

CHAPTER III

Probing the transition dynamics of chemisorbed states of O_2 on Pt(111)

3.1 O_2 states on Pt(111) surfaces

Because of its importance and relative simplicity, the O_2 /Pt(111) system is considered to be the model system for catalytic chemistry, and has been investigated both experimentally and theoretically in considerable detail. Four different adsorption states of oxygen on Pt(111) have been reported to date: one physisorbed state, two chemisorbed states, and one atomic state. It is important to review some of their properties before going further on investigating dynamics of oxygen molecules on Pt(111).

3.1.1 Physisorbed State

The physisorbed state of molecular oxygen can be stably deposited on a platinum surface when the surface temperature is below 30 K. In the case of physisorption, charge transfer or bond hybridization do not occur between the oxygen molecular bonds and the platinum d -band. The force holding the oxygen molecule to the platinum surface is a van der Waals attraction; hence, the physisorbed oxygen molecules do not reside on any specific sites on the platinum surface. Multiple layers of physisorbed oxygen molecules can

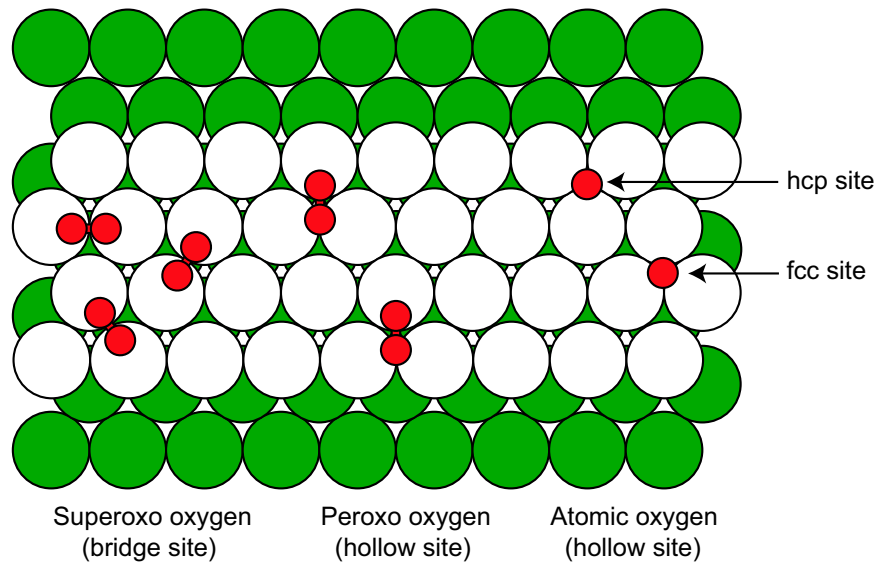


Figure 3.1: Schematic diagram of the surface configuration of oxygen on Pt (111), for the superoxo (O_2^-), peroxy (O_2^{2-}), and atomic (O) oxygen states.

reside on the metal surface, and these layers can be considered as a “condensed” phase of molecular oxygen. The electronic properties of these molecules are very similar to those of the gas-phase free oxygen molecules.

3.1.2 Superoxo and peroxy chemisorbed states

There are two different chemisorbed oxygen molecular states for the platinum (111) surface: superoxo oxygen (O_2^-), and peroxy oxygen (O_2^{2-}). When oxygen molecules are deposited on a platinum (111) surface at a temperature of about 77 K, thermal agitation of the oxygen molecules is stronger than the van der Waals attraction, and oxygen can no longer be physisorbed on the platinum surface. Instead, oxygen molecules attach to the platinum surface by chemisorption. Current wisdom is that during the chemisorption process, electrons transfer from the the platinum d -band to the molecular $1\pi_g^*$ orbital of the oxygen molecules, and the oxygen molecules become negatively charged. Therefore,

the electronic configuration of the oxygen changes considerably, especially for molecular orbitals with low binding energies.

“Superoxo” oxygen resides on a bridge site between two platinum surface atoms, with the intermolecular axis between the two oxygen atoms parallel to the surface (perpendicular to the surface normal). The O-O bond length of the superoxo state is calculated to be 1.39 Å using density functional theory, which is in good agreement with experimental measurements [63, 64]. The adsorption energy of the superoxo molecular oxygen is estimated experimentally to be -0.4 eV/molecule [65]. The adsorption bond between the superoxo oxygen and the platinum surface is formed by **one** electron transferred from the platinum surface to the now half-filled oxygen $1\pi_g^*$ orbital.

The “peroxo” chemisorbed state resides on the fcc three-fold-hollow site of the platinum surface. The intermolecular axis also nearly parallels the surface, but with a slightly tilted angle. The O-O bond length for the peroxo state is calculated to be 1.43 Å, and in agreement with experimental estimates [63, 66]. The adsorption energy of the peroxo molecular oxygen is experimentally measured to be -0.5 eV/molecule [67]. The adsorption bond between the peroxo oxygen and the platinum surface is formed by **two** electrons transferred to the molecule, resulting in a fully filled oxygen $1\pi_g^*$ orbital. The adsorption energies and bond length information for the different oxygen states on the platinum surfaces are summarized in Table 3.1.

Several properties of these two forms of chemisorbed molecular oxygen states differ. The peroxo oxygen is slightly more tightly bound to the platinum surface than superoxo. In the peroxo species, one more electron is transferred from the platinum surface to the

	Adsorption Energy (eV/molecule)	Bond Length (Å)
Gas-phase oxygen molecules (O_2)	—	1.21
Superoxo molecular oxygen (O_2^-)	-0.40	1.39
Peroxo molecular oxygen (O_2^{2-})	-0.50	1.43
Atomic oxygen (O) (fcc)	-1.65	—
Atomic oxygen (O) (hcp)	-0.98	—

Table 3.1: Comparisons of the adsorption energies and bond lengths between gas-phase oxygen molecules (O_2), superoxo (O_2^-), peroxo molecular oxygen (O_2^{2-}), and atomic oxygen (O) on fcc and hcp sites.

$1\pi_g^*$ orbital, forming two hybridized bonds between the peroxo oxygen molecule and the platinum surface. Increasing charge occupation in the $1\pi_g^*$ orbital strengthens the connection between the oxygen molecule and the platinum surface; the $1\pi_g^*$ orbital of the oxygen molecule is, however, an anti-bonding orbital with respect to the oxygen intermolecular bond. Therefore, the intermolecular bond connecting the two oxygen atoms is weaker when the oxygen is adsorbed on the peroxo state as opposed to the superoxo state; this property can be confirmed by the fact that the bond length of the peroxo oxygen is slightly longer than that of the superoxo oxygen. In fact, both of the oxygen molecular chemisorbed states (superoxo and peroxo) have a longer bond length (1.39 Å and 1.42 Å) compared to the free oxygen molecules (1.21 Å). Because of this, the two chemisorbed molecular oxygen states are often called the “intermediate” or “precursor” states of chemical oxidation processes on metal surfaces. For many chemical oxidation processes, dissociation of oxygen molecules into two atomic oxygens is necessary to initiate the process. It is suggested that the oxygen dissociation progresses gradually through weakening of the oxygen intermolecular bond (by transferring the oxygen molecules to these intermediate states) and finally to complete dissociation [68, 69, 70].

Another difference between these two chemisorbed states is that the superoxo oxygen tends to cluster on the adsorption sites, whereas the peroxo oxygen tends to be isolated. This property has been confirmed by observing the states through the technique of scanning tunneling microscopy (STM) [71]. This could indicate that intermolecular interactions, either attractive or repulsive, between the adsorbates can be a crucial factor in stabilizing these two chemisorbed states on the platinum surface. The clustering effect of the superoxo oxygen can explain why, at the same surface temperature, superoxo oxygen tends to dominate with high oxygen coverage and peroxo oxygen tends to dominate with low oxygen coverage. In addition, observation from STM measurement shows that both the chemisorbed states are stable, and diffusion of chemisorbed molecules after adsorption is not observed. This stability also indicates that superoxo oxygen clustering is not due to diffusion of chemisorbed molecules, but to the existence of a mobile precursor state upon adsorption [71].

STM work has also demonstrated that it is possible to use the STM tip to manipulate an oxygen molecule, moving it between these two chemisorbed states (superoxo and peroxo) from the bridge to hollow site, or vice versa [72]. The STM tip can be positioned directly above the oxygen molecule either in the bridge or the hollow site. After applying a very small current (nA) to the STM tip, the oxygen molecule gains energy to overcome the barrier of the potential energy surface, and finally stably resides on another adsorption site without perturbing other neighboring oxygen molecules.

3.1.3 Atomic Oxygen

Atomic oxygen can be formed on Pt(111) by dosing oxygen molecules at above 150 K surface temperature. At this temperature the oxygen molecules dissociate before becoming adsorbed to the platinum surface. Atomic oxygen can also be formed by dosing oxygen molecules at lower surface temperatures and subsequently heating the platinum surface to above 150 K for a short period of time to dissociate adsorbed oxygen molecules [73, 74]. Oxygen atoms are energetically favorable to reside at either the fcc or the hcp threefold hollow sites (fcc sites have no platinum atom directly beneath in the second surface layer) [71]. Theoretical calculations have estimated that the adsorption energy is much larger in the fcc hollow sites ($E = -1.65$ eV/molecule) and considerably smaller in the hcp hollows ($E = -0.98$ eV/molecule) [70].

