Direct Observation of Surface Chemistry Using Ultrafast Soft-X-Ray Pulses

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We present the first demonstration of the use of ultrafast extreme-ultraviolet pulses to directly monitor a surface chemical reaction on femtosecond time scales. By adsorbing molecular oxygen onto a platinum surface and exciting it with an ultrafast laser pulse, changes in the oxygen-platinum chemical bond on a subpicosecond time scale were observed through changes in the photoelectron spectra. This work demonstrates a powerful new technique for studying reactions of interest in catalysis and for probing changes of local order on surfaces on their fundamental time scales.

The study of ultrafast processes on surfaces has been a topic of increasing interest in recent years, from both an experimental and a theoretical point of view [1]. The driving force behind this interest is that recently developed ultrafast lasers [2] can now be used to monitor the evolution of these reactions on their fundamental time scales [3]. This prospect is of particular importance to processes such as heterogeneous catalysis, where the interaction dynamics between the molecule and the surface are fundamental to the process. However, in contrast to the case of gas or solution-phase chemistry, where pump-probe transient absorption spectroscopy and more sophisticated techniques can be used to obtain a clear picture of reaction dynamics [4], experimental surface science techniques are more limited in their ability to give directly interpretable data. In this paper, we present the first use of a powerful new technique to study molecular dynamics on surfaces. We use time-resolved photoemission spectroscopy and extreme-ultraviolet (EUV) light to monitor changes in the valence band of a surface adsorbate as a function of time. This enables us, for the first time, to directly observe changes in the chemical bond character of a molecule adsorbed on a surface, with the sub-100 fs time resolution necessary to follow the *entire* progress of the reaction.

Past time-resolved surface studies have used two-photon photoemission, infrared (IR) spectroscopy, sum-frequency generation, and resonant Auger spectroscopy to monitor phonon and electron substrate-adsorbate coupling on ultrafast time scales [5–8]. In a recent paper, by using two-photon photoemission, for example, Petek *et al.* [6] observed atomic motion corresponding to a fraction of a vibrational period of the Cs atom on the surface. By exciting the Cs atom to a relatively long-lived (≈ 100 fs) electronically excited state, the atomic motion corresponding to a fraction of a vibration period could be monitored. Photodesorption yield measurements and surface second harmonic generation [9–13], have also been used to monitor the final state after completion of a chemical reaction, and have made it possible to measure the overall time scale of femtosecond laser-induced desorption processes. Photoemission spectroscopy has been used extensively to charac-

terize surfaces and study slow changes in surface structure and composition [14]. However, all of these past experiments are limited in that the chemistry occurring at the surface itself—the making and breaking of chemical bonds, the intermediate reaction steps, and the existence of transient reaction products—has not been directly observed.

The techniques of valence- and core-level photoemission spectroscopy (UPS/XPS) are extremely sensitive to the chemical state of a surface-adsorbate complex [15]. To observe valence-band electronic structure, photon energies of a minimum of ~10 eV in the vacuum- and extreme ultraviolet (VUV/EUV) region of the spectrum are required, while core-level spectroscopy requires even higher photon energies. The "chemical shift" of a core level can act as an indicator of the chemical or charge state of an atom involved in a chemical bond. Valence-band spectra, on the other hand, provide information on the hybridization of the outermost molecular orbitals responsible for a chemical bond. Recent progress in the efficient generation of ultrafast pulses in the VUV [16] makes subpicosecond resolution UPS/XPS experiments feasible, to obtain direct, dynamic, information on the electronic structure of surface reactants. Past work applied ultrafast photoelectron spectroscopy to the observation of the decay dynamics of photoexcited electrons at surfaces [5,6,17–20]. Very recently, other experiments have used time-resolved hard-x-ray diffraction to monitor phase transitions in bulk materials with picosecond time resolution [21–23].

