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Anomalous branching ratio in the femtosecond surface chemistry of O_2/Pd(111)

J.A. Misewich [a], S. Nakabayashi [b], P. Weigand [a], M. Wolf [c], T.F. Heinz [d,*]

[a] *IBM Research Division, T.J. Watson Research Center, P.O. Box 218, Yorktown Heights, NY10598-0218, USA*
[b] *Department of Chemistry, Hokkaido University, Sapporo, Japan*
[c] *Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany*
[d] *Departments of Physics and Electrical Engineering, Columbia University, New York, NY10027, USA*

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Abstract

In this paper we examine the surface chemistry of O_2/Pd(111) under conditions of dense electronic excitation generated by femtosecond laser pulses. In contrast to the cases of conventional photo-activation and thermal activation, with femtosecond excitation the branching ratio for desorption/dissociation is found to favor desorption strongly. The results are discussed in terms of a recently developed model for desorption induced by multiple electronic transitions (DIMET).

Keywords: Laser methods; Low index single crystal surfaces; Metallic surfaces; Oxygen; Palladium; Photochemistry; Photon stimulated desorption (PSD); Surface photochemistry; Thermal desorption spectroscopy

1. Introduction

It has long been a goal to be able to control the branching ratio for competitive pathways in chemical systems. The extensive interest in coherent control of excited states under photoexcitation represents one of the current paths toward this goal [1,2]. In surface chemical reactions, the branching ratios can be influenced by the mechanism used to activate the reaction. In many systems there are significant differences between the outcome of thermal activation and photo- (or electron-) stimulated activation [3–6]. In this paper, we examine the branching ratio for the model surface chemical system of O_2/Pd(111) under conditions of high densities of substrate electronic excitation. Within this regime, attained with femtosecond laser excitation, novel multi-step activation processes become possible, and altered branching ratios may arise.

The absorption of femtosecond laser light in the surface region of a metal results in distinctive excitation conditions [7–15]. The initial absorption of light produces electron–hole pairs, which equilibrate among themselves on a sub-picosecond time-scale. Subsequently, on the time-scale of a few picoseconds, the electronic degree of freedom comes into equilibrium with the lattice excitations. Therefore, the effect of femtosecond laser pulses on the substrate may be modeled in a simple approximation by two temperatures: an electronic temperature T_{el} and a phonon temperature T_{ph}. For the laser fluences used in femtosecond surface

*Corresponding author.

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chemistry, peak electronic temperatures as high as several thousand degrees can be reached. The rise in the phonon temperature is, however, typically limited to a few hundred degrees because of the large heat capacity of the phonons compared with that of the electrons.

The first experimental studies of the surface chemistry of adsorbates under femtosecond laser excitation were performed on the NO/Pd(111) system [16–19]. This system serves as a model for non-dissociative behavior, since the only observed reaction channel is that of intact desorption of NO. The experimental results demonstrated that femtosecond excitation was very efficient in activating this desorption channel. The experiments also revealed some characteristic features of the desorption process, such as a strongly non-linear fluence dependence and a high degree excitation in the internal degrees of freedom of the desorbed molecules [16,18]. Subsequent time-resolved measurements of desorption, performed on the femtosecond time-scale by means of a two-pulse correlation technique, showed that the excitation responsible for the desorption exhibited a sub-picosecond lifetime [17].

