Vibrationally assisted electronic desorption: Femtosecond surface chemistry of O_2/Pd(111)

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The process of desorption for the system of O_2/Pd(111) under excitation by 100 fs pulses of visible light has been examined. Molecular desorption is found to occur with high efficiency and a nonlinear dependence on laser fluence. Direct time-domain measurements using a two-pulse correlation scheme reveal a dominant subpicosecond response together with a weaker, but significant correlation persisting for tens of picoseconds. These results imply a desorption process driven by the high electron temperatures produced by the femtosecond laser radiation. The slower component of the correlation response is interpreted as an enhancement of the desorption rate by adsorbate vibrational excitation.

Recently a new class of surface chemical processes has been demonstrated to be accessible through irradiation of the surface with laser pulses of femtosecond duration.[1–6] Results published on desorption in the chemisorption systems of NO/Pd(111)[1,2,4] and CO/Cu(111)[3] and O_2 [Pt(111)][5] excited by femtosecond radiation reveal several distinctive features: a very efficient channel for molecular desorption, a desorption yield scaling nonlinearly with laser fluence, and a subpicosecond response time for the desorption process. These characteristics cannot be reconciled with either a conventional thermal or photoinduced mechanism. Rather, desorption is attributed to the unique excitation conditions of high substrate electronic temperatures with little lattice heating arising from femtosecond laser pulses.

In this Letter, we present results of a study of the behavior of O_2/Pd(111) under excitation by femtosecond laser pulses. This system was chosen because of its interesting and well-characterized thermal chemistry[7–9] and photochemistry.[10,11] In contrast to the previously investigated cases, adsorbed O_2 on the Pd(111) surface exhibits dissociation as well as molecular desorption. As we report here, femtosecond laser radiation is capable of inducing efficient desorption even in this chemically more complex system. The broad similarity of the behavior for O_2/Pd(111) with the simple systems examined earlier suggests the generality of a desorption mechanism associated with the high electronic temperatures induced by femtosecond laser pulses. The present experiments do, however, exhibit an important new feature. In addition to the subpicosecond response observed previously, two-pulse correlation measurements for O_2/Pd(111) display a significant response for times > 10 ps. We explain this effect as a consequence of an enhancement of the desorption rate for vibrationally excited adsorbate molecules, i.e., as a vibrationally activated electronic desorption mechanism, with the longer time scale indicative of the cooling of the adsorbate vibrational excitation.

The experiments were conducted in an ultrahigh vacuum chamber (base pressure 1×10^{-10} Torr). The single-crystal Pd(111) surface was prepared by repeated cycles of argon-ion sputtering (0.5 kV) and annealing to a temperature of 950 K. Surface cleanliness and order were checked with Auger electron spectroscopy and low-energy electron diffraction (LEED). The concentration of surface carbon, whose Auger peak is obscured by an overlapping Pd peak, was gauged by the CO reaction product resulting from exposure of the sample to oxygen. The desorption measurements were performed starting with the Pd(111) surface dosed to saturation coverage at a base temperature of 140 K. Under these conditions, the α_1 and α_2 (peroxy) molecular adsorption states are formed.[7–9] The laser pulses required for the experiments were generated by an amplified colliding pulse mode-locked (CPM) ring dye laser. The system delivered pulses of 620 nm (2.0 eV) light at a 10 Hz repetition rate. The pulse duration at the Pd sample was 100 fs and an energy of 0.5 mJ/pulse was available. The desorbed O_2 was detected by a quadrupole mass spectrometer, the output of which was recorded on a transient digitizer.

Upon exposure to femtosecond laser pulses, desorbed O_2 could be readily detected. In contrast to observations for traditional thermal and photo induced processes, dissociation of the adsorbed molecular oxygen was not found to be a major reaction channel. The issue of branching ratios in the femtosecond surface chemistry of O_2 will be discussed in detail elsewhere. With respect to desorption, an absorbed fluence of 3.5 mJ/cm^2 gave rise to a yield of molecular oxygen of $\sim 10^{-4}$ ML. This corresponds to a cross section for a single photon process of $\sigma \sim 10^{-18}$ cm^2 per absorbed photon. In contrast to a simple photoinduced process, however, the desorption yield is strongly nonlinear in laser fluence, as shown in Fig. 1. The data can be fit to a power-law relation with an exponent of 6.0.