In our experiment, a femtosecond infrared pump pulse is used to excite molecular oxygen on a Pt(111) single crystal surface. Using ultrafast EUV light, we monitor the change in the characteristic photoemission spectrum from the surface as a function of time after excitation by the pump. We observe a change in the valence-level structure of the oxygen-platinum complex, on a time scale of approximately 500 fs. This change corresponds to a subpicosecond, reversible, laser-induced modification of the oxygen bond, corresponding to a fast change in the electronic configuration of the oxygen adsorbate.

In the experiment, a Pt(111) crystal is temperature controlled and mounted in a vacuum chamber with a base
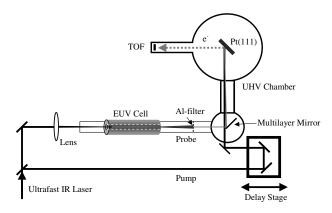
FIG. 1. Experimental setup for femtosecond time-resolved valence-state spectroscopy using EUV light.

pressure less than 1×10^{-10} torr (Fig. 1). We use an amplified Ti:sapphire laser system that generates 1.4 mJ, 800 nm, 25 fs pulses at a 1 kHz repetition rate [2]. An 800 nm pump beam of duration 55 fs (broadened due to dispersion) is used to excite the oxygen, at an absorbed laser fluence of 10 μJ/mm^2. An 800 nm probe beam is upconverted using phase-matched high harmonic generation (HHG) [16], to give an EUV probe pulse of duration <25 fs. A 2000 Å aluminum filter is used to maintain a pressure differential between the HHG cell and the main chamber, and to eliminate the copropagating laser light while transmitting the EUV beam without temporal distortion. Because of the phase-matched conditions under which the EUV light is generated, most of this light emerges in 3–5 harmonics of the pump beam, corresponding to the 23rd–31st harmonics at energies between 34.5 and 46.5 eV. This, in combination with a 45° EUV energy-selective multilayer reflector and the filter transmission, partially monochromatizes the EUV probe beam. The 27th, 29th, and 31st harmonics reach the sample, with more than half of the beam energy in the 29th harmonic (43.5 eV). The pump and probe beams have a relative angle <1° to minimize geometrical errors. The kinetic energies of the photoemitted electrons from the sample are determined by their flight time through a 600-mm-long time-of-flight (TOF) tube. The UHV chamber is equipped with a sputter gun for sample cleaning, as well as a temperature-programmed desorption setup to identify the adsorbate.

The time resolution of our measurement was determined by performing a cross correlation between the IR pump beam and the IR light used to generate the EUV light, after removing the aluminum filter. The FWHM of this cross correlation was 62 fs, and represents an upper limit to our time resolution given that the x-ray pulse duration is shorter than that of the driving laser.

In our experiment, we deposit oxygen on Pt at a temperature of $-195\,°C$. Under these conditions, oxygen is known to chemisorb as a molecule, where—depending on the coverage—either a superoxo (O_2^-) or peroxo (O_2^{2-}) configuration is preferred [24–28]. At high coverage, the superoxo state is predominant, whereas at low cov-

erage the peroxo state is dominant. Figure 2(a) shows the measured photoemission spectrum, with no pump beam present, for a saturation layer of oxygen adsorbed on a Pt(111) single crystal surface maintained at liquid nitrogen temperature. Figure 2(b) shows the spectrum obtained with the probe coincident in time with the pump beam (i.e., time zero), and with an absorbed pump fluence of about 10 μJ/mm^2 per pulse. In the data of Fig. 2, there is no significant difference between Figs. 2(a) and 2(b). However, at pump-probe delays of 250 fs, well after the 55 fs pump light has been absorbed, a distinct peak shows up on the low energy side of the valence band, which is also visible at 500 fs delay. To confirm that this feature is not due to a permanent change of the sample conditions, Fig. 2(e) shows a spectrum taken at time zero immediately after the 500 fs scan. For low irradiation fluences and times, the observed changes are thus reversible. Figure 3 shows a plot of the integrated strength of this peak, as a function of time delay, fit to a curve corresponding to an exponential onset with a time constant of 550 ± 140 fs.

