

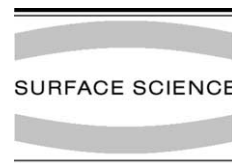


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# Time-resolved UPS: a new experimental technique for the study of surface chemical reactions on femtosecond time-scales

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## Abstract

Recent progress in the generation of ultrashort XUV-pulses by means of high harmonic generation provides a means to monitor the dynamics of surface chemical reactions using photoemission spectroscopy. In this paper we describe details of an experimental setup for time-resolved photoemission spectroscopy using high harmonic generation. We also present results where the different steps involved in the laser-induced change of an adsorbate–surface bond were monitored with sub-100 femtosecond time-resolution.

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## 1. Introduction

The study of ultrafast processes at surfaces has been a topic of increasing interest in recent years, from both experimental and theoretical point of view. One of the challenging goals in this field is to monitor the evolution and the different steps of a chemical surface reaction in real-time. Valence-band spectra and Core-level spectra as obtained by ultraviolet photoemission spectroscopy (UPS) and XPS, respectively, provide information on the chemical state e.g. of an adsorbate-covered surface [1]. Therefore, these techniques are also

potential probes for the *changes* in the chemical state during the course of a chemical reaction. The fundamental time-scales of these processes lie in the range of vibrational and rotational periods of molecules, thus in the range of some tens of femtoseconds [2]. Within a real-time experiment these time-scales are only accessible by means of pump–probe experiments and require sources of ultrashort photon-pulses (a) to initiate the process to be studied and (b) for dynamical sampling of the process. Ultrashort, intense laser systems in the visible regime are sufficient for step (a), however, to monitor the change in the chemical state of a surface by means of photoemission spectroscopy, the photon energy of the probe pulse has to be high enough to emit from levels involved in the chemical bond (valence states), or levels sensitive to chemical change (i.e. core levels).

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Thus, photons in the VUV or XUV, with energy  $\geq 10$  eV, are required. Recent progress in the creation of ultrashort pulses in this energy range at sufficient flux by means of high harmonic generation makes time-resolved UPS at femto-second time resolution feasible [3,4]. Herein, we describe details of an experimental setup capable of time-resolved UPS, and present experimental results where we observed a change in chemical bond of a surface-adsorbate system, on a sub 100 fs time-scale.

## 2. Experimental

A schematic overview of the experiment is shown in Fig. 1. The set-up can be divided into three major parts: (1) the laser system, (2) the pump-probe line, including the generation of ultrashort XUV-pulses and (3) the ultrahigh vacuum (UHV) system. The laser system used here is a two stage multipass Ti:Sapphire amplifier that generates 1.4 mJ (maximum possible output: 4.5 mJ), 800 nm (1.5 eV), 22 fs pulses at up to 2 kHz rep-