3.2 Experimental results of O₂/Pt (111)

3.2.1 Thermal Desorption Spectroscopy

Thermal desorption spectroscopy (TDS)¹ is a well-known and commonly used technique for characterizing chemical reaction processes on surfaces. The idea of TDS is to adsorb the molecules under study to the metal surface at a low non-reactive temperature. The temperature of the metal surface subsequently increases at a constant rate to a temperature well above the temperature where the adsorbates react and desorb. By measuring the yield of the desorbing molecular species and the corresponding desorbing temperatures, information about adsorption energy of the adsorbates, activation energy, and the reaction channels of the chemical reactions can be extracted. For oxygen on platinum (111), TDS

¹Some literature refers to temperature programmed desorption spectroscopy

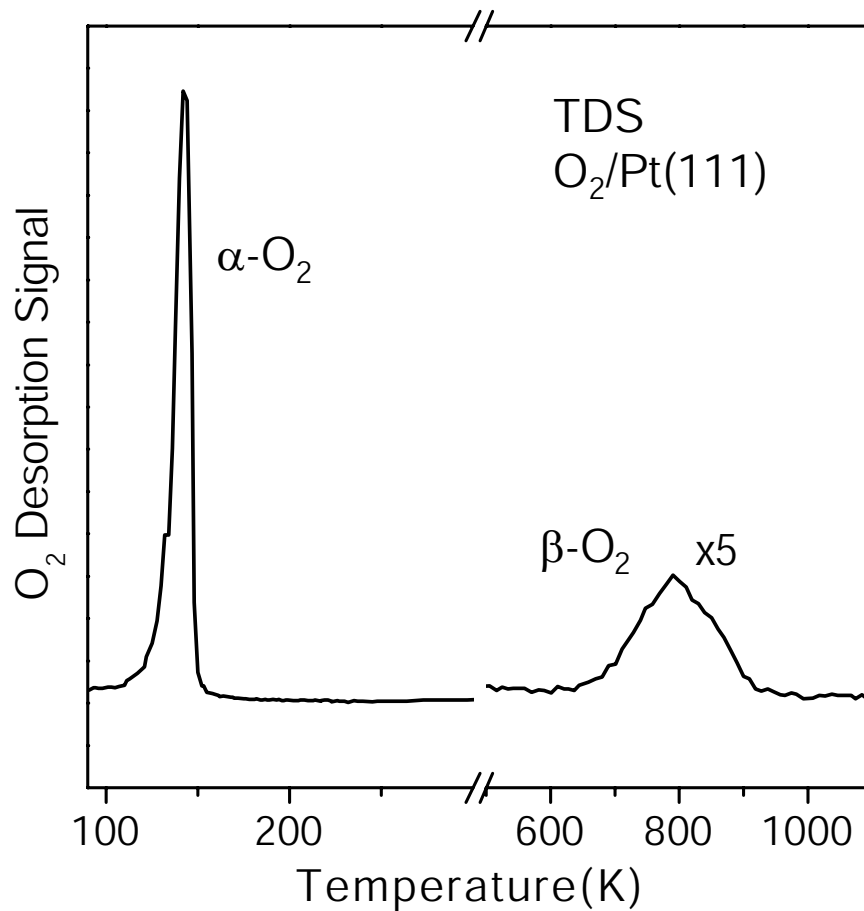


Figure 3.2: TDS for Pt(111) covered with O₂: the rate of temperature increase is 3 K/sec from 77 K to 300 K; then 10 K/sec from 300 K to 1100 K

can help us understand the oxygen chemisorbed states and their corresponding properties.

Figure 3.2 shows the TDS spectrum of O₂⁻ on Pt (111) taken using our setup. Oxygen was initially dosed onto the platinum sample at 77 K, to saturation coverage. Two distinct desorption peaks can be observed in the TDS spectrum: An intense $\alpha - O_2$ peak at 145 K, and a weaker high temperature $\beta - O_2$ peak (the symbols of α and β are used for identification purposes only; the oxygen molecules desorbing from these two peaks are the same). A reasonable explanation for the TDS spectrum of O₂/Pt is as follows: As discussed in

the previous section, superoxo oxygen (O_2^-) dominates at the bridge site at high coverage when oxygen is dosed to full coverage at liquid nitrogen temperature. When the surface temperature is heated above 145 K, a large fraction of oxygen molecules desorbs from the platinum surface, since the oxygen molecules have gained enough energy to overcome the energy barrier for desorption. Once some of the oxygen molecules desorb, the oxygen coverage becomes much lower on the platinum surface, and there will not be enough oxygen molecules left on the surface to cluster at adjacent bridge sites. The oxygen molecules now tend to move from the bridge site to the three-fold-hollow sites to lower their total energy, leading to a state transition from the superoxo (O_2^-) into the peroxo (O_2^{2-}) state for the remaining oxygen molecules. When the surface temperature increases above 200 K, the intermolecular bond of the adsorbed oxygen molecule will gain enough energy to be broken. This causes the oxygen molecule to dissociate into two identical oxygen atoms (O), and the two oxygen atoms absorb on two different three-fold-hollow sites on a platinum surface. Since the atomic oxygens have a much higher adsorption energy, they will remain on the platinum surface until the surface temperature reaches temperatures higher than 800 K. Finally, the atomic oxygen will desorb recombinatively to form oxygen molecules and leave the platinum surface.

3.2.2 Static photoemission spectra of the different oxygen states

From the knowledge gained from TDS investigation, we can now selectively prepare the oxygen adsorbed on the platinum surface preferentially for a certain oxygen state. Experimentally, saturation coverage leads to superoxo oxygen as dominant state. Therefore, to prepare superoxo oxygen, oxygen can simply be dosed onto a platinum surface to the sat-

uration coverage at liquid nitrogen temperature, so that most of the oxygen molecules will cluster and reside on the bridge sides of the platinum surface. By heating the platinum surface to 145 K, a partial desorption of molecular oxygen increases the occupation of three-fold-hollow sites for the oxygen molecules, and leads to a predominance of the peroxo chemisorbed state. At temperatures above 145 K, oxygen molecules will gain enough energy to dissociate into oxygen atoms; therefore, heating the sample to room temperature is the preferable way of obtaining atomic oxygen [14, 63, 65, 69, 72, 75].

Static photoemission spectra have been taken using our TR-UPS setup by blocking the pump pulses to avoid excitation for the clean Pt(111) surface, $\text{O}_2^-/\text{Pt}(111)$, $\text{O}_2^{2-}/\text{Pt}(111)$, and $\text{O}/\text{Pt}(111)$. Comparing the spectrum of the clean Pt(111) surface to the other oxygen covered spectra reveals that the intensity of the platinum *d*-band, where the binding energy is close to the Fermi-edge, is strongly reduced for the latter spectra. This surface sensitivity is expected – when oxygen molecules adsorb on the platinum surface, the electrons emitting from the platinum are scattered back into the platinum due to the presence of the oxygen molecules.

At a binding energy of about 6 eV (referenced to the Fermi level), an oxygen-related feature appears in the oxygen covered spectra. This feature has been observed previously by others using synchrotron radiation sources, where it has been assigned to the occupied oxygen $1\pi_g^*$ orbitals of the free oxygen molecule [66]. The position of this feature appearing at about 6 eV binding energy agrees with calculations of density functional theory [70, 76] that the oxygen molecule adsorbed at the three-fold-hollow site has a higher density-of-states at this energy. At the EUV photon energy of 42 eV used in our setup, this

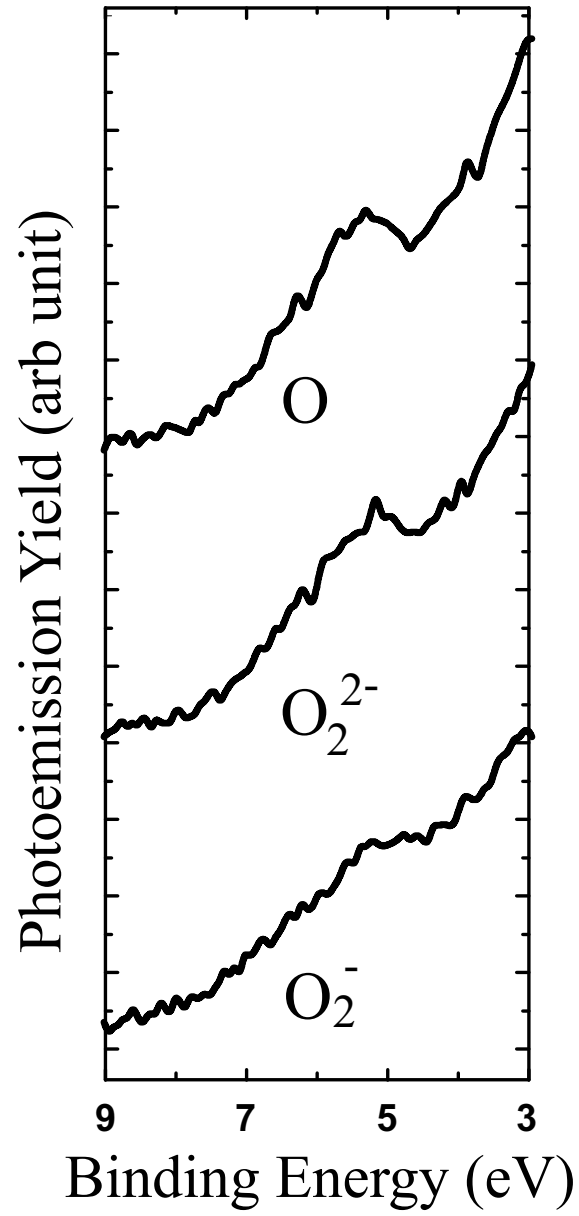


Figure 3.3: Static photoemission spectra taken for the superoxo (O_2^-), peroxo (O_2^{2-}) and atomic (O) oxygen states on Pt(111).