The transient peak of Figs. 2 and 3 appears at a binding energy of ≈ 6 eV with respect to the Fermi edge, and is located within the energy range of the oxygen valence states that are strongly hybridized due to the interaction of the oxygen with the platinum d bands [26,29–31]. The detailed UPS study of Puglia *et al.* on the adsorption states of oxygen on Pt(111) reported a peak at about 6 eV binding energy both for peroxo and atomic oxygen adsorbed on platinum [28]. This peak was not observed in the high coverage regime of O_2 on Pt(111), where the superoxo state dominates. Figure 4 shows the static photoelectron spectra we obtain for O, O_2^-, and O_2^{2-} on Pt, under coverage and temperature conditions where the different species coexist at different ratios [26,29]. Three peaks are observed near the Fermi edge because our probe pulse consists of three harmonics. A schematic diagram of the surface configuration for the superoxo and peroxo states is also shown.
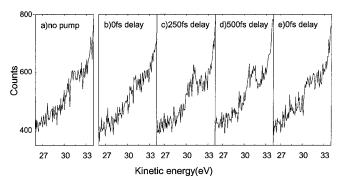

FIG. 2. Time-resolved high-resolution photoemission spectra from a saturation layer of molecular oxygen adsorbed on a Pt(111) surface, at liquid nitrogen temperature: (a) no pump beam; (b) with pump beam, zero delay between pump and probe; (c) 250 fs delay between pump and probe; (d) 500 fs delay between pump and probe; (e) repeat of (b), taken immediately after (d).
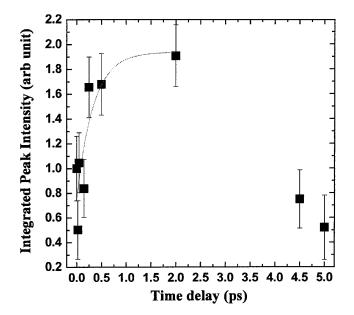
FIG. 3. Integrated amplitude of the transient 6 eV valence-band feature as a function of pump-probe time delay. A fit to the data indicates an onset time of 550 ± 140 fs.

Thus, past work as well as static spectra indicate that we detect a transient change in the photoelectron spectrum, in a region that is sensitive to the oxidation state of O and that is characteristic of the appearance of either peroxo
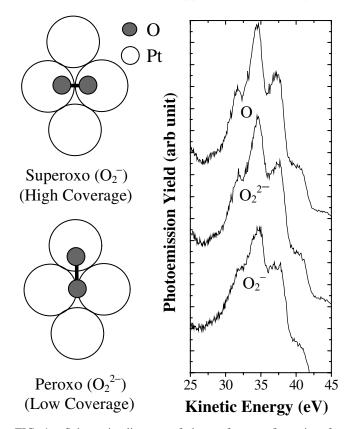

FIG. 4. Schematic diagram of the surface configuration for oxygen on Pt, for the superoxo and peroxo states (O_2^- and O_2^{2-}). The graphs on the right are static photoelectron spectra taken at different sample temperatures after coverage by a saturation layer of O_2 at LN temperature.

(O_2^{2-}) or atomic oxygen. This is a direct observation, on a subpicosecond time scale, of a change in character of the oxygen-platinum chemical bond. In addition to this reversible change in the valence-band structure, we also observe a long-term *nonreversible* change in the sample induced by the IR pump pulse. Over a period of 2 h, a stable peak appears in the photoemission spectrum, at the same position as the transient peak of Fig. 2.