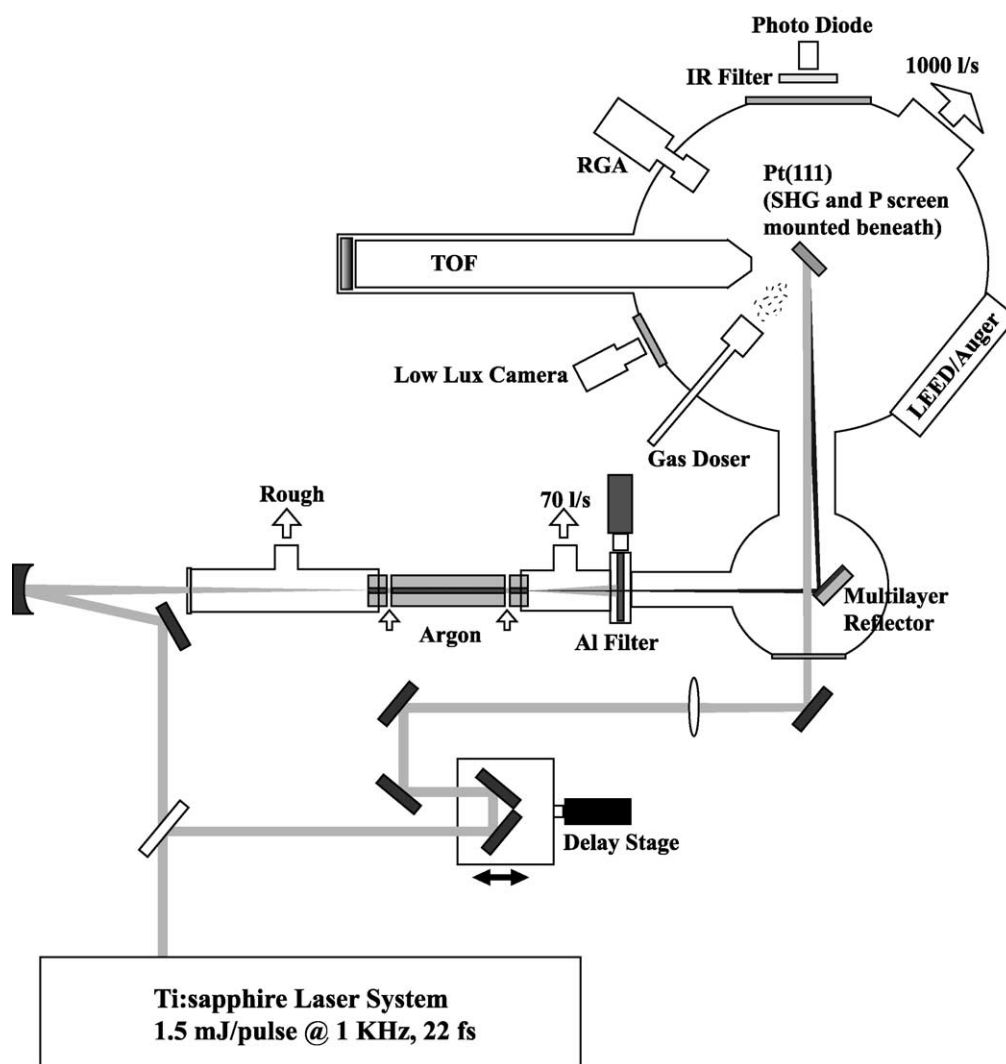


Fig. 1. Experimental setup for time-resolved ultraviolet photoemission spectroscopy. See text for details.

etition rate. A beam-splitter at the output of the amplifier system separates the beam into pump and probe beams, with a ratio of 30%/70%. The pump beam incorporates an optical delay stage to adjust the pump–probe delay. A slight focusing of the beam results in a beam diameter of approximately 3 mm at the sample surface mounted inside the UHV chamber. The pump beam intensity and, therefore, the level of excitation of the surface, can be adjusted continuously using a polarizer and half wave plate. The fluence incident on the surface is measured outside the chamber, after passing the beam through a reference viewport. The actual absorbed fluence at the surface is calculated using literature values for the respective optical constants from reference [5].

The high intensity (probe) part of the beam is used to generate ultrashort XUV pulses by means of phase-matched high harmonic generation in an Argon filled cell. This cell consists of a three section hollow core fiber (ID 150  $\mu\text{m}$ ), as described in detail in Ref. [3]. This source delivers a spectrum of odd harmonics of the driving fundamental laser field ( $h\nu = 1.5$  eV), separated by an energy of 3 eV. The  $\sim 450$  mJ driving pulse energy that is coupled into the fiber creates photons with energies up to 50 eV at sufficient flux for our photoemission experiment. In addition to its high efficiency, the hollow fiber geometry is also quite convenient for use with an UHV system. In contrast to high harmonic sources using gas jets or pulsed valves [6,7], in our setup only a single differential pumping stage using a small turbo pump (70 l/s or smaller) is required to reduce the pressure from a constant  $\sim 50$  Torr inside the cell to  $5 \times 10^{-11}$  Torr inside the main chamber. The pressure is stepped-down to UHV in two stages: first, the fiber end piece (5 mm length, ID 150  $\mu\text{m}$ ) provides for differential pumping to a pressure of about  $1 \times 10^{-4}$  Torr; and second, a 0.2  $\mu\text{m}$  thick aluminum filter, also required to block the residual fundamental (800 nm) laser pulse, isolates the UHV system from the intermediate vacuum.

