Femtosecond Laser Induced Processes: 
Ultrafast Dynamics and Reaction Pathways for O$_2$/Pd(111)

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ABSTRACT

The processes of desorption and dissociation for O$_2$ on Pd(111) under femtosecond laser irradiation have been investigated. Desorption is characterized by a high yield, a nonlinear fluence dependence, and a dominant subpicosecond feature in two-pulse correlation measurements. These observations are consistent with a process driven by the high substrate electronic temperature produced by the femtosecond laser pulse. The correlation measurements also reveal the existence of a weaker feature persisting $\approx$10 ps which is attributed to an enhancement of the desorption rate by adsorbate vibrational excitation. Under the same conditions where efficient desorption is occurring, an upper limit of 5% is found for the dissociation of molecular oxygen. This is in contrast to the high branching ratio for dissociation found in thermal activation and conventional photoactivation for the same system. Explanations for the anomalous branching ratio in the femtosecond surface chemistry for O$_2$/Pd(111) within a model involving multiple cycles of electronic excitation are examined.

1. INTRODUCTION

The activation of chemical reactions at solid surfaces by both thermal and photo-induced means is well-known; however, recent experiments have shown that femtosecond laser light can induce a new class of chemical processes at metal surfaces.$^{1-9}$ In studies of desorption of femtosecond laser excitation several distinctive features were observed. The desorption yield$^1$ was found to be much higher than expected based upon a conventional thermal or photoactivated mechanism. Although a linear fluence dependence is observed for conventional photoactivated processes, the femtosecond desorption experiments are characterized by a highly nonlinear fluence dependence.$^{1,3,6,7}$ Also, time-resolved experiments$^{2,3,6,7}$ performed under femtosecond excitation conditions reveal a subpicosecond response time for the desorption. These features have been attributed to the influence of the high electronic temperatures attained in the metal substrate under femtosecond excitation. The initial absorption of photons leads to creation of electron-hole pairs. Because of the low electronic heat capacity and the $\approx$1 picosecond time scale required for electronic excitation to couple with the phonons, the metal surface may reach a transient electronic temperature of thousands of degrees. The unique features of femtosecond laser activation are then the result of the interaction of the adsorbate with this substrate electronic excitation. One proposed model,$^9$ desorption induced by multiple electronic transitions (DIMET), involves repetitive cycles of electronic excitation and deexcitation of the adsorbed species as

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a mode of energy transfer from the substrate into the reaction coordinate. Such a model accounts for many of the salient features of femtosecond laser induced desorption.

The existence of a new mechanism for activation of chemical reactions at metal surfaces suggests the possibility of obtaining distinctive branching ratios in the case where multiple reaction channels are open. Indeed, recent examinations of the branching ratio for reactions involving oxygen on Pt$^5$ and Pd$^d$ reveal novel branching ratios for femtosecond surface chemistry. On Pd, two reaction channels for adsorbed O$_2$ exist: molecular desorption and dissociation to form adsorbed atomic oxygen. Under both thermal activation and photo-activation the two reaction channels are readily observed. In contrast, the results for femtosecond excitation in this system indicate a strong propensity for desorption.

In this paper we present the results of our studies of desorption and dissociation in the femtosecond surface chemistry of O$_2$/Pd(111). For desorption, we examine the yield, fluence dependence, and correlation response. The branching ratio for the competition between desorption and dissociation is also studied.

2. THE O$_2$/Pd(111) SYSTEM

Fig. 1: A temperature programmed desorption (TPD) spectrum for a saturation dose of oxygen on Pd(111) at 110 K showing the molecular desorption peaks at low temperature and recombinative desorption of atomic oxygen in a broad peak at high temperature.