These experimental observations suggested that a distinctive electronic mechanism was operative under femtosecond laser excitation and led to the model of desorption induced by multiple electronic transitions (DIMET) [20]. The DIMET model is a generalization of the Menzel–Gomer–Redhead (MGR) model for desorption induced by electronic transitions (DIET) [21,22]. Like DIET, the first step in the DIMET process is a transition to an excited electronic state of the adsorbate complex. In order for desorption to occur in the DIET model, the adsorbate must stay in the excited state long enough to acquire sufficient energy for desorption, which for short excited-state lifetimes characteristic of chemisorbed species on metals is a very improbable event. In the DIMET process, however, the adsorbate only needs to acquire a small amount of energy on any given cycle of excitation and de-excitation. The energy necessary for desorption accumulates through a series of excitation–de-excitation cycles made possible by the high density of substrate electronic excitation. Thus, a single improbable event is replaced by a sequence of probable events and a significant enhancement in desorption efficiency may be realized. A complementary description of the flow of energy between the substrate electronic excitations and the motion of the adsorbate and the ensuing desorption process has also been elaborated. In this approach [23–27] explicit excitations of adsorbate-localized electronic states are eliminated and the influence of non-adiabatic effects is incorporated in a Langevin equation by means of frictional damping and the corresponding fluctuating forces. This methodology has been extensively developed in the context of vibrational dynamics [28–36] and has attained particular importance in view of recent ultra-fast time-domain probes of adsorbate vibrations [37–45]. While the formalism employed in the DIMET and frictional approaches is clearly quite different, both methods are capable of capturing the same physics and have been shown to give similar results within the appropriate limits [24,25]. In the case of decreased density of electronic excitation, however, only the DIMET formalism reduces naturally to the DIET picture of a non-equilibrium process induced by a single adsorbate-localized excitation.

The experimental studies of the response of NO/Pd(111) to femtosecond laser excitation have been complemented by several investigations of the intact molecular desorption in the CO/Cu(111) and O_2/Pt(111) systems [46–49]. In a time-resolved measurement of surface second-harmonic generation following femtosecond excitation of CO/Cu(111), Prybyla et al. [46] concluded that the CO molecules leave the surface in less than 0.4 ps. For O_2 desorption from the Pt(111) surface, both Ho et al. [47] and Mazur et al. [49] observed a non-linear fluence dependence for the desorption rate and a dominant sub-picosecond response time in two-pulse correlation measurements. In recent measurements on the O_2/Pt(111) system by Ho et al. [50] correlations between the translational energy of the desorbed molecules and the properties of the femtosecond laser excitation were reported. Such results, while not compatible with a traditional DIET picture, can be understood either in the context of a DIMET or frictional coupling model. These findings suggest a certain generality to the key features exhibited in

the femtosecond surface chemistry of the NO/Pd(111) system.

In addition to these investigations of intact molecular desorption, Ho et al. [48] have also demonstrated the possibility of inducing bimolecular surface reactions by femtosecond laser excitation. In a study of the coadsorption system of CO and O_2 on Pt(111), they observed the desorption of both O_2 and the reaction product CO_2. As in the earlier experiments on femtosecond surface photochemistry, these processes exhibited a strongly non-linear fluence dependence. (The variation of the fluence dependence with laser wavelength was recently examined in a related study by Mazur et al. [49].) Interestingly, Ho et al. [48] discovered that the branching ratio for desorption/reaction of O_2 was significantly higher for femtosecond laser activation than for conventional photochemical activation with nanosecond laser pulses.

Another system that offers the flexibility to examine competitive pathways is that of O_2/Pd(111). A study of desorption induced by femtosecond laser excitation in this system has been undertaken by our group [51,52]. Again, the characteristic features of femtosecond desorption, such as a high yield and a non-linear fluence dependence, were seen. In time-domain measurements using the two-pulse correlation technique, a dominant sub-picosecond response was observed. In addition, weaker long time-scale features (tens of picoseconds) were discerned in the correlation data. These results (and similar findings for the O_2/Pt(111) system by Mazur et al. [49]) have been attributed to the influence of vibrational preheating in enhancing the desorption yield in a DIMET process [49,51].

In this paper, we examine how femtosecond laser activation of surface processes can influence branching ratios in a system where multiple reaction paths are possible. The O_2/Pd(111) system discussed above in the context of desorption measurements is an attractive choice for such studies. Two well-known reaction channels of adsorbed oxygen molecules exist: intact molecular desorption and dissociation to form two adsorbed atomic oxygen atoms. The nature of the two channels under conventional photostimulated activation [53–58] and under thermal activation [59–61] has been thoroughly characterized. We show here that while femtosecond laser activation leads to efficient desorption in this system, the dissociation channel is strongly suppressed. This behavior differs sharply from that found under conventional photo- and thermal activation, where dissociation is an important reaction pathway. The distinctive results for femtosecond laser activation are discussed in terms of the multiple-excitation scheme for surface chemistry introduced above.