For the experiment described below we used a flat Mo/Si multilayer to limit the spectrum used for photoemission to three harmonics (27th, 29th and 31st, corresponding to  $h\nu = 40.5, 43.5, 46.5$  eV), with more than half of the beam energy in the 29th

harmonic. The spectral distribution was characterized by use of a free-standing transmission grating (100 nm period) temporarily placed between mirror and sample. Dispersive (temporal) broadening induced by the multilayer reflector and the aluminum filter is estimated to be less than 1 fs, due to their minimal thickness. The spot diameter of the XUV beam at the sample surface (at a distance of 1.5 m from the capillary exit) is 2 mm, measured at a phosphor screen (P1) mounted just below the sample. Thus it is sufficiently small in comparison to the pump beam to guarantee the probing of a homogeneously excited surface area. Spatial overlap of pump and probe is verified by monitoring the image at the phosphor screen of both beams using a CCD camera. Temporal overlap is determined from a cross-correlation signal from a SHG-crystal at the sample position, between the pump beam and the light used to generate the probe, with the aluminum filter temporarily removed from the beam path. The FWHM of this cross-correlation trace is measured to be 62 fs, and represents the highest time resolution to date for observing a dynamic structural process using short wavelength light. This resolution represents an upper limit given that the XUV pulse duration is shorter than that of the driving laser. Time-resolved photoemission data using XUV pulses as presented below confirm this high temporal resolution.

The surface investigated in this study is a Pt(1 1 1) single crystal attached to a manipulator in a UHV chamber. The sample temperature can be varied and controlled over a range from 77 to 1500 K. The UHV system is equipped with standard surface preparation and analysis tools such as sputter gun, LEED, Auger and TDS to clean the sample and check its sample state. For electron spectroscopy we use a home built time-of-flight (ToF) electron energy analyzer with a 600 mm drift tube and a 40 mm diameter detector ( $1 \times 10^{-2}$  steradian). Special care has been taken to impedance match the entire transmission line from the front of the detector anode to the time to digital converter (TDC) of the detection system. We use a detector scheme [8] that minimizes signal reflection due to 50  $\Omega$  mismatch and, therefore, allows for multihit detection per laser (harmonic-)

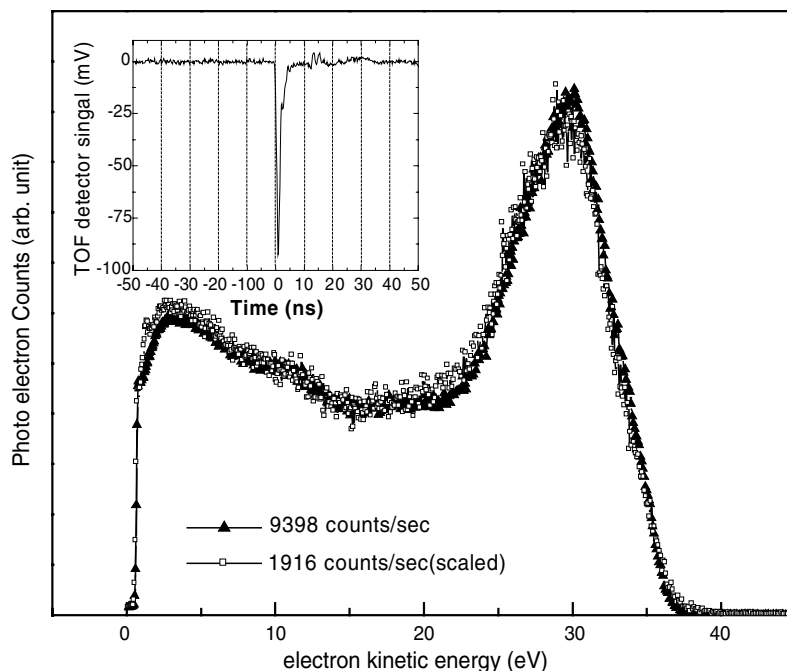


Fig. 2. Electron ToF spectra taken at different count rates. The repetition rate of the laser system used here is 2 kHz. The use of an impedance matched detector system (signal output see inset) and a multihit capable TDC allows for up to 8 counts/lasershot without significant spectral distortions due to pile-up effects.<sup>1</sup>

shot. This significantly reduces data acquisition times for recording photoemission spectra. The dead time between two detectable electron hits is determined by the pulse pair resolution of the timing discriminator, and is specified to be less than 10 ns. At a temporal spread of the spectrum of the order of 500 ns (sample is biased by  $-2$  V, energy spread of about 40 eV) we are able to drive the detector with up to 8 counts/laser shot without noticeable distortion of the spectrum due to pulse pile-up effects (see Fig. 2<sup>1</sup>).