There are four possible transitions that might lead to either a permanent or reversible peak structure at 6 eV binding energy in the oxygen spectrum at a sample temperature of 77 K: (1) a population transfer between the two molecular-bonded states (superoxo O_2^- to peroxo O_2^{2-}); (2) dissociation of the O_2^- molecule into highly excited atomic O followed by recombination; (3) dissociation of the molecular oxygen, resulting in strongly bonded atomic oxygen on the surface; or (4) desorption of molecular oxygen. Of the possibilities listed above, we can exclude the possibility that the *transient* peak is related to oxygen desorption. We do not observe any feature at a binding energy of 6 eV from a clean surface. We can also exclude a "reversible" replenished desorption: the probability of refilling a depleted oxygen site within 1 ms is negligible given the ambient pressure of 1×10^{-10} torr [32]. At higher fluences than those used in our experiment, we can observe laser-induced desorption by using our mass spectrometer, consistent with previous observations [9]. For fluences used in this experiment, we can extrapolate from the data of Ref. [33] to estimate that we are slowly desorbing oxygen from the surface over a period of hours. Peroxo oxygen tends to be the preferred adsorption site at low surface coverage, with a maximum peroxo-state population at about 0.1 ML of oxygen coverage [25]. Thus, the *permanent,* nontransient change in the valence-band structure may be due to desorption [34]. A buildup of atomic oxygen on the surface on long time scales is a second possibility. However, since atomic oxygen is by far the most energetically stable configuration of oxygen on Pt(111), this process is unlikely to be reversible—therefore the transient change is unlikely to be due to the recombination of strongly bonded atomic oxygen.

Comparison of data from this work and others [28,30,31] suggests that the reversible *dynamic* change observed in the valence structure of oxygen on platinum is due to either dissociation of the excited superoxo (O_2^-), to generate highly excited atomic O, or charge transfer from the superoxo to the peroxo (O_2^{2-}) state. These processes are similar—the O-O bond in excited peroxo (O_2^{2-}) oxygen is weak compared to superoxo oxygen, because of an additional electron in the antibonding π orbital of the molecule. Thus, excited peroxo oxygen is often referred to as a precursor state for dissociation. Such an excited peroxo state is likely to exist in our experiment, and can be interpreted as a transient state that could be characterized as either an excited peroxo state or a precursor to excited atomic oxygen. Regardless, the *transient* peak we observe is a subpicosecond, reversible,

laser-induced change in bonding between the adsorbate and the surface. In support of this interpretation, other work assigns this changing 6 eV feature to the π orbital of O_2, which is the orbital that changes when O_2 makes the transition from the superoxo to the peroxo state [30,31].

The excitation mechanism of the oxygen molecule is likely to result from the high density of hot electrons in the femtosecond laser-excited substrate [35]. The laser energy rapidly and effectively heats the electron gas while leaving the lattice cold. The hot substrate electrons can induce adsorbate excitations by tunneling into unoccupied orbitals of the adsorbate. Oxygen is known to adsorb on Pt(111) with the intramolecular bonding axis nearly parallel to the surface. In the case of superoxo oxygen, the bond to the platinum is established by hybridization of platinum d bands with the $\pi_\perp^*$ antibonding state of the oxygen molecule oriented perpendicular to the surface. Peroxo oxygen is double bonded to the platinum surface, where the $\pi_\parallel^*$ orbital is oriented parallel to the surface. Changes to these bonds involve a charge flow into the respective π^* orbital from the substrate to the adsorbate [25], corresponding to the different charge states of the two species. In the superoxo case, the $\pi_\parallel^*$ orbital is only half-filled and, therefore, is located exactly at the Fermi level. As the temperature of the platinum electron gas rises, the density of electrons just above the Fermi level, in resonance with the $\pi_\parallel^*$ orbital, increases dramatically. This could explain the strong signature we obtain from the excited state at an energy of 6 eV.

The observed delay between the arrival of the pump pulse and the appearance of the peak could arise due to the picosecond-to-subpicosecond hot-electron thermalization times [36]. Alternatively, it could result from atomic dynamics. To establish the new peroxo state, reorientation of the molecule (involving rotation and stretching) from a bridge to an fcc site is necessary to some extent [26,27], as shown schematically in Fig. 4. Time scales of such processes typically lie in the range of molecular vibrations—tens to hundreds of femtoseconds.

In conclusion, we have demonstrated the use of ultrafast x-ray pulses to directly monitor a surface chemical reaction on femtosecond time scales for the first time. This work demonstrates a powerful new technique for probing changes of local order on surfaces on their fundamental time scales.

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