Time-resolved studies provide important additional information about the nature of the desorption process.[2,3] In our measurements, time-domain data have been obtained by a correlation technique in which the total desorption yield is monitored as a function of delay time between two excitation pulses. The experimental results are displayed in Fig. 2. In this figure, the uncorrelated background signal (i.e., the sum of the yield for each pulse individually) has been subtracted from the data for each run. The results in Figs. 2(a) and 2(c) were obtained with excitation pulses of

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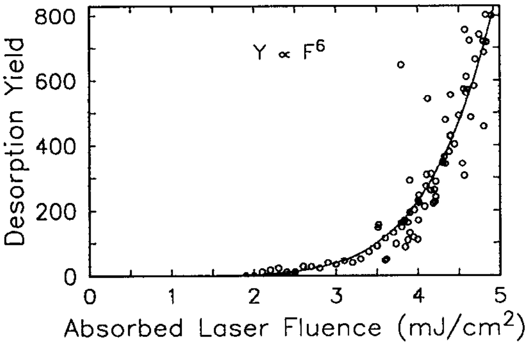

FIG. 1. O_2 desorption yield as a function of absorbed fluence for excitation by a 100 fs laser pulse. The solid line is a fit to a power law.

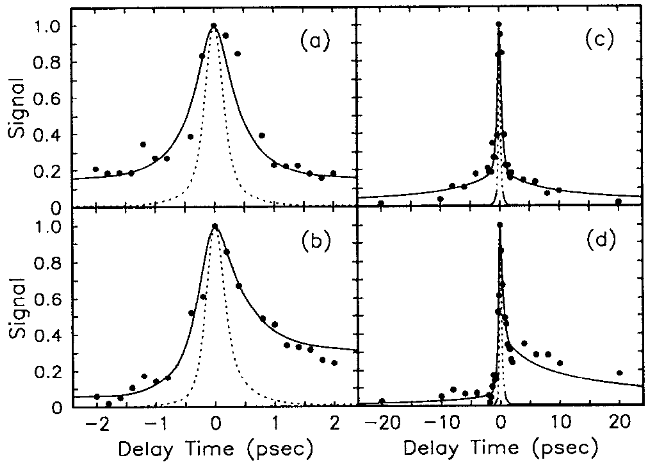

FIG. 2. Two-pulse correlation data. The O_2 desorption yield (solid circles) is plotted as a function of the delay between pairs of femtosecond excitation pulses. Panels (a) and (b) examine the short time-scale response (±2 ps); (c) and (d) show the data for pulse separations up to ±20 ps. Results in (a) and (c) correspond to excitation pulses with adsorbed fluences of 1.7 mJ/cm^2 in each beam; (b) and (d) were obtained with unequal absorbed fluences of 1.5 and 2.3 mJ/cm^2. At positive times, the weak excitation pulse precedes the strong one. The dotted curves are based on a phenomenological model of the desorption process in which only the electronic temperature of the system is considered. The solid curves include the effect of vibrational activation, as discussed in the text.

equal fluence of 1.7 mJ/cm^2. The results in panels (b) and (d) correspond to unequal fluences of 1.5 and 2.3 mJ/cm^2, with positive time delay denoting the situation where the weak pulse precedes the strong one. Two features in these data are noteworthy. First, both the equal and unequal fluence data sets show a narrow peak of width $\lesssim 1$ ps. Second, the wings of the correlation traces do not fall rapidly to the value expected for uncorrelated pulses. The slowly decaying correlation response, particularly prominent in Fig. 2(d), has a lifetime $\gtrsim 10$ ps.

The experimental observations just summarized provide clear evidence that the desorption process induced by femtosecond laser pulses is neither a conventional thermal process nor a conventional photochemical one. A conventional thermal process associated with the lattice temperature profile of the substrate would not exhibit the strong subpicosecond response time present in the correlation measurements. This point has been discussed previously with respect to NO/Pd(111).[2] Further, the few hundred degree rise in the substrate lattice temperature induced by the laser pulse (see below) would not be expected to give a significant desorption yield based on an Arrhenius rate law. With respect to the operation of a conventional photochemical desorption mechanism, several experimental features are incompatible. First, a striking departure from a usual photochemical process is found in the nonlinear dependence of the desorption yield on laser fluence. Second, the photon energy of 2.0 eV lies below the threshold of approximately 3.5 eV quoted in the literature. Third, the cross section for femtosecond desorption at this subthreshold photon energy ($\sigma_{\text{fs}} \sim 10^{-18}$ cm^2) exceeds even the largest reported value for nanosecond photochemistry[11] ($\sigma_{\text{ns}} \sim 4 \times 10^{-19}$ cm^2 at $\hbar\omega = 6.4$ eV). Finally, the correlation response is considerably longer than the laser pulse. This observation precludes, e.g., a conventional photochemical process occurring through multiphoton excitation.