feature is particularly sensitive to the chemical bond character of the oxygen chemisorbed configuration. Close-up photoemission spectra are shown in Fig. 3.3 for the superoxo (O_2^-), peroxy (O_2^{2-}) and atomic (O) oxygen states on Pt (111) around the binding energy from 3 to 9 eV. In qualitative agreement with results by Puglia and co-workers [63], we observe a change in the spectral shape of the $1\pi_g^*$ orbital between the superoxo and peroxy states, but no significant difference in this energy region between the peroxy oxygen and the atomic oxygen states. This change is due to the different degree of hybridization of the particular oxygen state to the platinum d -band. Comparatively, the spectrum of the superoxo oxygen remains relatively flat in this energy region, similar to the clean platinum surface, while the spectrum of peroxy and atomic oxygen has a “peak” at about 6 eV binding energy. The spectra of peroxy oxygen and atomic oxygen have similar features in this region because the peroxy oxygen resides in a geometry similar to the atomic oxygen, and also the peroxy oxygen is considered to be the “precursor” state in the process of molecular dissociation. In the following experiment to probe the oxygen dynamics, this peak will be used as a valuable “signature” to indicate whether the oxygen is changing its chemisorbed configuration, by observing the change of this peak after the O_2/Pt system is triggered by an intense ultrafast pulse.

3.2.3 Oxygen desorption induced by intense ultrafast pulses

Desorption by intense femtosecond laser pulses of $O_2/Pt(111)$ has been studied previously by photo-desorption yield measurements [14, 77]. In particular, a nonlinear dependence of desorption yield with increasing laser intensity has been reported. In fact, this nonlinear dependence has been reported for many adsorbate/metal systems and proposed

as the result of direct coupling between excited hot surface electrons and adsorbates, without conventional heating from the surface lattice, or phonons [78]. In Mazur's desorption work [77], he proposed that after the sample was excited by an ultrafast pulse, a new "configuration" for the adsorbed oxygen molecules is created. The oxygen molecules could settle in a configuration that differs from a "fresh" platinum surface. This new configuration might complicate further subsequent laser desorption and deposition cycles resulting in a decreasing desorption yield. Figure 3.4 shows femtosecond-induced desorption yield traces for two adjacent desorption cycles with oxygen redosing in between. This observation indicates that a surface modification other than complete oxygen depletion occurs, resulting in a diminished number of free adsorption sites in subsequent desorption cycles. One reasonable explanation is that the high intensity laser pulse not only desorbs the oxygen from the platinum surface, but the oxygen molecules are also dissociated into oxygen atoms. These oxygen atoms then block the adsorption site. In general, nonreversible effects, such as dissociation, are not desirable for time-resolved photoemission experiments and should be minimized. Each photoemission spectrum at each time delay needs to be accumulated through many pump-probe excitations. Hence, a large advantage is realized if the system under study reverts to its original state before another excitation cycle starts. Otherwise, reversible and irreversible changes are superimposed making data interpretation difficult. Therefore, in all of our experiments, we used a low ($10\text{-}15 \mu\text{J}/\text{mm}^2$) pump fluence to minimize nonreversible processes, such as desorption and dissociation. From extrapolation of control experimental data, we estimate that significant irreversible oxygen desorption requires a time scale of more than an hour for the pump excitation levels used

in our time-resolved work.

3.2.4 Probing O₂/Pt(111) by TR-UPS

We start by adsorbing a saturation layer of molecular oxygen onto the platinum surface at liquid nitrogen temperature (77 K). Photoemission spectra were taken at different time delays between the pump infrared pulse and the EUV probe pulse. Significant changes were observed in the spectra as a function of time delay between the pump and the probe in two different energy regions: at the Fermi edge, and at a binding energy of 6 eV reference to the Fermi level, where the oxygen-induced feature ($1\pi_g^*$) appears.

Figure 3.5 shows the transient modifications at the Fermi edge as observed at different delays. At time zero (i.e., when the pump and probe pulses arrive temporally coincident at the surface), the shape of the Fermi edge is modified by a “step” at energies above the Fermi edge with a width of about 1.5 eV, corresponding to the energy of the exciting photons. Some evidence of this feature is still visible at 150 fs delay. Within another 100 fs, or 250 fs after the pulse pulse arrives, this nonthermal contribution has completely disappeared. At longer time delays, no further changes in this energy region were observed. The experimental distribution at time-zero is best reproduced by an excitation level of about 6% (at a photon energy of 1.5 eV). Referring to the insert of Fig. 3.5, the solid line is the calculated distribution for this excitation level, convolved with the estimated detector resolution of 370 meV. For reference, a spectrum taken with solely with the probe EUV beam (ground-state distribution) is fitted to a Fermi-Dirac distribution at 100 K, which is also convolved with the detector resolution.

Figure 3.6(b-e) shows the pump-probe spectra at various time delays, focusing on

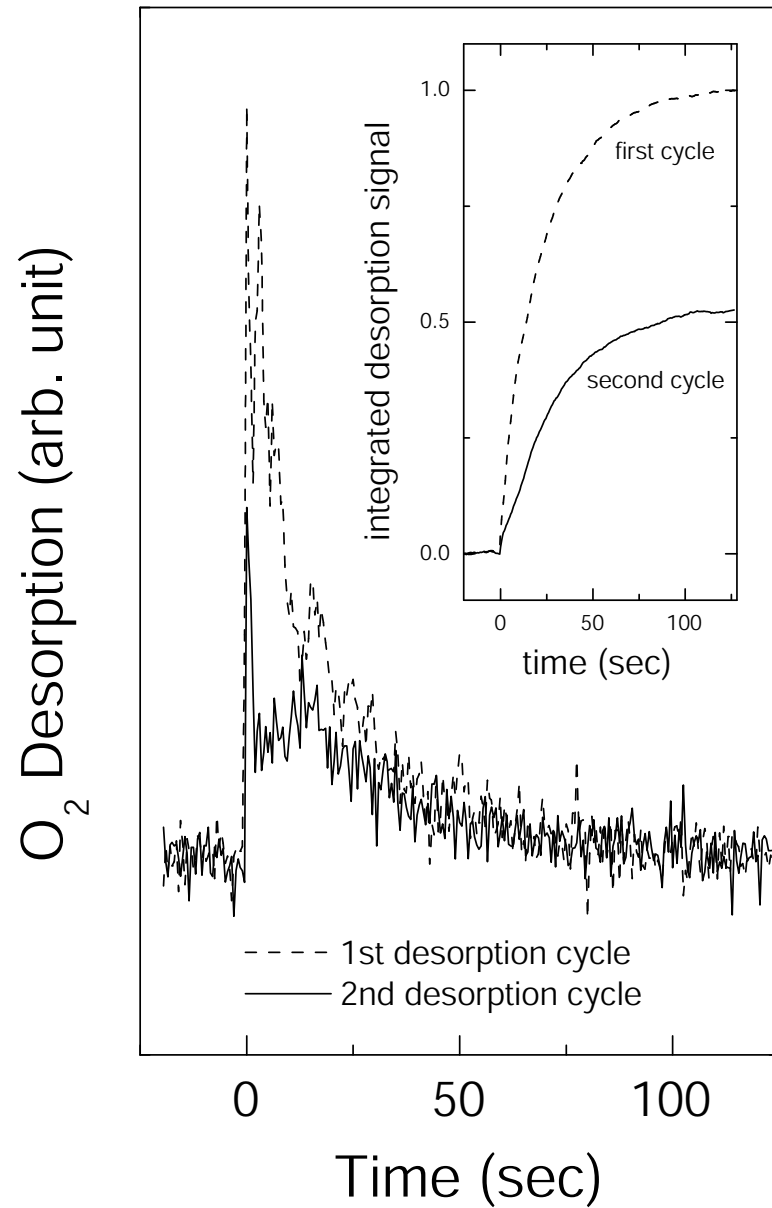


Figure 3.4: Femtosecond laser-induced desorption for the two adjacent desorption cycles with oxygen redosing between the two laser excitations. Insert shows the integrated desorption signal for the two cycles.