2. The O_2/Pd(111) system

Several complementary surface techniques have been applied to examine the system of O_2/Pd(111) [59–62]. From electron energy-loss spectroscopy (EELS) data [60,62], we know that exposure of Pd(111) surfaces to O_2 at low temperatures (<150 K) results in molecular chemisorption for all doses. In the adsorbed state, there is significant charge transfer into the π^* orbital of oxygen with the appearance of both superoxo (O_2^-) and peroxo (O_2^{2-}) species on the surface. Fig. 1 shows a temperature-programmed desorption (TPD) spectrum for the O_2/Pd(111) system taken in our laboratory following exposure at 100 K. The first molecular state to form, corresponding to the α_1 TPD feature, is characterized by the highest binding energy and is associated with the peroxo form of oxygen. After saturation of the α_1 feature, the α_2 and α_3 features

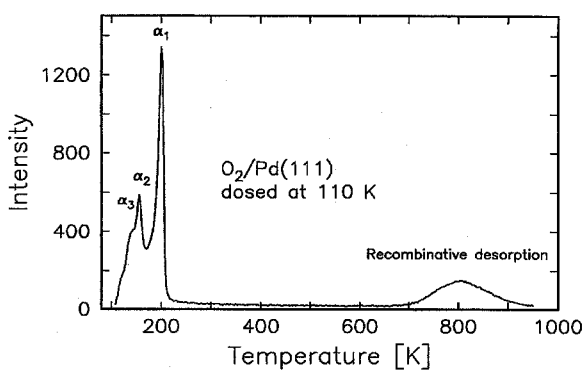

Fig. 1. Temperature-programmed desorption (TPD) spectrum for O_2/Pd(111) after exposure to a saturation dose of oxygen at 100 K.

appear sequentially with increasing oxygen exposure.

Upon heating a Pd(111) surface exposed to a saturation dose of O_2, one first observes desorption from the α_3 and α_2 states. At temperatures of approximately 200 K, the desorption of the α_1 species occurs, together with the appearance of adsorbed atomic oxygen. The desorption of the α_1 species of molecular oxygen is thought to result from a displacement process accompanying the dissociation of adsorbed molecular oxygen. This conclusion is supported by the strong inhibition of α_1-oxygen formation upon predosing with atomic oxygen [59]. In experiments at low initial coverages of O_2, heating of the surface leads to complete dissociation rather than to molecular desorption. Adsorbed atomic oxygen leaves the surface through a recombinative desorption process, as manifested by a broad TPD peak at a temperature of approximately 800 K.

Photo-induced effects have also been investigated extensively for O_2/Pd(111) [53–58]. Both photodesorption of molecular oxygen and photodissociation into adsorbed atomic oxygen have been observed. The two 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 and in parallel with one another as a function of photon energy. At the highest photon energy of 6.4 eV, maximum cross-sections of $\sim 4 \times 10^{-19}$ cm^2 were reported.

3. Experimental

The experiments reported here were conducted in an ultra-high vacuum chamber with a base pressure not exceeding 1×10^{-10} Torr. The system was equipped with capabilities for low-energy electron diffraction (LEED), Auger electron spectroscopy (AES), and quadrupole mass spectrometry (QMS). The procedure for preparing the single-crystal Pd(111) surface consisted of repeated cycles of argon-ion sputtering (at 0.5 keV) and annealing to a temperature of 950 K. Cycles of oxygen exposure and annealing were also found to be helpful in reducing the degree of carbon contamination. LEED measurements were used to verify ordering of the surface, and Auger spectroscopy was employed to verify surface cleanliness. The sensitivity of Auger spectroscopy to the critical surface contaminant of carbon is, however, very low because of the presence of a strong Pd feature at nearly the same energy. In place of Auger spectroscopy, a sensitive measure of carbon contamination was the strength of the CO peak in TPD traces obtained after exposing the surface to oxygen. For the results reported here, the Pd(111) sample was dosed at a temperature of 157 K, where only the α_1 molecular adsorption state forms.