Before turning to the experiment itself, we briefly review some of the key points in the literature on the thermal chemistry and photochemistry of O$_2$/Pd(111).$^{10-15}$ At low temperatures (< 150 K), exposure of Pd(111) surfaces to O$_2$ results in molecular chemisorption at all doses. There is significant charge transfer into the $\pi^*$ orbital of oxygen with the appearance of both superoxo (O$_2^-$) and peroxo (O$_2^2-$) species on the surface.$^{11}$ The first molecular state to form, the $\alpha_1$ species, is characterized by the highest binding energy and largest shift in the intramolecular vibrational frequency from gas-phase oxygen. After saturation of the $\alpha_1$ state, the $\alpha_2$ and $\alpha_3$ species form sequentially. These states are characterized by decreasing binding energies and frequency shifts. A temperature programmed desorption (TPD) trace is shown in Fig. 1 for molecular oxygen after dosing the Pd(111) surface to saturation coverage. Desorption from the $\alpha_3$ state (the low-temperature shoulder of the first peak) and $\alpha_2$ state (the central part of the first peak) occurs initially, with desorption of the $\alpha_1$ species following at a temperature of ~200 K. From EELS data,$^{11}$ adsorbed atomic oxygen is formed at temperatures which coincide with the appearance of the $\alpha_1$ TPD peak. The desorption of the $\alpha_1$ molecular oxygen species is thought to result from a displacement process accompanying the dissociation of adsorbed molecular oxygen. This conclusion is supported by the strong inhibition of $\alpha_1$ oxygen formation upon predosing with atomic...
oxygen. At low initial coverages of O₂, heating of the surface leads to complete dissociation rather than to molecular desorption. In addition to the molecular desorption features observed at low temperature, a broad desorption peak is observed around 800 K. This peak corresponds to the recombinative desorption of atomic oxygen which was formed by the dissociation of the molecular species at 200 K. The photochemistry of O₂/Pd(111) has also been investigated extensively. Three different photo-induced processes have been observed: photodesorption of molecular oxygen, photodissociation into adsorbed atomic oxygen, and interconversion between the molecular adsorption states. All of these processes were found to have similar cross sections and to display a threshold photon energy of about 3.5 eV. The cross sections increased strongly with photon energy up to the highest energy used (6.4 eV), where the maximum cross sections approached ~ 10⁻¹⁸ cm².

3. EXPERIMENTAL

The experiments were conducted in an ultrahigh vacuum chamber (base pressure 1 x 10⁻¹⁰ Torr) equipped with capabilities for low-energy diffraction (LEED) and Auger spectroscopy. 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 level of surface carbon, whose Auger peak is obscured by an overlapping Pd peak, was gauged through the CO reaction product after exposure of the sample to oxygen. For the experiments reported here, the base temperature of the Pd(111) sample generally was 100 K. Oxygen desorbed from the sample was detected by quadrupole mass spectrometry.

The laser pulses required for the experiments were generated by an amplified colliding pulse mode-locked ring dye laser (CPM). 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 with an energy of 0.5 mJ. In order to determine the energy absorbed by the sample, the reflectivity was measured directly. Further, energy and transverse characteristics of the laser could be determined on a shot-by-shot basis with a beam profiling camera. Typically the beam was focussed to a spot of millimeter size, yielding absorbed fluences on the order of a few mJ/cm². The quoted fluences refer to the peak value across the profile.

4. RESULTS

An examination of the femtosecond desorption process for this system was recently reported by our group. Upon irradiation of the surface with femtosecond laser pulses, the desorption of molecular O₂ from Pd(111) was easily detected by capturing mass spectrometer transients, suggesting the high efficiency of the process. More precisely, an absorbed laser fluence of 3.5 mJ/cm² desorbed ~ 10⁻⁴ ML of molecular oxygen. In linear photochemistry, this would correspond to a cross section of σ ~ 10⁻¹⁸ cm² per absorbed photon. The desorption induced by femtosecond laser pulses is, however, not a simple linear photoinduced process. The fluence dependence shown in Fig. 2 indicates a highly nonlinear process. The solid line in Fig. 2 is a fit to a power law which indicates an exponent of 6.0.
Fig. 2: O$_2$ desorption yield as a function of absorbed fluence for femtosecond surface chemistry. The solid line is a fit of the data to a power law.

Important clues to the nature of the femtosecond surface chemistry activation process have been obtained from time-resolved studies\textsuperscript{2,3,6} of desorption. In our approach, time-domain data is obtained by a correlation technique in which the desorption yield is monitored as a function of delay time between two excitation pulses. Fig. 3 shows correlation data for the case where the absorbed fluences for the two pulses are 1.5 and 2.3 mJ/cm$^2$. Positive delay times correspond to the weak pulse preceding the strong pulse. Although symmetric correlation traces are obtained when equal pulse fluences are used\textsuperscript{7}, the asymmetric data are shown here since the asymmetry more clearly indicates the long time feature of the process. Two features are prominent in the time-resolved data: the dominant subpicosecond feature of width $\sim$0.8 ps and a weaker correlation feature lasting $\approx$10 ps.