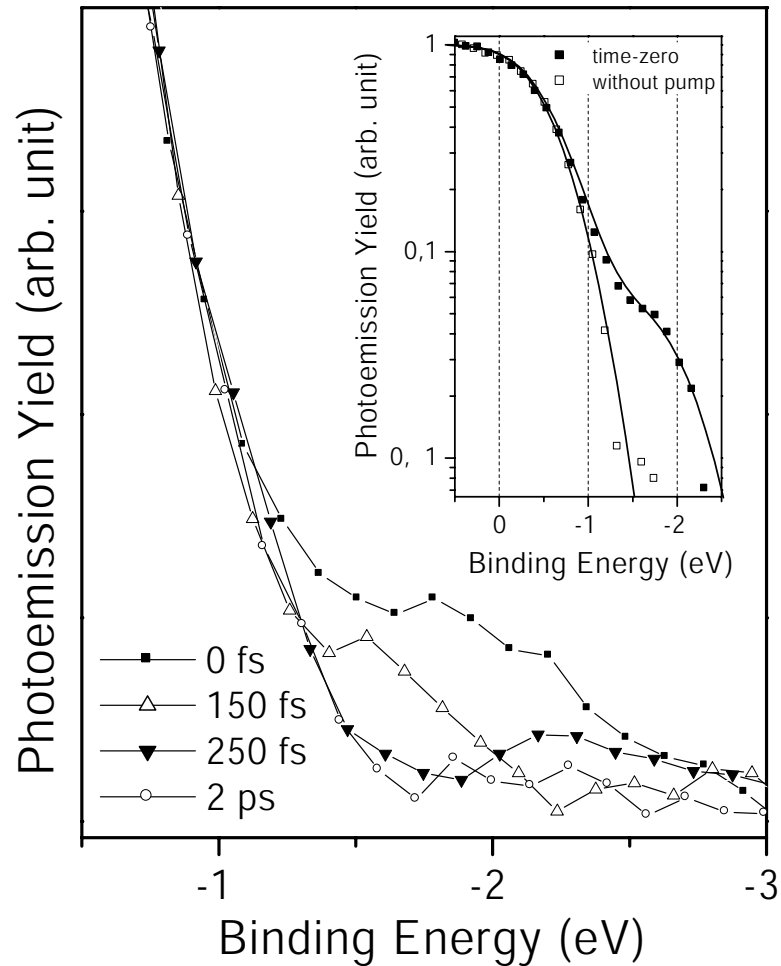


Figure 3.5: Electron energy distribution at Fermi edge of $O_2/Pt(111)$, for time delays of 0 fs, 150 fs, 250 fs, and 2 ps. Nonequilibrium hot electrons can be seen at 0 and 150 fs; however, at 250 fs, the energy distribution has thermalized. Inset: Fermi edges at 0 fs time delay (black square) and static spectrum without pump pulses excitation (hollow square), plotted in log scale. The electron distribution at 0 fs time delay can be fit to a 100 K Fermi-Dirac distribution with 6% of the electrons excited by the pump photon energy (1.5 eV).

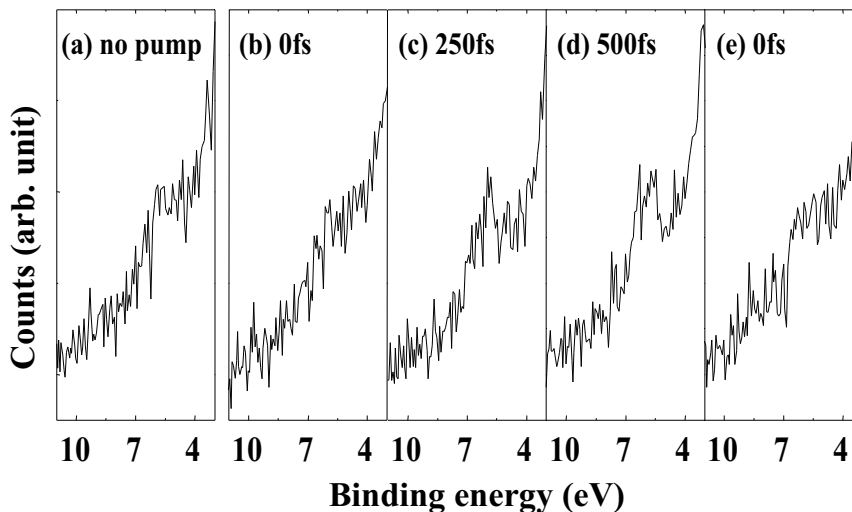


Figure 3.6: Time-resolved high-resolution photoemission spectra from a saturation layer of molecular oxygen adsorbed on a Pt(111) surface at liquid nitrogen temperature: (a) no pump beam; (b) with pump beam, zero time delay between pump and probe; (c) 250 fs time delay between pump and probe; (d) 500 fs time delay; (e) repeat of (b), taken immediately after (d).

the higher binding energy part of the valence band spectra. For comparison purpose, a photo-electron spectrum without pump beam excitation was taken in the very beginning, as shown in Fig. 3.6(a). In these spectra, the feature appears at around 6 eV binding energy corresponding to the oxygen $1\pi_g^*$ orbital hybridized with the platinum surface, as discussed in previous paragraphs. Figure 3.6(b) shows the spectrum obtained at zero time delay; no significant changes are visible when compared to the static spectrum. This contrasts with the changes above the Fermi-edge at zero time delay, as shown in Fig. 3.5, where the non-thermal distribution happens at zero time delay. However, at 250 fs time delay – well after the 55 fs pump pulse has been adsorbed and the nonthermal distribution at the Fermi edge has disappeared – a significant peak-like structure emerges out of the background. This peak-like structure is even stronger at a pump-probe delay of 500 fs, and it persists for

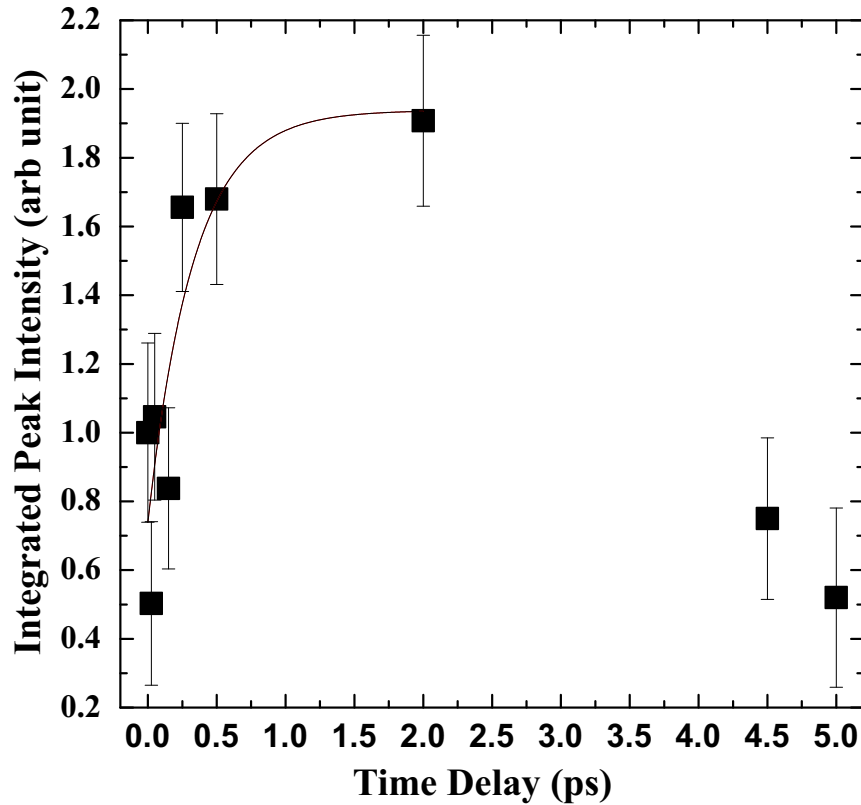


Figure 3.7: Integrated amplitude of the characteristic 6 eV peak feature as a function of pump-probe delay. A fit to the data indicates an onset time of 550 ± 140 fs.

several ps. Although our spectra were taken sequentially in this experiment with increasing time delays, this observed feature is not a permanent change of the sample through continuous pump pulse excitation, but rather a transient change. This can be verified by taking another spectrum at zero time delay immediately after the 500 fs spectrum is taken. This final time-zero spectrum is identical to the spectra of (a) and (b), which are taken at the beginning of the pump-probe scans. Therefore, in this experiment, the observed changes are definitely reversible, and a transient modification of the adsorbate bonding is monitored with femtosecond timing resolution for the first time.

By repeating this experiment to acquire more detailed scans, we are able to extract

the characteristic population and relaxation rates of this transient (meta-stable) excited adsorbate state. Figure 3.7 is a plot of the integrated strength of this transient peak as a function of time delay. The data points can be fitted by an exponential growth function:

$$y = y_0 + Ae^{\left(\frac{x-x_0}{t_0}\right)} \quad (3.1)$$

where t_0 is the rise time of the exponential increase function. By using this fitting equation to the extracted data, we estimate that the observed peak has an exponential rise time $t_0 = 550 \pm 140$ fs. Together with the information at longer time delays, we know that the signal decays within about 5 ps after the pump pulse arrives.