The femtosecond radiation used to initiate surface chemistry was produced by an amplified colliding pulse mode–locked ring dye laser (CPM) system. The laser supplied 0.5 mJ pulses of 620 nm (2.0 eV) light at a 10 Hz repetition rate. The pulse duration at the Pd surface, measured by an autocorrelator arranged with optics identical to that traversed by the beam in reaching the sample, was 100 fs. The absorbed laser fluence was found to be a critical parameter in our earlier experiments. In order to determine the energy absorbed by the sample, the reflectivity was measured directly. Further, the energy content and spatial character of the laser pulses could be determined on a shot-by-shot basis with the aid of 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 cm^{-2}.

The response in the desorption reaction channel was observed by recording transient mass spectrometer signals for mass 32 synchronized to the femtosecond laser pulses. No atomic oxygen ejection was seen. As previously reported [51], the desorption of O_2 from Pd(111) is an efficient process and can readily be observed in the transient QMS signal for a single femtosecond laser pulse. However, since the product of the dissociation reaction channel remains on the surface, a determination of the extent of the dissociation reaction channel is not quite as straightforward.

Before discussing the details of the dissociation measurement, we need to make some preliminary observations relevant for the validity of the chosen method. Although laser-induced desorption of O_2 from Pd(111) is readily observed when there is molecular oxygen on the surface, the case is quite

different for Pd(111) with adsorbed atomic oxygen on the surface. We have prepared the Pd(111) surface with atomic oxygen in two ways: (i) by dosing with O_2 at low temperature (100 K) and then heating well above the α_1 desorption temperature of 200 K and (ii) by dosing with molecular oxygen at 300 K. Both procedures result in presence of absorbed atomic oxygen, as was verified by the appearance of a high-temperature recombinative desorption peak in TPD spectra, with procedure (ii) providing a slightly higher coverage of atomic oxygen. From such a saturated surface of O/Pd(111), we found no evidence of femtosecond laser-induced desorption of (atomic or molecular) oxygen even with twice the fluence used in these experiments. We conclude, therefore, that femtosecond laser radiation does not lead to the desorption of adsorbed atomic oxygen.

The following procedure may then be employed to gauge the extent of dissociation of O_2/Pd(111) in femtosecond laser activation. First, the surface is exposed to a prolonged irradiation by the femtosecond laser. The irradiation is chosen to be sufficiently long (i.e. to be comprised of a sufficient number of laser pulses) to drive all reactions to completion. To ensure that the sample is irradiated uniformly, the laser beam is carefully scanned over the entire surface. If dissociation of the adsorbed molecular oxygen occurs, the result will be the creation of adsorbed atomic oxygen on the surface. As noted above, this species is unaffected by femtosecond laser pulses and will accumulate on the surface during the laser irradiation. After a thorough exposure to femtosecond laser radiation, the extent of dissociation is determined from the area of the recombinative desorption peak in a TPD spectrum.

In order to apply the method just outlined to determine the efficiency of laser-induced dissociation, we need to calibrate the sensitivity of our QMS for oxygen TPD spectra. This is accomplished by comparing our TPD data for the recombinative desorption peak with previously published spectra for which an absolute calibration has been established [61]. In particular, for a surface prepared with atomic oxygen according to procedure (i) above, the saturation coverage is reported to be at 0.17 ML; procedure (ii) above leads to a saturation coverage of 0.25 ML, as indicated by a $p(2\times2)$ LEED structure [61]. Fig. 2 shows a series of TPD spectra obtained by dosing Pd(111) at 300 K with four different oxygen exposures. Prior to making these measurements, it should be noted that we performed several O_2 adsorption/desorption cycles to saturate subsurface oxygen sites and to remove any residual carbon contamination. The top trace in Fig. 2 shows a TPD spectrum for exposure to a saturating dose, which corresponds to an atomic oxygen coverage of 0.25 ML. The bottom trace in Fig. 2 shows a spectrum for a surface coverage of 0.05 ML. Based on these measurements, we conservatively estimate our sensitivity to atomic oxygen to be 0.02 ML.