Fig. 3: Two-pulse correlation data for O$_2$/Pd(111) in which desorption yield is plotted versus delay time between two pulses with absorbed fluences of 1.5 and 2.3 mJ/cm$^2$. Positive time corresponds to the weak pulse preceding the strong pulse.

We next examine the dissociation of O$_2$ on Pd(111) under the same femtosecond laser excitation conditions that led to the desorption described above. From experiments performed on Pd(111) surfaces saturated with atomic oxygen (obtained by dosing with molecular oxygen at sample temperature of 300 K), we have established the femtosecond laser pulses do not initiate recombinative desorption. Therefore, dissociation of molecular oxygen will result in atomic oxygen which remains on the surface. Con-
sequently, the extent of dissociation can be gauged by the amount of atomic oxygen present on the surface after irradiation with the femtosecond laser. We measure the surface oxygen coverage using temperature programmed desorption (TPD) spectra. As mentioned above, at low oxygen coverages only the recombintive desorption peak is observed in TPD spectra. We calibrate mass spectrometer sensitivity using the fact that the peak saturates at 0.25 monolayer (ML) coverage (O/Pd atom). Figure 4 shows a series of recombintive desorption TPD spectra for increasing oxygen exposure. The area of the recombintive desorption peak is plotted versus exposure in Fig. 5. From these data we conservatively assign a sensitivity of 0.02 ML for observation of surface oxygen.

Fig. 4: Recombinative desorption peaks versus exposure of O₂ for a Pd(111) surface temperature of 300 K.
With this information, we now irradiate the surface with the femtosecond laser and record TPD spectra. These measurements are performed by scanning the beam across the sample to produce uniform exposure. The experimental results are shown in Fig. 6 as a function of increasing laser exposure. The data were obtained with the sample at a base temperature of 100 K, but with oxygen dosing at a temperature of 157 K for which only the \( \alpha_1 \) molecular oxygen state is formed. This procedure allows us to look simultaneously for another possible process: the conversion of molecular oxygen in \( \alpha_1 \) states into \( \alpha_2 \) and \( \alpha_3 \) molecular states.

![Fig. 6: TPD spectra taken as function of the extent of femtosecond laser scanning for an absorbed laser fluence of 3.6mJ/cm\(^2\). The sample was dosed with oxygen at 157 K (to produce only the \( \alpha_1 \) state) and then cooled to 100 K for laser irradiation.](image)

5. DISCUSSION

The high yield at a photon energy below threshold for conventional photochemistry, the nonlinear fluence dependence and the subpicosecond correlation feature observed for desorption induced by
femtosecond laser pulses in the O₂/Pd(111) system cannot be explained by a conventional thermal or photochemical mechanism. These features confirmed the generality of the excitation mechanism first observed in the NO/Pd(111) system\(^1\) and were consistent with the multiple excitation model suggested in Ref. 9.

A feature not previously recognized in femtosecond surface chemistry studies is the appearance of the long time-scale component in the correlation data. Using a model relying solely on rapid coupling of the substrate electronic excitation to the adsorbate center-of-mass motion (desorption reaction coordinate), one can reproduce many of the key features of the data including the high yield and nonlinear fluence dependence. Such a model\(^7\), constructed from the fluence dependence and the calculated electronic temperature profiles, is shown in Fig. 3 as a dashed curve. Although it reproduces some of the trends (i.e. sharp subpicosecond correlation feature, proper asymmetry and long time correlation), it fails quantitatively because of small asymmetry in peak electronic temperature (only 50 K on a peak of 2800 K) leads to a very weak long-time correlation feature. We conclude that an additional mechanism acts to retain memory of the femtosecond laser excitation in the system from one pulse to another. A candidate for such an excitation is vibration in the molecule-surface bond or another closely coupled vibration. Our simulations of DIMET as well as the single-excitation analog, DIET, indicate that such excitation strongly influences the desorption yield. A simplified phenomenological model for vibrationally assisted electronic desorption was presented (Ref. 7) in which the yield was calculated by activating the pure electronic model in an Arrhenius fashion by the degree of excitation in the molecule-surface vibration. Approximating the degree of molecule-surface vibration using a frictional coupling of the vibration to the electronic excitation (relaxation time 5 ps) and using an activation energy of 1500 K leads to the solid curve in Fig. 3, which fits the data reasonably well. We note however that the data could also be well fit using a model in which the femtosecond laser results in nonthermalized vibrational excitation of the molecule-surface bond if a vibrational lifetime of ~10 ps is used. In principle, two contributions to the long-time correlation response could exist: the time-scale of equilibration of the vibrational excitation with the substrate electronic temperature and the time-scale of cooling of the substrate electronic temperature. However, when these two are similar, it is difficult to extract both from our data. Additional experiments in which a nanosecond laser is used to preheat the surface and separate the role of thermalized vibrational excitation are planned.