3.2.5 Permanent modification of O₂ on Pt(111)

In addition to the reversible change observed in the valence band structure, over the time scale of several hours of continuous pump pulse excitation, we also observe a long-term nonreversible change of the surface state induced by the ultrafast infrared pump pulses. Figure 3.8 shows a series of spectra taken during a period of 2 hours of irradiation by the ultrafast infrared pump pulses. During the first hour of the pump pulse irradiation, after a saturation coverage of oxygen was adsorbed to the platinum surface, no significant changes in the spectrum are observed. However, further irradiation from the ultrafast infrared pulse pulses alters the 6 eV binding energy feature from a shoulder-like structure to a peak-like structure. This peak-like structure is similar to the spectra of the peroxo and atomic oxygen states on the platinum surface of their static spectrum; it is also similar to the transient peak appearing in the pump-probe scans. This differs from the transient feature, which disappears when the time delay returns to zero. By continuing ultrafast

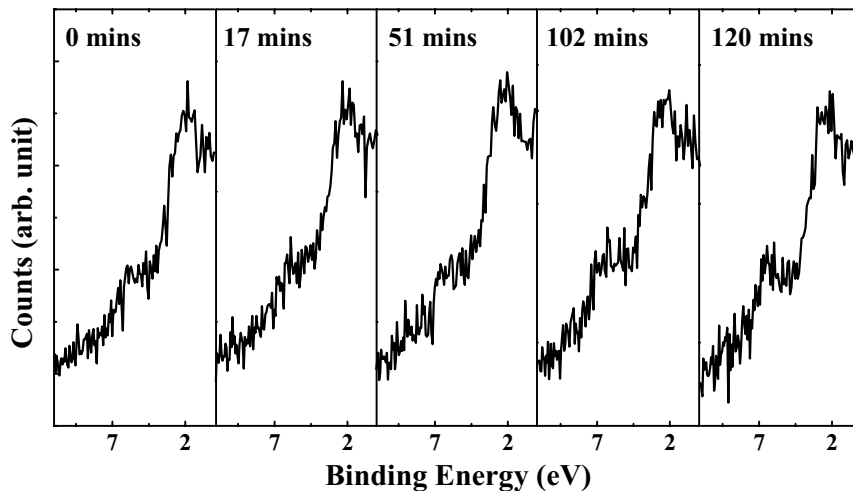


Figure 3.8: Spectra taken during pump beam irradiation of the sample over a period of 2 hours. During the first ≈ 50 min, the spectra are unchanged. However, after ≈ 100 min, the characteristic 6 eV peak gradually increases and is permanently present on the subsequent spectrum taken.

infrared pump pulses irradiation over several hours, this feature remains after the pump pulses have stopped, indicating the sample condition does not return to its original state. This feature in the photoemission spectrum seems to represent a stable configuration of the $O_2/Pt(111)$ system, resulting from continued irradiation by the ultrafast infrared pump pulses over several hours.

3.3 Discussion

The reaction pathways of surface chemical reactions induced by an intense, ultrafast infrared pulse could possibly proceed in following order:

1. Creation of a nonthermalized or “hot” electron distribution at the metal surface results from the energy adsorption of the excited ultrafast pulse.
2. Internal energy redistribution between the hot electrons to achieve a thermalized

configuration.

3. Adsorbate excitation caused by the energy transfer mediated by hot electrons from the metal surface.
4. Modification of the adsorbates-surface chemical bond character leads to translational and rotational motions of the adsorbates.
5. Thermalization between the electrons and the surface photons.
6. Traditional “phonon induced” chemical surface reaction caused by the elevated phonon temperature, but this step happens in a much longer time scale (\sim ps).

In the pump-probe experiment, the transient feature of the photoemission spectrum observed above the Fermi edge could be assigned to the step 1; while the transient peak observed at the higher binding energy side of the valence band could be assigned to the step 3. Furthermore, knowledge of the adsorbed fluence as well as the measured excitation rate of the electron gas allow us to reconstruct steps 2, 4 and 5.

3.3.1 Nonthermal surface electrons on Pt(111) surface

3.3.1.1 Nonthermal surface electrons observed in the experiment

Laser energy adsorbed by the adsorbate layer (in this case, a saturated layer of molecular oxygen) is extremely low; therefore, direct excitation from the ultrafast infrared pump pulse is highly unlikely [78, 79]. The energy of the incident infrared pulse is adsorbed entirely by the electrons on the top ~ 100 Å thick of the platinum (111) surface. Because of the extremely short (~ 65 fs) and intense ($> 10^{12}$ W/mm²) excitation, this energy

results in a extremely nonthermal energy distribution of the electron gas. This nonthermal distribution can be observed at the spectrum taken at zero time delay, that shows a transient “step” above the Fermi-edge. The adsorbed fluence of 1 mJ/cm^2 results in an estimated excitation of about 6% of the electrons at the platinum surface [80]. Comparable excitation levels have been reported for heating a 300 \AA thick gold film [32] and a Pt(110) surface [81] by ultrafast pulses. The fact that the transient nonthermal feature of the “hot” electron step at the Fermi-edge disappears within the first 250 fs after the zero time delay is in agreement with the measurement of the Pt(110) surface [81]. In contrast, significantly longer lifetimes of the nonthermal contribution (up to 400 fs) have been reported for gold. This time difference between the platinum and the gold surfaces can be explained as a much slower electron thermalization process in noble metals in comparison to transition metals, because of a reduced electron-electron scattering rate at the relevant energies [82, 83]. The measurement is extremely surface sensitive because the 42 eV EUV probe photons we used can only liberate electrons from the top 5 \AA of the platinum surface due to the short electron penetration depth at these kinetic energies.

3.3.1.2 Two temperature model and nonthermal surface electrons lifetime

Knowledge of the absorbed fluence allows us to calculate the time evolution of the electron and lattice temperatures. Due to its low heat capacity, the surface electrons are heated quite efficiently by ultrafast infrared pulses. Although the electron distribution immediately after the excitation is nonthermalized and technically cannot be fully described quantitatively by a simple temperature, nevertheless the calculated electron temperature is a useful indicator of the actual excitation degree of the surface electrons.

Thermalization of the electron distribution occurs within 250 fs, followed by subsequent cooling of the hot electrons due to coupling to the surface lattice phonons (electron-phonon coupling). The electron-phonon effective collision time is actually of the same order as the electron-electron scattering time. It is, however, quite inefficient with respect to collisional energy exchange, because of the typical phonon energies required for the energy transition (about some tens of meV), where significant excitation of the surface lattice occurs on a much longer time scale than the electron dynamics. In addition, the higher heat capacity of the lattice limits the maximum lattice temperature to a much lower temperature than that of the electrons. On the other hand, since only the electrons at the top ~ 100 Å of the platinum surface are excited by the ultrafast pulses, thermal diffusion between the electrons at the metal surface and the electrons at the bulk also has a significant effect on the thermalization process.

The interplay between ultrafast pulses, hot electrons, and the lattice (phonons) can generally be calculated by a simplified model, or so-called “two-temperature model” [84]. A set of coupled equations is used to determine the electron temperature (T_e) and the lattice temperature (T_p) as a function of time:

$$C_e \frac{\partial}{\partial t} T_e = \frac{\partial}{\partial z} \left(\kappa \frac{\partial}{\partial z} T_e \right) - g(T_e - T_p) + \hat{F} \quad (3.2)$$

$$C_p \frac{\partial}{\partial t} T_p = g(T_e - T_p) \quad (3.3)$$

where $C_e = \gamma T_e$ and C_p are the electron and lattice heat capacities, respectively. $\kappa = \kappa(T_e/T_p)$ is the thermal conductivity and g is the electron-phonon coupling constant. The

Electron specific heat γ	748 J/m ³ K ²
Thermal conductivity $\kappa_0(77\text{ K})$	71.6 W/mK
Electron-phonon coupling constant g	6.76×10^{17} W/m ³ K
Lattice heat capacity $C_p(77\text{ K})$	2.69×10^6 J/m ³ K
Absorbed laser peak intensity I_0	1.71×10^{14} W/m ²
Pulse width τ	55 fs
Optical penetration depth λ (800nm)	12.56 nm

Table 3.2: Parameters of platinum(111) used in the calculation of electron and lattice temperatures

term \hat{F} is used to describe the femtosecond pump pulse in the form of

$$\hat{F} = \frac{I_0}{\lambda} e^{-4\log(2)t/\tau - z/\lambda} \quad (3.4)$$

where I_0 is the adsorbed laser peak intensity, λ is the optical penetration depth, and τ is the pump pulse width. All the parameters used in this simulation are listed in Table 3.2.