4. Results

Here we present data on the amount of atomic oxygen adsorbed on the surface following femto-

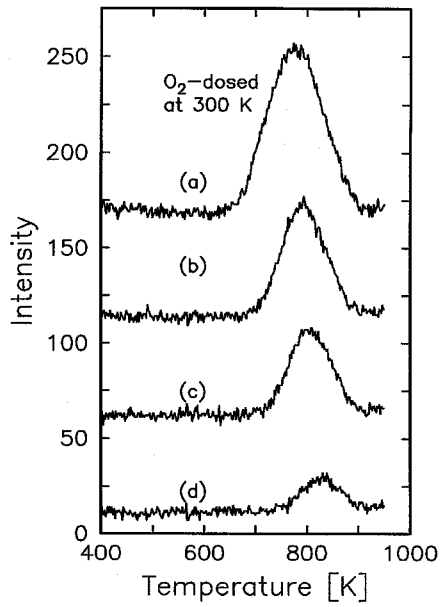

Fig. 2. A series of TPD spectra for the O_2/Pd(111) system after dosing with O_2 at 300 K. The top curve (a) corresponds to a saturation dose 0.25 ML of atomic oxygen. The other curves correspond to coverages of (b) 0.175, (c) 0.1, and (d) 0.05 ML of atomic oxygen.

second laser irradiation of the O_2/Pd(111) system. In the case of efficient dissociation, adsorbed atomic oxygen will accumulate on the surface during laser irradiation and a substantial recombinative desorption peak will result. On the other hand, in the limit of negligible dissociation, a thorough irradiation will leave the surface clean.

Fig. 3 shows a series of TPD spectra for the O_2/Pd(111) surface obtained after irradiating the sample with varying numbers of femtosecond laser pulses. For simplicity of interpretation, the O_2/Pd(111) surface was prepared with adsorbed molecular oxygen only in the α_1 state. This was accomplished by dosing with oxygen (to saturation) with the sample held at a temperature of 157 K. The presence of adsorbed oxygen solely in the α_1 state also has the advantage of facilitating the identification of a possible channel for femtosecond laser-induced transformation of oxygen in this state into adsorbed molecular oxygen in the α_2 and α_3 states. Such interconversion between different states of adsorbed molecular oxygen in the O_2/Pd(111) system has been observed in conventional photochemistry by Hasselbrink et al. [54]. After the surface preparation was complete, the temperature of the sample was lowered to 100 K. This lower temperature was maintained during irradiation by the femtosecond laser pulses and was the base temperature for the TPD measurements. In this manner, any molecular oxygen formed in the α_2 or α_3 states would be stable during the irradiation process. Trace a of Fig. 3 shows a

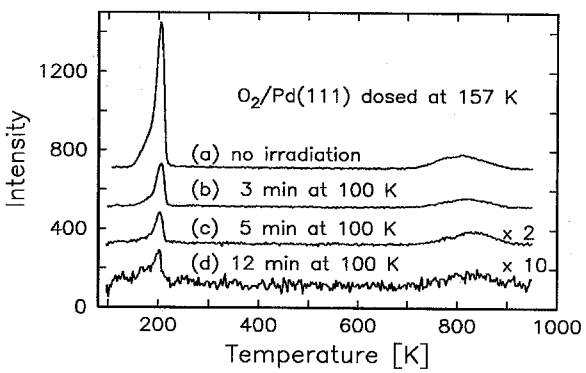

Fig. 3. A series of TPD spectra for the O_2/Pd(111) system after dosing at 157 K with a saturation exposure as a function of the extent of femtosecond laser irradiation.

TPD spectrum taken in the absence of any laser irradiation. As expected, only the α_1 molecular desorption peak and the recombinative desorption peak are observed.