In order to discuss the experimental results, we first briefly describe the response of the Pd metal substrate to femtosecond laser pulses.[12] The absorption of optical photons at a metal surface leads to the creation of electron-hole pairs. This electronic excitation equilibrates with the lattice modes (phonons) on a time scale of ~1 ps. For irradiation by subpicosecond laser pulses, the substrate excitation can be described to a reasonable approximation by two temperatures, one for the electrons (T_{elec}) and one for the lattice (T_{latt}). Since the heat capacity of the lattice is much greater than the heat capacity of the electrons, it is possible to attain peak electronic temperatures of thousands of degrees with a rise in lattice temperature limited to a few hundred degrees. Typical behavior of the elec-

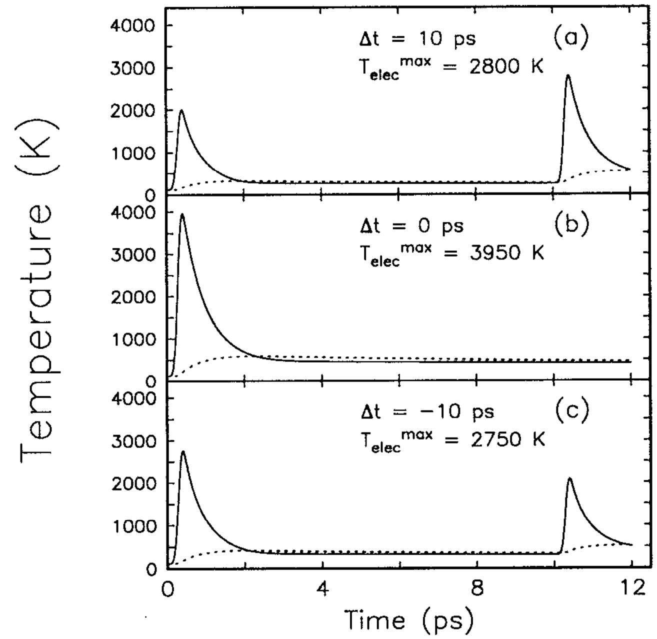

FIG. 3. Calculations of the electronic (solid curves) and lattice (dotted curves) temperature profiles for excitation of a Pd surface with pairs of 100 fs pulses of 1.5 and 2.3 mJ/cm^2 fluence.

tronic and lattice temperatures, computed by the coupled diffusion equation formalism,[13] is portrayed in Fig. 3(b). For an absorbed fluence of 3.8 mJ/cm^2, peak electronic and lattice temperatures of $T_{\text{elect}}=3950$ K and $T_{\text{latt}}=450$ K are obtained. As can be seen in the figure, the electronic temperature transient has a duration of ~ 1 ps before substantial equilibration with the lattice occurs. The equilibrated excitation then decays on a time scale of tens of picoseconds as diffusion into the bulk occurs.

Many of the key experimental findings can be explained at a qualitative level by postulating a strong coupling between the nonequilibrium substrate electronic excitation created by the femtosecond laser pulse and the adsorbate center-of-mass motion. Among these are: the high desorption yield (a consequence of the elevated electronic temperature), the nonlinear fluence dependence (a consequence of activation by the electronic temperature), and the dominant subpicosecond correlation response (a consequence of the rapid electronic cooling in the Pd substrate). Microscopic models of the adsorbate–substrate electronic coupling have been considered within a frictional formalism[14,15] for a single adsorbate potential energy surface, as well as in a picture involving desorption induced by multiple electronic transitions (DIMET)[16] between distinct adsorbate potential surfaces.