The calculated result is shown in Fig. 3.9, and the measured nonthermal electron integrated intensity is shown in parallel for comparison purposes. For a platinum surface excited by a $10 \mu\text{J}/\text{mm}^2$ and 55 fs ultrafast pulse, we predict the maximum electron temperature to be 1082 K at 35 fs after zero time delay, i.e., immediately after the laser pulse (55 fs) has totally arrived. The same value for the maximum temperature (about 1000 K) can be calculated from the measured excitation of the electron gas of 6% [80]. In contrast, the calculated maximum temperature of the lattice is 174 K, and is reached at 1.2 ps after the ultrafast pulse excitation. At this long time scale, the electron and lattice temperatures are equilibrated and the condition of the sample heating is similar to conventional thermal surface chemical reaction, at which the electron and lattice temperatures are equal.

Figure 3.9 shows that at long delays (> 1 ps), the calculated lattice temperature is a little higher than the electron temperature. This is a numerical simulation artifact that is

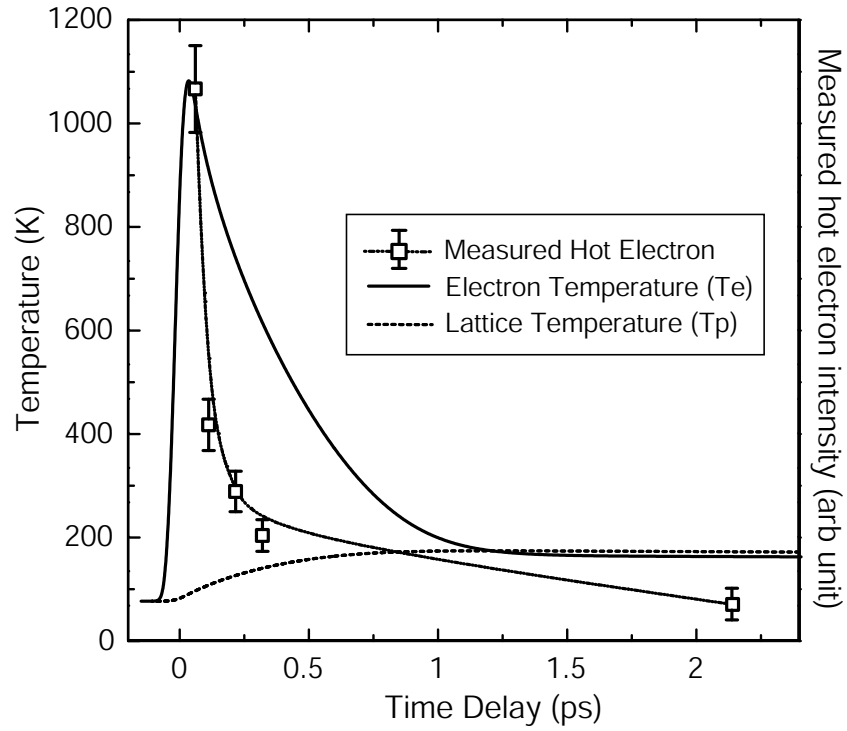


Figure 3.9: Calculated electron temperature (T_e) and lattice temperature (T_p) using the “two-temperature model” at the platinum (111) surface excited by a $10 \mu\text{J}/\text{mm}^2$, 55 fs ultrafast infrared pulse. The measured nonthermal electron integrated intensity (square) is also shown in the figure for comparison purposes.

caused by the simple two-temperature model. This artifact happens because only electron heat diffusion is considered in Eq. 3.2, and the lattice thermal diffusion is completely neglected due to the fact that the electron thermal diffusion is significantly more efficient than the lattice thermal diffusion. The optical excitation of the surface electrons only happens within the optical penetration depth of the platinum surface, and at around several picoseconds after the optical excitation the temperature of the surface electrons is still much higher than the bulk. Therefore, the surface electrons keep losing energy to the bulk electrons to achieve thermal equilibrium for the whole crystal. However, most of the energy initially adsorbed by the surface electrons has been transferred to the surface lattice by this time. The surface lattice has to give back its stored energy to the surface electrons, which continue to lose energy to the bulk electrons. Therefore, the surface lattice temperature is slightly higher than the surface electron temperature to maintain an energy gradient to give up energy from the surface lattice to the surface electrons for thermal diffusion. True equilibrium will happen at a very long time delay, when the whole sample achieves thermal equilibrium and no gradients remain.

The two-temperature model is often criticized for being too “simple” to describe the actual ultrafast electron heating process. Since the rapid heating of electrons by an intense ultrafast pulse will cause the surface electrons to become highly excited, the excited electrons cannot be described by a “temperature” that can only be defined when the electrons are in thermal equilibrium, especially in the first several hundred femtoseconds after the excitation. In fact, more complicated models are needed to accurately describe the non-thermal electrons excited by ultrafast laser pulses. However, by integrating the nonthermal

electrons measured in Fig. 3.5, Fig. 3.9 compares the measured nonthermal electron integrated intensity with the calculated electron temperature. This comparison does show that the de-excitation rate of the calculated electron temperature is quantitatively similar to the measured nonthermal electron intensity. Therefore, the two-temperature model provides insight into understanding the role of surface hot electrons in femtochemistry on metal surfaces.

Hot-electron temperature at longer time scales can, in principle, be obtained by measuring the slope of the Fermi-edge from the pump-probe spectrum. However, due to the resolution limitation of our detector and the limited statistics of our measurements, the gradual tilting of the slope of the Fermi-edge cannot be distinguished from our spectrum, and we are not able to further compare the two-temperature model with the actual measurement at a longer time scale.

3.3.1.3 Excitation of O₂ by nonthermal surface electrons

As discussed in Sec. 3.2.4, a transient feature appears at about 6 eV binding energy on the time scale of about half a picosecond on our measured spectra. This raises a question of how this transient change is created. There are three possible mechanisms to explain the transient effect observed, including: (1) pure electronic artifact, (2) phonon-mediated oxygen state transition, and (3) nonthermal electron-mediated oxygen state transition.

Figure 3.10 compares the integrated intensity of the measured transient feature to the calculated electron and lattice temperatures by the two-temperature model. Figure 3.10(a) clearly shows that the maximum intensity of the transient feature is delayed about 1 ps with respect to the time when the maximum electron temperature is reached. Also, the oxygen

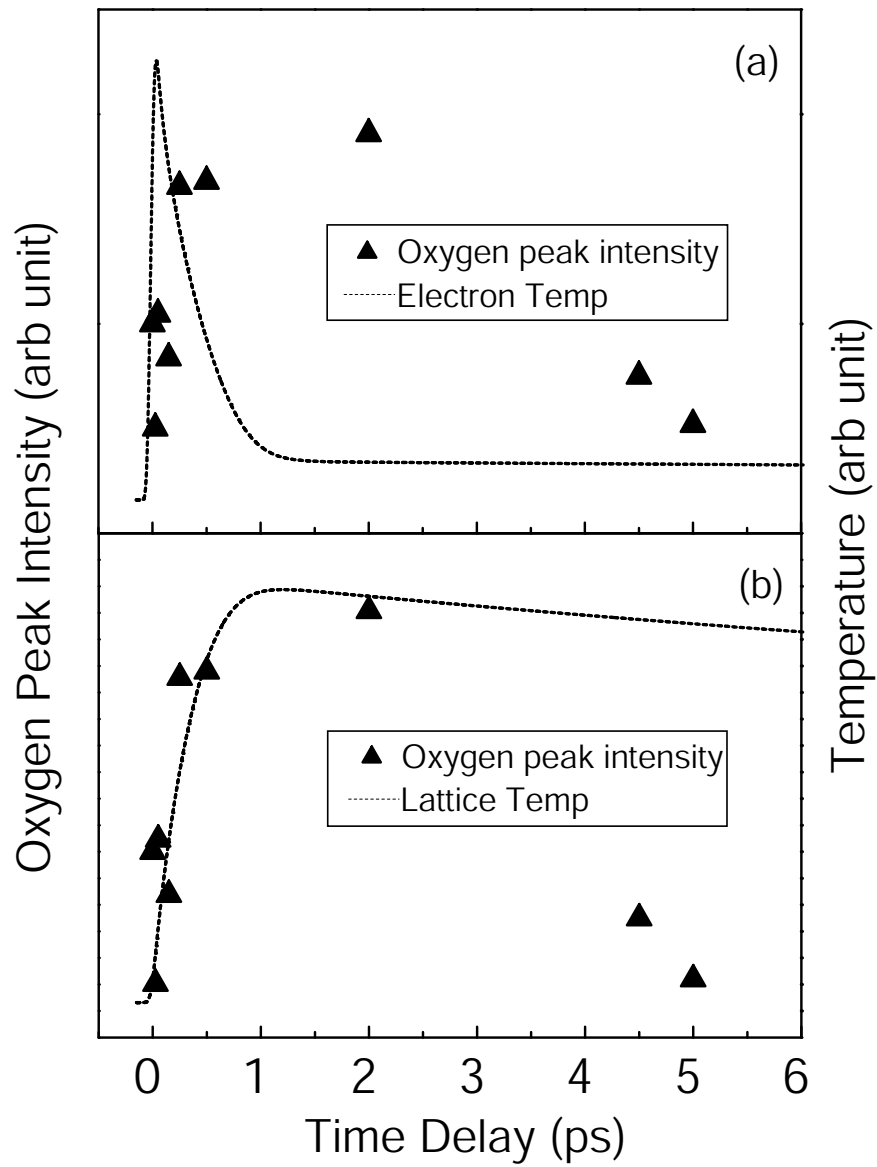


Figure 3.10: Integrated intensity of the peroxy signature peak compared to the rescaled (a) electron and (b) lattice temperature.

peak relaxes at about 5 ps, by which time the surface electrons have long been cooled for several picoseconds. Therefore, if the transient feature is a pure electronic excitation of case (1), the peak-like transient feature should have a rise and relaxation time similar to that of the nonthermal surface electrons. Hence, the possibility that the observed transient feature is a purely electronic artifact is not likely.