The other traces in Fig. 3 illustrate the effect of femtosecond laser irradiation on the O_2/Pd(111) surface. In all of these measurements, the absorbed fluence for the femtosecond laser pulses was 3.5 mJ cm^{-2}. This fluence was chosen to produce efficient electronically driven desorption of O_2, as determined by direct QMS measurement of gas-phase oxygen leaving the surface [51]. Although the lattice temperature is high enough for thermal desorption and dissociation, it must be remembered that the time duration of the lattice transient is far too short for any significant yield of thermal activated processes. The set of TPD data in Fig. 3 confirm the existence of an efficient channel for molecular desorption activated by the femtosecond laser pulses. This process leads to the rapid depletion of the low-temperature molecular peak in the TPD spectra of the irradiated surfaces. Concurrent with the depletion of the molecular TPD peak, the data also show that the recombinative desorption peak in the TPD traces (at ~800 K) falls sharply. In trace d, the recombinative desorption peak has been reduced to 0.014 ML. The lack of atomic oxygen on the surface following thorough laser exposure leads us to conclude that dissociation is inefficient compared to the desorption channel. If this were not the case, we would expect a build up of atomic oxygen on the Pd(111) surface. More quantitatively, these measurements allow us to obtain an upper boundary of 0.05 for the branching ratio of dissociation/desorption under femtosecond laser excitation. The effective dissociation cross-section is then $<5\times10^{-20}$ cm^2 (for a laser fluence of 3.5 mJ cm^{-2}); the corresponding effective desorption cross-section is 10^{-18} cm^2.

It should be noted that the recombinative peaks observed in the TPD spectra for lesser amounts of laser irradiation are to be understood as resulting from the influence of molecular oxygen remaining on the surface. In addition to desorbing in its molecular form, these adsorbed oxygen molecules also undergo thermal dissociation during the TPD heating ramp. At still higher temperatures (above 750 K), the newly formed adsorbed oxygen atoms

leave the surface recombinatively. Thus, the existence of recombinative desorption peaks in the TPD spectra for relatively low laser exposures is not indicative of the presence of adsorbed atomic oxygen. The presence of a molecular desorption peak in the TPD spectra for low coverages of adsorbed oxygen (high laser exposure) reflects the somewhat inhomogenous nature of the laser irradiation of the sample. As a further result, we mention that the TPD spectra after femtosecond laser excitation show no evidence for interconversion of adsorbed molecular oxygen from the α_1 state to either the α_2 or α_3 state.

5. Discussion

In comparison with the results for conventional photo- and thermal activation, the desorption/dissociation branching ratio for the O_2/Pd(111) system under femtosecond laser activation is seen to be anomalous. For thermal activation, heating of the Pd(111) surface with saturation coverage of molecular oxygen gives rise to a substantial coverage of atomic oxygen [59]. Indeed, starting at sufficiently low coverage of molecular oxygen, dissociation is the only reaction observed. In the case of conventional photostimulated activation [53–58], both desorption and dissociation are observed and have roughly comparable cross-sections. An analogous dramatic change in branching ratio in going from conventional (nanosecond) photoactivation to femtosecond laser activation has also been observed by Ho et al. for the O_2+CO/Pt(111) system [48].

Since the femtosecond laser-induced desorption process occurs through a distinctive mechanism, such as that represented by the DIMET model, a significant change in branching ratios is perhaps understandable. In the DIMET model [20], the high substrate electronic temperature created by the femtosecond laser pulse may induce a transition from the ground electronic state to an excited-state potential energy surface of the adsorbate. Since excited-state lifetimes are thought to lie in the femtosecond range [63,64], this electronic excitation will generally relax to the ground state before much energy is exchanged. This fact accounts for the low desorption probabilities usually associated with conventional photostimulated excitation of chemisorbed molecules on metal surfaces. In the DIMET model, however, the electronic temperature remains high for a time much longer than the excited-state lifetime, and multiple cycles of excitation–de-excitation may occur. If these cycles (and the associated energy transfer) occur sufficiently rapidly, the adsorbate can acquire the energy needed to overcome the activation barrier of a chemical reaction. Stochastic trajectory calculations of DIMET show enhancements in the reaction yield of many orders of magnitude beyond that obtained for a single excitation–de-excitation cycle [20].