For our immediate purposes, we restrict ourselves to a phenomenological treatment. While clearly incomplete, we believe that this level of analysis is sufficient to draw some important conclusions about the nature of the desorption mechanism. In this approach, we first compute the electronic temperature profiles for various laser fluences. From the measured fluence dependence of the desorption yield, we then construct a relation between the electronic temperature and desorption rate (taken for definiteness as instantaneous in time). This relation, when combined with the calculated temperature profiles (such as those of Fig. 3), can be used to predict the shape of the two-pulse correlation traces. As shown by the dotted curves in Fig. 2, the procedure reproduces the dominant subpicosecond correlation response reasonably well. The short-time behavior reflects the increased substrate electronic temperature for pairs of excitation pulses falling within the electron–phonon coupling time of the solid.

For longer pulse separations, this simple model reproduces some of the *trends* in the correlation data. Both the presence of a long-time (> 10 ps) correlation response and its characteristic asymmetry are predicted. These features arise from the influence of the first pulse in raising the equilibrium temperature of the substrate. Such a preheating effect, as can be seen in Fig. 3, leads to a slightly higher peak electronic temperature for the second pulse and, hence, to a higher desorption yield than in the absence of the first excitation pulse. The effects are, however, very weak. For example, the presence of the first pulse in Fig. 3(a) only raises the peak T_{elec} of the second pulse from 2750 to 2800 K. As a consequence, the model is not capable of reproducing the substantial effects observed experimentally. Indeed, the long-time correlations predicted by the model are not even visible on the scale of Fig. 2. We conclude that an additional contribution must act to retain the memory of the excitation in the system from one pulse to the other.

The excitation that is most likely to enhance the electronically driven desorption process is vibration in the molecule–surface bond (or another closely coupled adsorbate motion). Simulations of DIMET processes (as well as the single-excitation analog, DIET) indicate a strong increase of the desorption yield with the temperature of the molecule–surface vibration.[17] We introduce this effect into our model by a desorption yield that depends on the electronic temperature, but is activated (in an Arrhenius manner) by the degree of excitation of the molecule–surface vibration. The extent and time evolution of the adsorbate vibrational excitation produced by the first laser pulse is not presently determined by any direct experimental observation. As an approximation, we calculate the adsorbate vibrational temperature using a frictional coupling[4,18] to the substrate *electronic* excitation with a relaxation time of 5 ps. This approach reflects the strong coupling of adsorbate vibrational modes to substrate electron-hole pair excitation known to be present at low electronic temperatures.[19–23] Clearly, at elevated electronic temperatures where the desorption rate is high, this approximation does not predict the correct molecule–surface vibrational temperature. However, the calculation provides a description of the initial condition (i.e., the degree of vibrational excitation remaining from the electron transient of the first pulse) for desorption induced by the second laser pulse. With an activation energy for the molecule–surface vibration of 1500 K, the model (solid lines in Fig. 2) provides a satisfactory qualitative fit to the experimental data.

Within the present model, the long-time correlation arises from the decay of adsorbate vibrational excitation, which is in turn controlled by the substrate (electronic) temperature. While this treatment reproduces the experimental data in a natural manner, the initial adsorbate vibrational excitation following the first excitation pulse may, as noted above, exceed that assumed in our calculation. This effect might manifest itself in the appearance of two distinct relaxation times in the correlation trace, one associated with the equilibration of the adsorbate vibration with the substrate electronic excitation and the other (considered in the analysis above) with the cooling of the substrate itself. With the available experimental data, only a single decay time can be identified with certainty. In addition to an explanation based on cooling of the adsorbate vibration while in equilibrium with the substrate, the long-time correlation response can also be reproduced by the phenomenological model in the limit of a slow relaxation of the adsorbate vibrational excitation to the substrate temperature. In this case, a vibrational lifetime > 10 ps is required. The roles of these two contributions to the correlation decay should be separable experimentally by comparing the present results with those obtained using a nanosecond laser pulse to heat the sample before inducing desorption with a femtosecond pulse. Such experiments are planned in our laboratory.

In conclusion, the results of the O_2/Pd(111) system reported here confirm the generality of surface processes driven by coupling to the high substrate electronic temperatures created by femtosecond laser pulses. More specifically, the experiments demonstrate an efficient desorption process with a nonlinear fluence dependence, a dominant ~1 ps response, and a weaker correlation persisting for > 10 ps. The appearance of these distinct time constants in the time-domain data, a feature not recognized in previous studies, cannot be reconciled with a model for desorption relying solely on a rapid electronic coupling. The behavior is attributed to a vibrationally assisted electronic mechanism in which the initial degree of vibrational excitation of the adsorbate significantly affects the rate of electron desorption process.

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