For case (2), it might seem possible that the transient feature could be a phonon mediated process, since the lattice temperature has a rise time similar to that of the transient feature. However, the lattice temperature actually takes a very long time to cool down when compared to the relatively short relaxation time (~ 5 ps) of the oxygen peak, as shown in Fig. 3.10(b). Therefore, if the observed transient feature was actually driven primarily by phonon excitation, as in conventional surface chemistry, the relaxation time of the oxygen peak would be much longer than the 5 ps that we observed. It ought to be comparable to the lattice relaxation time. Furthermore, comparable rise time between the lattice temperature and the transient feature actually indicates that the excitation process cannot be phonon-mediated. The reason is because a finite time delay is actually required between the rise times of the lattice temperature and the transient feature, since a finite coupling time is needed to transfer energy from the lattice to excite the adsorbates, as required by the frictional model [85]. Therefore, the nonthermal electrons at the platinum surface are most likely to be directly driving the changes in the oxygen configuration.

By excluding the first two possible mechanisms, the transient feature is most likely mediated by the nonthermal surface electrons of case (3).

3.3.2 Mechanism of O₂ excitation

3.3.2.1 Identification of the transient feature

From the discussion of Sec. 3.2.2, the difference in the photoemission spectrum at 6 eV binding energy between superoxo and peroxo chemisorbed states is assigned to the difference in the electron occupancy of the $1\pi_g^*$ orbital of the oxygen molecules. For superoxo, the $1\pi_g^*$ orbital is half-filled; whereas for peroxo, the $1\pi_g^*$ orbital is fully occupied. This difference changes the density of state of the oxygen molecules and causes the photoemission spectra of peroxo chemisorbed state to have a peak-like feature at the 6 eV binding energy below the Fermi-edge [63, 70]. Together with the discussion from the previous section, the appearance of this transient feature possibly reflects a state transition for the chemisorbed oxygen molecules mediated from the coupling of the nonthermal surface electrons on the platinum surface.

As mentioned in Sec. 3.1.2, the $1\pi_g^*$ orbital of the oxygen molecule is important to the interaction between the adsorbed oxygen molecules and the platinum surface. Since the $1\pi_g^*$ orbital is “anti-bonding” in nature, the bond length between the two oxygen atoms is slightly longer for the peroxo oxygen (fully filled) than the superoxo oxygen (half-filled). However, the $1\pi_g^*$ orbital also is hybridized with platinum d -band; thereby it is “bonding” in nature with respect to the oxygen molecule and the platinum surface. This causes the peroxo oxygen to bond more tightly to the platinum surface. Therefore, as is widely accepted in conventional investigations, the spectral changes we observed in the pump-probe measurements could not merely reflect electronic transients. It is very likely to reflect modifications to the chemisorbed state of the oxygen initiated by changes at the surface-adsorbate bonding.

The similarity between the static spectrum of the peroxy oxygen, the static spectrum of the atomic oxygen (Fig. 3.3), and the transient pump-probe spectrum at about 500 fs time delays (Fig. 3.6) reveals two possibilities for the nature of this transient state transition of the adsorbed oxygen molecules. The initial superoxy oxygen (O_2^-) on the platinum surface can be excited by the ultrafast pulses into either: (1) two transient dissociated atomic oxygen atoms, or (2) an excited peroxy oxygen (O_2^{2-}).

In fact, these two possible processes are closely related, or even identical to a certain extent. Previous calculations using density functional theory [69, 86] have suggested that the peroxy oxygen can actually be considered to be a “precursor” state in the process of dissociation to two oxygen atoms. According to calculations, superoxy oxygen has a comparatively higher energy barrier to dissociate; however, after the superoxy oxygen transfers to the site of peroxy oxygen and subsequently changes its bonding character through charge transfer with the platinum *d*-band, the energy barrier for dissociation is reduced. The reduction of the energy barrier for dissociation can be explained by the weakening of the intermolecular bond between the two oxygen atoms when an additional electron is tunneled to the $1\pi_g^*$ orbital from the platinum *d*-band. Moreover, this charge transfer will cause the oxygen molecule to move from its original bridge site to the three-fold-hollow site, due to the creation of an extra bond to the platinum surface.

Complete dissociation into two oxygen atoms is not possible because the transient features are observed in the pump-probe scans are in fact reversible. If the transient feature is identified as two fully dissociated oxygen atoms, these two oxygen atoms will need to recombine back into an oxygen molecule in a short period of time (~ 5 ps). In addition,

atomic oxygen has the highest binding energy to the platinum surface of all the adsorption states. Thus it is very unlikely that the stable oxygen atoms would recombine back into a less-stable molecular configuration. Moreover, the probability for two separate atomic oxygens to get close enough for recombination would be rather low if the two dissociated oxygen atoms adsorb at two non-adjacent three-fold-hollow sites (2x2 structure).

Finally, a reversible replenished desorption process is also unlikely. The reason is that significant oxygen re-adsorption to the depleted oxygen sites in the time interval between the ultrafast pulses (1 ms) requires an oxygen ambient pressure of higher than 10^{-3} torr², but the chamber pressure is kept in the 10^{-10} torr range during the whole experiment. Lateral oxygen diffusion to replenish the depleted oxygen sites is also not possible because the following test was performed to ensure that lateral diffusion rate is low in the experimental surface temperature (77 K): An oxygen covered surface was first depleted by intense ultrafast pulses. Then, the sample sat still for several minutes to allow possible lateral diffusion to happen. Intense ultrafast pulses were reintroduced onto the depleted spot, but no further oxygen desorption could be detected on the second laser desorption. In addition, pictures taken by STM on an oxygen covered platinum surface cannot identify any possible oxygen redistribution after the oxygen dosing, indicating oxygen lateral diffusion is insignificant [71].

In conclusion, the transient feature that appears in the pump-probe scans can be identified as the superoxo molecular oxygen state (O_2^-) is transferring into a highly-excited peroxo molecular oxygen state (O_2^{2-}) or equivalently, a transient dissociated oxygen atomic

²1 Lamuire (L) $\equiv 10^{-6}$ torr·sec. In general, dosing 1 L of molecules will deposit a surface to the saturation coverage. For 1 ms, pressure of 10^{-3} torr will be required.

state (O), in a half-picosecond time scale.

3.3.2.2 Excitation rate of molecular oxygen

By comparing the peak height observed in the pump-probe spectra with that observed in the static spectrum of the atomic oxygen, the actual excitation rate of molecular oxygen by the pump ultrafast pulse can be estimated. As discussed in Sec. 3.2.2, heating an superoxo oxygen covered platinum sample to different surface temperatures can transform the oxygen into the peroxo and the atomic oxygen states. For both the TDS and UPS static spectrum, conventional lattice heating is used to transform the superoxo oxygen to the peroxo and atomic oxygen, and hence the transformed peroxo and atomic oxygen coverage on these two cases should, in principle, be the same.

The total amount of adsorbed oxygen on the platinum surface is proportional to the combined area of the the α and β peaks from the TDS spectrum. By comparing the ratio of the total areas of the α and β peaks, we estimated that the dissociation ratio $d = 25\%$, in which 25% of the oxygen molecules of the saturated layer are dissociated thermally. Then, by comparing the intensity ratio i of the characteristic peak of the peroxo oxygen pump-probe spectra to the static atomic oxygen spectrum, the total excitation rate induced by the ultrafast pump pulses is equal to $i \times d$. The ratio of the peak intensities between the peroxo transient and the atomic static spectra is measured to be $i = 70\%$. Therefore, the total excitation rate of the peroxo oxygen state is about $70\% \times 25\% = 18\%$. At first glance this number seems to be surprisingly high. However, even higher excitation rates for molecules due to femtosecond laser pumping have been reported. For example, complete depletion of the adsorbed oxygen molecules by a single intense ultrafast pulse

has been reported to the system of $O_2/Pt(111)$ [12], in which the fluence used was several orders of magnitude higher than in our experiment.

3.3.2.3 Energy transfer mechanism from nonthermal electrons to adsorbates

The excitation mechanism of the adsorbate – the coupling between the excited surface electron and the adsorbate – can be described on the microscopic scale by means of direct electron (hole) transfer process between the excited surface electron into the LUMO (HOMO) of the adsorbate.³ The schematic drawing for the orbitals of superoxo and peroxo oxygen is shown in Fig. 3.11 [12, 87]. Several schemes of transfer processes have been proposed to explain the desorption processes induced by ultrafast pulses for adsorbates. In particular, for $O_2/Pt(111)$, it has been proposed that the transition is due to the excited surface electron coupling to the unoccupied $3\sigma_u^{+*}$ level [77]; for $O_2/Pd(111)$, hole transferring into the occupied part of the $1\pi_g^*$ level is an important process [88].