There are two unique features of the DIMET model for activation using femtosecond lasers that can dramatically affect the observed surface femtosecond chemistry compared to that expected for conventional photochemistry. The first effect is simply the possibility of large enhancements in reaction yield that was discussed above. A certain reaction channel might be energetically allowed in conventional photochemistry, but might not be observed because of its low yield. For example, a very short excited-state lifetime in a DIET process may lead to vanishingly (exponentially) small reaction probabilities. The second effect is that certain energetically forbidden processes in conventional photochemistry may be allowed in a multiple-excitation model. A reaction channel which requires activation over an energy barrier will not be allowed in a single-step mechanism unless the excitation energy exceeds that of the barrier. In a multiple-step process such as DIMET, however, this restriction is relaxed, since the required energy to cross the reaction barrier can be accumulated through several adsorbate–substrate interactions.

In order to apply these considerations to the O_2/Pd(111) system under study, we need at least a qualitative picture of the electronic structure of the adsorbate-localized levels. Fig. 4 shows the expected ordering of the oxygen adsorbate levels for the superoxo- and peroxo-states on Pd(111). The ordering was taken from that calculated by Panas and Siegbahn [65] for the Pt(111) system. Also shown for reference are the gas-phase molecular orbitals for oxygen. The positions of the energy

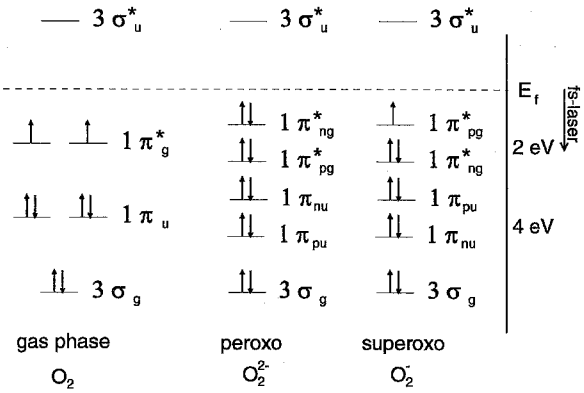

Fig. 4. A qualitative view of the electronic structure of O_2/Pd(111) for both the superoxo- and peroxo-states. The molecular orbitals of gas-phase O_2 are also shown for reference.

levels in this qualitative picture are certainly not accurately defined, but we do expect the gerade states to lie a few eV below the Fermi level. As the molecule approaches the surface, the degenerate π orbitals normal to the intramolecular axis in the gas phase split into orbitals parallel (subscript p) and normal (subscript n) to the surface. The gerade orbitals have antibonding character with respect to the oxygen intramolecular coordinate; however, they have bonding character with respect to the molecule/surface coordinate and the chemisorption bond stabilizes as they are filled.

Both the desorption and dissociation channels in conventional photostimulated activation have been attributed to the capture of a hot electron in the unoccupied oxygen $3\sigma^*$ level [54]. This level is thought to lie 3–5 eV above the Fermi level, in rough accord with the apparent threshold for conventional photoprocesses at a photon energy of $\hbar\omega \approx 3.5$ eV. Even at the elevated electronic temperatures attained in our experiment by femtosecond laser pulses, negligible excitation of this high-lying state would be expected. (It may be noted that a significant role for substrate electrons that have been excited by a multiphoton process to high energies may be ruled out. This inference follows from examination of the time-domain data obtained for the O_2/Pd(111) system [51]. The width of the two-pulse correlation peaks is too large to be attributed to such hot electrons, which can be produced only when the laser pulse is present and which rapidly relax thereafter.) Rather than invoke the $3\sigma^*$ state, we suggest that femtosecond activation is mediated by capture of a hole in the $1\pi^*_{ng}$ level located $\sim$1–2 eV below the Fermi level. Since femtosecond laser pulses create substrate electronic temperatures in the range of thousands of degrees K, this state could be excited repeatedly by hole capture. (We note that the hole temperature for femtosecond laser excitation in a metal system should be approximately in equilibrium with the electron temperature.) It is thus a natural candidate as an intermediary in a multiple-excitation model. On the other hand, it still remains to explain why this state does not appear to be active in conventional photostimulated processes, which appear to reflect a threshold of $\sim$3.5 eV [54]. We note that although the capture of a hole in this level will strengthen the intramolecular oxygen bond and weaken the molecule–surface bond, this does not mean that excitation through this level cannot lead to dissociation. Since the capture of a hole in this state leads to a different equilibrium bond length, energy can be transferred into the intramolecular vibration by such a capture. Such excitation can lead to dissociation of the adsorbate. This situation is analogous to the desorption model of Antoniewicz, where excitation to a bound excited state which has an even shorter equilibrium bond length than the ground state (and therefore tends to pull the adsorbate closer to the surface) can lead to desorption [66].