The temporal resolution (and thus energy resolution) of the detector can be determined from the FWHM of the photon peak visible at the leading edge of the spectrum. It is result of UV-photons reflected from the sample surface into the MCP-

detector of the ToF system. We measure a timing resolution of 300 ps mainly determined by the resolution of the used TDC ( $\Delta t = 220$  ps). This corresponds to an energy resolution of 190 meV at kinetic electron energies of 45 eV, the high energy end of a typical electron spectra.

### 3. Results and discussion

For our first real-time experiments with this setup we studied a substrate electron-induced transient excitation of molecular oxygen adsorbed on a Pt(111) surface [9]. One saturation layer of molecular oxygen is adsorbed on Pt(111) at a surface temperature of 77 K. For this coverage oxygen prefers adsorption in a superoxo configuration ( $O_2^-$ ) [10,11]. For excitation of the surface we use a 55 fs pulse at 800 nm and a (absorbed) fluence of  $1 \text{ mJ/cm}^2$ . Due to the low optical density of the adsorbate layer the 800 nm light is dominantly absorbed by the electron gas of the plati-

<sup>1</sup> The spectra in Fig. 2 have been recorded with a Mo/Si based double mirror multilayer implemented in our setup recently that allows side-band free selection of the 27th harmonic.

num. On sub-ps time-scales the electron gas is effectively decoupled from the lattice and has a low heat capacity; therefore, it can be heated quite easily [12]. For the experimental parameters used, the maximum in electron temperature is estimated to be about 1100 K, while leaving the lattice essentially cold. Subsequent excitation of the adsorbed oxygen molecule can occur via transfer processes of hot substrate electrons into unoccupied molecular orbitals [13]. The energy gained by this process is transferred to vibrational, rotational or translational degrees of freedom of the molecule and can finally result in a change in the intra-molecular or molecule–surface bond, e.g. dissociation or desorption. More details on the experiment from the surface science point of view can be found in Ref. [9].

It is possible using this setup to follow at least three different steps within this process. Fig. 3a shows the high energy part of the valence spectrum of the O<sub>2</sub>-covered Pt(1 1 1) surface near the Fermi edge. The different time delays between pump and probe pulse correspond to different times within the course of this adsorbate–surface excitation process. At time zero (i.e. when the pump beam

hits the sample) a step-like contribution appears in our spectrum, with a width corresponding to the pump photon energy of 1.5 eV. Part of the occupied electron distribution just below the Fermi level is increased in energy by exactly the absorbed photon energy, leaving the electron–gas in a very non-thermal excitation state. This observation is in qualitative agreement with previous investigations on thin gold films [14] and on Pt(1 1 0) [6]. Note that this feature has already weakened significantly after 50 fs, and has almost completely disappeared at 250 fs. This demonstrates that the setup is capable of monitoring dynamical processes at surfaces with sub-50 fs time-resolution. The next step, as expected for this scenario, would be the relaxation of these hot electrons into a somewhat-elevated thermal distribution. Unfortunately, the energy resolution of the current setup is insufficient to directly observe this.

The second step within this process that shows up in our photoemission spectra is a transition of the adsorbed oxygen molecule into a new (meta-stable) bond state (Fig. 3b). A spectral feature for the adsorption state of the oxygen molecule is a peak in the photoelectron distribution located at a