In the present case, we propose that an excited surface electron is transferred from the platinum surface to the unoccupied $1\pi_g^*$ orbital of oxygen, in which the orbital orientation is parallel to the platinum surface. There are two justifications:

1. Excitation to the $1\pi_g^*$ orbital is the most direct way to achieve the required charge configuration for the peroxo oxygen, in which its $1\pi_g^*$ orbital has one more electron when compared to the superoxo oxygen [69].
2. For the superoxo oxygen, the $\pi_{||}$ orbital, which the $1\pi_g^*$ hybridized with the platinum d -band, is only half-filled and is located right at the Fermi-edge. Therefore, the observed high excitation level for this state transition can be explained because the

³LUMO = Lowest unoccupied molecular orbital, HOMO = Highest occupied molecular orbital

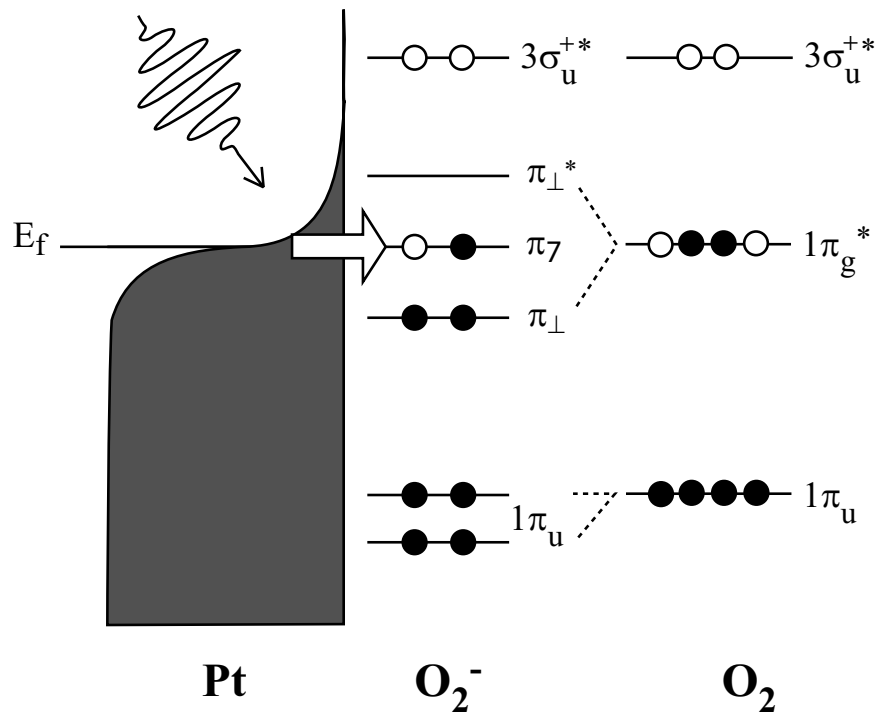


Figure 3.11: Because of the increased population of the surface electrons above the Fermi level induced by the ultrafast pump pulse excitation, the surface electrons will start to tunnel to the $1\pi_g^*$ orbital of the oxygen molecule and this leads to energy transfer to the oxygen center-of-mass.

excited surface electrons has the highest population at the Fermi-edge, and hence the transition probability for the excited surface electrons tunneling into the $\pi_{||}$ orbital can be very high. In contrast, since the $3\sigma_u^*$ orbital lies > 1 eV above the Fermi-edge, much fewer surface electrons will be able to reach this energy level for the same pump pulse intensity. If the electron transition into the $3\sigma_u^*$ is the correct mechanism, much higher laser intensities would be expected and be necessary to achieve the electron temperature needed [13].

3.3.2.4 Possible molecular motion during state transition

From the previous discussion, it becomes clear that excitation rate of the adsorbed oxygen by surface electrons reaches its highest level at the maximum temperature of surface electrons, which is several tens of femtoseconds after the pump pulse. After that, the excitation rate gradually decreases as the surface electrons cool. Therefore, the appearance of the transient peak-like feature at about 500 fs, which has a significant delay relative to the maximum electronic excitation of the oxygen molecules, does not reflect the electronic excitation level. Rather, this transient feature result from changes in the chemisorbed state accompanied by motions of the oxygen molecule. In general, the adsorption sites are the local minima of the potential energy surfaces (PES): for the superoxo oxygen, it is the bridge site, and for the peroxo oxygen, it is the hollow site. In addition, the PES defines the route for the transition between two chemisorbed states [69, 70]. For superoxo state to peroxo state, the oxygen will need to move from the bridge site to the hollow site (see Fig. 3.1). In order to move from the bridge site to the hollow site with the correct molecular orientation and configuration, the oxygen molecular motion could involve rotational

and vibrational motions. The oxygen molecule is pulled by the extra bond created when the hot surface electron transfers to the LUMO state of the oxygen molecule.

Theoretically, the rise time of the transient feature can be related to an effective coupling time τ_e between the surface electrons and oxygen center-of-mass motion by using a “frictional model” for the description of substrate-adsorbate interaction [85]. The typical value of the coupling time τ_e for direct energy exchange between the electron gas and the adsorbate lies in the range of a few 100 fs to several ps, in good agreement with our observations [8, 16, 89].

3.3.2.5 Decay channels for the excited state

The decay of the transient feature in several picoseconds can be interpreted as the actual lifetime of the meta-stable intermediate oxygen state. In case of the peroxy oxygen transformation, the decay can occur through molecular kinetic energy relaxation scattering with the surface electrons and phonons.

For our experiment, since the excited oxygen state (peroxy) is observed to relax to its ground state (superoxy) in about 5 ps, relaxation to the superoxy oxygen must be the dominant channel; however, it might not be the only possible decay channel. Typically, several different decay channels are present for conventional thermal excitation; For example, desorption and dissociation often co-exist. For excitation by ultrafast pulses, desorption and dissociation for the adsorbates are always observed together [8, 16, 89]. Therefore, the permanent feature shown in the photoemission spectrum of Fig. 3.8 after several hours of ultrafast excitation could likely result from the cumulative effects of slow oxygen desorption and dissociation. Since peroxy oxygen tends to be the preferred configuration for

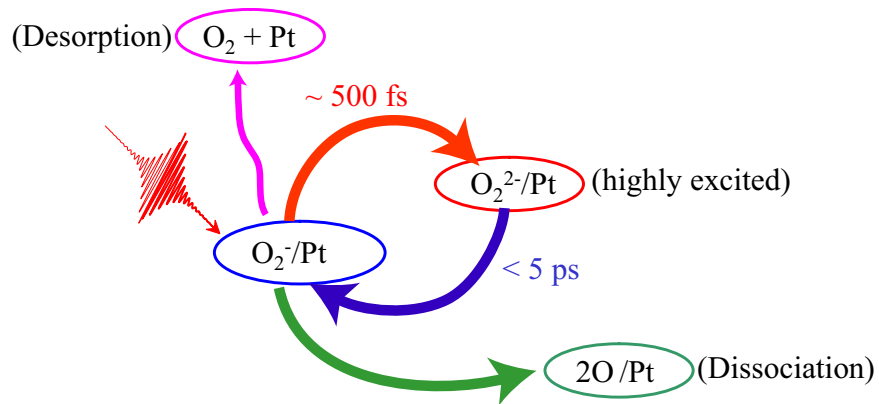


Figure 3.12: Possible reaction diagram of how oxygen molecules react after excited by an intense ultrafast pulse on the platinum surface

chemisorbtion at low surface coverage [75], a reasonable explanation for the permanent feature in valence band may result from slow desorption of oxygen over time and slowly increase the stable peroxy population on the platinum surface. Another explanation could be slow dissociation into oxygen atoms by the ultrafast pulses after extended pumping. However, it is unlikely that surface contamination causes this permanent feature, since the chamber is maintained in ultra high vacuum during the data taking, and the contaminant is not likely to contribute to the 6 eV peak that we observed.

3.4 Conclusion

After a lengthy discussion, a complete picture of how oxygen molecules adsorbed on Pt(111) surface response after the platinum surface is excited by an intense ultrafast pulse is illustrated in Fig. 3.12 [90, 91]. The oxygen molecules, originally residing on the bridge site as superoxo state (O_2^-) with one extra electron transferred from the platinum, are excited by the hot surface electrons to gain another electron from the platinum surface. After 500 fs, an extra chemical bond between the oxygen and platinum surface is created

due to the excess electron, and this pulls the oxygen molecule to the hollow site (peroxo O_2^{2-}). In about 5 ps, the excited oxygen will relax back to the bridge site (superoxo O_2^-) by giving up the excess electron to the platinum surface. In addition, slow desorption and dissociation happens on a longer time scale and ultimately reduces the molecular oxygen coverage.