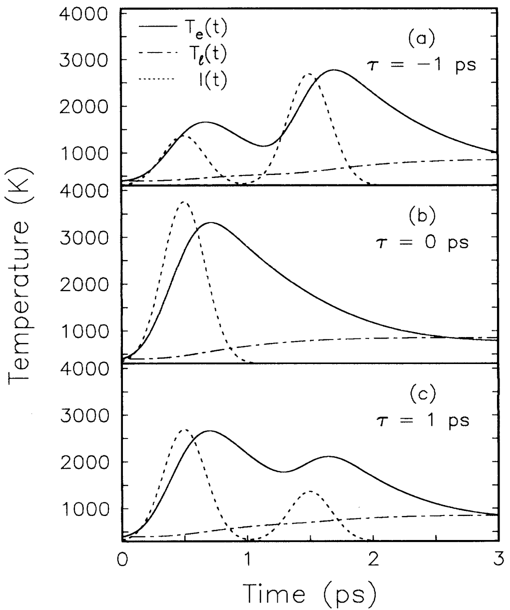

FIG. 2. Calculations of the electronic (solid curve) and lattice (dot-dashed curve) temperatures from the coupled diffusion equations for heat flow under excitation conditions corresponding to Fig. 1(c). The results are displayed for pulse delay times $\tau = -1$, 0, and 1 ps. The dotted curves indicate the laser excitation profiles.

ing of the equilibrated excitation occurs over tens of picoseconds and is not visible in the figure. For the case of two-pulse excitation, the peak temperature attained by the second pulse is influenced by the heating produced by the first pulse. The effect on the peak electronic temperature can be observed even if the excitation of the first pulse has thermalized. The influence is most pronounced, however, if the electronic excitation from the first pulse has not yet equilibrated, i.e., for delays < 1 ps. For excitation pulses of differing intensities, as shown in Fig. 2, the peak electronic temperature T_e^m also depends on the order of the two excitation pulses. Since T_e^m is governed by the strong pulse, a higher value is reached when the weak pulse arrives first and provides preheating for the strong pulse [Fig. 2(a)] rather than for the reverse ordering [Fig. 2(c)]. Thus, for pump pulses with different absorbed fluences, T_e^m is a sharply peaked (~ 1 ps) and asymmetric function of the delay time. On the other hand, the peak lattice temperature T_l^m shows little variation for delay times $\tau < 10$ ps because of the slow rate of diffusion of the equilibrated excitation.

From the analysis just described, we obtain the peak electronic and lattice temperatures T_e^m and T_l^m at the Pd surface for two-pulse excitation as a function of delay time τ. We now consider how this relates to the desorption signals. To assess the relative importance of the lattice and electronic heating on desorption, it is instructive to consider two limiting cases: complete equilibration of the NO-Pd vibration with the lattice temperature and complete equilibration with the electronic temperature. We then take the desorption rate to be given by an Arrhenius form with an activation energy E_a and the appropriate temperature. The curves in Figs. 1(d)-1(f) indicate the predicted behavior in the different limiting cases for an activation energy[25] of $E_a = 1.0$ eV. We observe immediately that the characteristic form of the correlation traces is reproduced using the peak electronic temperature T_e^m, but not with the lattice temperature T_l^m. The increasing degree of asymmetry in the correlation peak of Figs. 1(b) and 1(c) is reflected in the corresponding curves 1(e) and 1(f) for the electronic desorption mechanism. In addition to the asymmetry of the peak, the calculations show small but distinct shifts in the base-line level. This offset arises from the equilibrium preheating occurring when the weak pulse precedes the strong one. The sign of the effect agrees with the experiment, although the magnitude of the calculated shift is considerably smaller than that of the experimental data. The calculated shift would increase, however, for a smaller electronic heat capacity $C_e(T_e)$ at high T_e (see above), since the preheating would then be more effective in raising T_e^m. Overall we see that the exponentiated peak electronic temperature (but not the peak lattice temperature) is capable of reproducing the main qualitative features and the approximate width of the experimental correlation traces.

It should be stressed that the analysis above, while demonstrating the important influence of electronic excitation in the substrate on desorption, makes several simplifying assumptions. Certainly a finite coupling time exists between the electronic excitation in the bulk and motion of the adsorbate. From the observed width of the correlation feature, however, we infer that this coupling time should be < 1 ps. This time involves an average of the coupling for different levels of the molecule-surface vibration excited in the desorption process. As such it is related to, but distinct from the recently reported time-domain measurements of relaxation for weak excitation of vibrational modes of adsorbates,[7,10,11] which for the case of internal vibrations of diatomic molecules chemisorbed on metal surfaces gave relaxation times[10] of 3-5 ps. The discussion above is also simplified by restricting ourselves to the limiting cases of coupling to electronic *or* lattice excitation. A more realistic model would include simultaneous coupling to both degrees of freedom, possibly with different relative strengths depending on the degree of molecule-surface vibration.[26] We are currently developing a microscopic treatment of the desorption process induced by electronic and lattice excitations at differing temperatures that permits us to examine these issues in detail.

In summary, we have performed direct time-resolved measurements of desorption from a surface induced by femtosecond laser pulses. On the subpicosecond time scale highly nonequilibrium conditions arise in which the lattice and electronic excitations in the substrate are decoupled. The observed two-pulse correlation signal for desorption exhibited a strong peak of <1 ps width and showed a pronounced asymmetry for excitation by pulses of unequal strengths. These characteristic experimental features can be understood by consideration of the electronic temperature in the metal substrate, but cannot be explained by the lattice temperature. The results demonstrate unambiguously that low-energy electronic excitation in the substrate can play a significant role in coupling substrate energy to the motion of an adsorbate on a metal surface.

The authors acknowledge critical technical contributions by B. D. Smith.

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