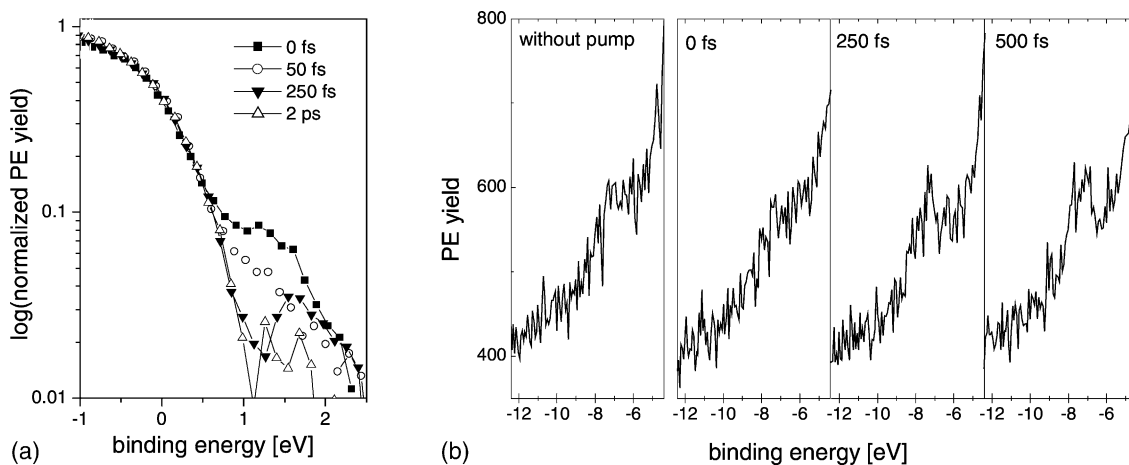


Fig. 3. Time-resolved UPS of a femtosecond laser-induced bond-change of O<sub>2</sub>/Pt(1 1 1). (a) The incident laser-pulse for excitation is absorbed by the platinum electron gas. This can be observed by a step-like, strongly non-thermal distortion at the Fermi-edge of the photoemission spectrum right at time zero. Spectral changes are visible on a sub 50-fs time-scale, reflecting the time resolution of the system. (b) A temporally delayed chemical modification of the oxygen-molecule is visible at the low energy part of the valence band. The shoulder feature at a binding energy of about 6 eV is due to photoemission from the  $1\pi$  orbital of oxygen and reflects the ground-state configuration of the molecule (superoxo state). Efficient population of an excited state configuration (peroxo state) as result of laser-excitation is delayed by several hundred femtoseconds with respect to time zero (right).

binding energy of about 6 eV with respect to the Fermi edge. This signature has been observed before using photoemission spectroscopy, and has been assigned to the  $1\pi$ -orbital of the adsorbed  $O_2$  [11,15]. In Fig. 3b (left) this feature appears as a shoulder at the low energy part of the platinum d-bands, representing the ground state of the superoxo adsorbed oxygen molecule. In response to excitation by the pump pulse, no spectral changes are observed at time zero (Fig. 3b, 0 fs—note that for this time delay we observe maximum modifications at the Fermi-edge). However, efficient population of a new oxygen state is indicated by a change of the shoulder-like feature into a peak-like structure, clearly visible at 250 and 500 fs delay. An exponential fit into the integrated peak-intensity as function of delay gives a characteristic rise-time (population time) of about 550 fs.

In a final relaxation step (not shown, see Ref. [9]), the peak structure disappears again over a period of several picoseconds, and the entire final spectrum (both the Fermi edge as well as the oxygen-related feature) is identical to the original ground state spectrum. We interpret this step as relaxation of the metastable oxygen state back into the superoxo ground-state. It is noteworthy that the lifetime of a few picoseconds excludes a phonon driven excitation of the oxygen. After laser excitation the lattice stays hot for several tenth of picoseconds and would, therefore, keep the adsorbate in its intermediate state for much longer times.

The delayed appearance of the metastable oxygen state with respect to excitation of the electron gas, as well as its long lifetime, shows that the observed spectral modifications do not reflect the (charge transfer induced) electronic excitation of the oxygen. These kinds of processes are known to happen on time-scales of a few femtoseconds, and are possible for only as long as the hot substrate electron gas is present [2]. The signal maximum from the metastable state is definitely reached after the electron gas has cooled down significantly [14]; furthermore, the lifetime of the state exceeds this time-scale by an order of magnitude. From this, we conclude that the spectral changes in the  $\pi$ -orbital are rather characteristic of actual modifications in the chemical bond character between

oxygen–oxygen and/or oxygen–platinum following the electronic excitation, than of the electronic excitation itself. This is affirmed by comparison of the excited state spectra with photoemission results of different chemical modifications of oxygen/Pt(111). We find an almost identical spectral feature for the stable peroxy and atomic adsorption state of oxygen/Pt(111) [9]. The most likely interpretation is that the observed spectral changes correspond to a transient population of a metastable peroxy state with a lifetime of several picoseconds.

#### 4. Conclusion

In summary, we have described in detail an experimental setup for time-resolved photoemission spectroscopy capable of monitoring dynamics of surface chemical reactions on femtosecond time-scales. The fiber-based high harmonic cell required for the creation of ultrashort XUV pulses can be coupled to an UHV system in a convenient way, and gives sufficient photon flux for time-resolved photoemission experiment up to photon energies of 50 eV. The specific design of the TOF detector allows for distortion free multihit detection so that integration times are reduced significantly. Our first experiment on a model-like adsorbate–surface system shows that the setup is capable of synchronously monitoring different steps of a surface chemical reaction. The time resolution that could be achieved within this experiment was shown to be  $\sim 50$  fs or better.

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