As suggested above, the lack of conventional photochemistry mediated by the $1\pi^*_{ng}$ level may result from its having a very short excited-state lifetime. This would act to reduce sharply the reaction (desorption or dissociation) yield in a single-step process. In the limiting case, the excitation energy of the $1\pi^*_{ng}$ level may fall short of the barrier height for reaction, making this pathway energetically inaccessible in a single-excitation process. The reaction pathway may, however, be made observable through a multiple-excitation mechanism, which causes the energy constraint to vanish and can lead to high efficiencies even for very short excited-state lifetimes [20]. Within this picture, the distinctive branching ratio observed for femtosecond laser activation may then be attributed to the role of an excited state, such as the $1\pi^*_{ng}$ level,

different from that responsible for conventional surface photochemistry.

From a more phenomenological point of view, we may also examine the preference for desorption of O_2 relative to dissociation under femtosecond excitation in terms of rate laws for the two processes. As discussed in the literature [20,24,25] the femtosecond-laser activated processes occur under conditions in which the vibrational excitations of the adsorbate are attempting to come into equilibrium with those of the substrate electrons. Since a true steady state is not reached during the brief (ps) duration of the electronic temperature transient, one should not consider the process to be one occurring under equilibrium conditions at the electronic temperature. Nonetheless, on a qualitative basis, we expect the behavior to resemble that encountered in a thermal process taking place at a temperature approaching that of the electronic system. This observation provides a means of rationalizing the experimental findings. Suppose that the desorption channel is characterized by a rate law with a higher pre-exponential factor, but also with a somewhat higher activation energy than for the dissociation. For processes occurring slowly (at low temperatures), dissociation will then be favored. For a process occurring rapidly (at high temperatures), desorption may, however, be favored. Indeed, such a preference towards desorption (frequently characterized by high preexponential factors) over other surface reactions is known to take place for thermal processes induced by nanosecond laser pulses. While the same description cannot be rigorously applied for the femtosecond time-scale relevant in the present experiments, we may expect the same trend to prevail.

6. Summary

The branching ratio between the competing reaction channels of desorption and dissociation in the O_2/Pd(111) system has been investigated under the conditions of elevated substrate electronic temperatures produced by femtosecond laser activation. In contrast to the case of conventional photostimulated and thermal activation, negligible dissociation is observed for femtosecond laser activation, despite the efficiency of the femtosecond desorption channel. The results were interpreted in the light of models for activation through multiple electronic transitions, such as DIMET [20]. Activation through a multiple-excitation process may serve to enhance significantly channels that have low probability for a single-step process. Indeed, a multiple-excitation mechanism may even allow reaction pathways to be followed that would be energetically inaccessible in a single-excitation process. For the case of O_2/Pd(111), we have suggested that femtosecond laser activation enables reactions to proceed by repeated hole capture in the $1\pi^*_{ng}$ state lying slightly below the Fermi level. Femtosecond laser excitation results in a new mechanism for activation of surface chemical processes, and as such offers researchers a new tool to influence chemical reaction pathways on surfaces.

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