We now turn to an examination of the extent of dissociation under the conditions which lead to the desorption discussed above. In the case where dissociation competes with desorption (as is the situation for thermal activation or conventional photoactivation), scanning the laser over the surface would result in significant accumulation of atomic oxygen and a substantial recombinative desorption peak in the TPD spectrum. With limited scanning of the femtosecond laser (e.g., traces b and c in Fig. 6), there is no evidence of dissociation since the relative sizes of the molecular and recombinative desorption peaks remain unchanged. In the limit of no dissociation, a thorough scanning of the surface with the femtosecond laser would desorb all of the molecular oxygen and leave a clean surface. Indeed we find that with modest scanning (trace d in Fig. 6), the area of the recombinative desorption peak has been reduced to only 0.014 ML, the limit of our detection for atomic oxygen. This implies a dissociation/desorption branching ratio for femtosecond laser activation of < 0.05. This result is quite different from the results found for thermal chemistry or conventional photochemistry. In thermal chemistry\(^12\) the branching ratio is 0.27 for saturation coverage. However, at low coverages, all of the oxygen dissociates. In conventional photochemistry\(^13\), the cross-sections for dissociation and desorption are about equal for all wavelengths leading to a unity branching ratio. The data of Fig. 6 also indicate that little internal conversion to other adsorbate states is occurring.

Much like the final-state and time-domain data for desorption on O₂/Pd(111), the branching ratio in femtosecond surface chemistry studies suggests a distinctive mechanism may be responsible for the femtosecond laser-induced processes. The previous femtosecond surface studies led to the suggestion of a mechanism of desorption induced by multiple electronic transitions (DIMET).\(^9\) The operation of a multiple excitation mechanism for activation of the chemical processes at a surface could also lead to a different branching ratio. Consider the case of an adsorbate state close to the Fermi level which couples to one channel (desorption), but not another channel (dissociation). Further assume that this state
has a very short lifetime. Because the short lifetime results in a low yield for a conventional photo-induced process, no chemistry will be observed at photon energies which can excite this state. Higher energy photons accessing different states - and capable of leading to different branching ratios - would be required to observe conventional photochemical processes. Modelling suggests that the yield from states with short lifetimes may enhanced by many orders of magnitude by multiple excitations. Thus a state like the one described could show an appreciable desorption yield, but not exhibit dissociation. We also note that another departure of DIMET mechanism from conventional photoactivation is that a state can be chemically active for single excitation because of energy constraints resulting from the placement of the state relative to the chemical bond strength. In a DIMET mechanism, such a state could be chemically active since the energy would be gained in several steps.

More specifically with regard to states, the conventional photochemistry might reasonably be associated with the oxygen $3\sigma^*$ state, thought to lie 3-5 eV above the Fermi level. This would be consistent with the threshold observed for conventional photoprocesses. For the femtosecond laser chemistry our electronic temperature of a few thousand K would be insufficient to couple effectively to this state. The electronic energy distribution might, however, contribute to the capture of holes by the occupied $\pi_m$ level located 1-2 eV below the Fermi level. This state is thought to be largely responsible for adsorbate binding and therefore capture of a hole could couple to a desorption channel more effectively than to a dissociation channel. Although this state might have an unobservably small conventional photochemical cross-section, as suggested in the previous paragraph, with multiple excitations it could become much more active.

6. SUMMARY

In summary, the activation of surface chemical processes in the O$_2$/Pd(111) system under femtosecond irradiation has been studied. The desorption results show a high yield at subthreshold photon energy, a nonlinear fluence dependence and a dominant subpicosecond correlation response. These features confirm the generality of surface processes driven by coupling to the high electronic temperature of the substrate. The long-time feature is attributed to a vibrationally assisted electronic mechanism. In contrast to conventional thermal activation and photo-induced activation where both desorption and dissociation are significant, only desorption is observed for femtosecond excitation. An upper limit of 5% has been established for the fraction of the adsorbed oxygen which dissociates.

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REFERENCES