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Zefeng Ren
Dalian Institute of Chemical Physics

Chuanyao Zhou
Dalian Institute of Chemical Physics

Zhibo Ma
Dalian Institute of Chemical Physics

Chun-lei Xhao
Dalian Institute of Chemical Physics

Xinchun Mao
Dalian Institute of Chemical Physics

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Zefeng Ren, Chuanyao Zhou, Zhibo Ma, Chun-lei Xhao, Xinchun Mao, Dongxu Dai, Jerry L. LaRue, Russell Cooper, Alec M. Wodtke, and Xueming Yang

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ARTICLE

A Surface Femtosecond Two-Photon Photoemission Spectrometer for Excited Electron Dynamics and Time-Dependent Photochemical Kinetics

Ze-feng Ren[a†], Chuan-yao Zhou[a†], Zhi-bo Ma[a], Chun-lei Xiao[a], Xin-chun Mao[a], Dong-xu Dai[a], Jerry LaRue[b], Russell Cooper[b], Alec M. Wodtke[b], Xue-ming Yang[a*]

a. State Key Laboratory of Molecular Reaction Dynamics, Dalian Institute of Chemical Physics, Dalian 116023, China

b. Department of Chemistry and Biochemistry, University of California at Santa Barbara, CA 93106, USA

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A surface femtosecond two-photon photoemission (2PPE) spectrometer devoted to the study of ultrafast excited electron dynamics and photochemical kinetics on metal and metal oxide surfaces has been constructed. Low energy photoelectrons are measured using a hemispherical electron energy analyzer with an imaging detector that allows us to detect the energy and the angular distributions of the photoelectrons simultaneously. A Mach-Zehnder interferometer was built for the time-resolved 2PPE (TR-2PPE) measurement to study ultrafast surface excited electron dynamics, which was demonstrated on the Cu(111) surface. A scheme for measuring time-dependent 2PPE (TD-2PPE) spectra has also been developed for studies of surface photochemistry. This technique has been applied to a preliminary study on the photochemical kinetics on ethanol/TiO_2(110). We have also shown that the ultrafast dynamics of photoinduced surface excited resonances can be investigated in a reliable way by combining the TR-2PPE and TD-2PPE techniques.

Key words: Femtosecond two-photon photoemission spectropy, Time-resolved, Ultrafast excited electron dynamics, Surface photochemical kinetics

I. INTRODUCTION

The discovery of photoelectric effect by Heinrich Hertz in 1887 has made a tremendous impact on modern physics. Single photon photoemission spectroscopy has been widely used in investigating the electronic structures of atoms, molecules, solid materials, and their surfaces [1]. For solid surfaces, the vast majority of recent single-photon photoemission (1PPE) studies were focused on the valence electronic structures. The two-photon photoemission (2PPE) technique was developed about three decades ago when strong pulse lasers had just became widely available [2−7]. Recent research developments using 2PPE have been described in several related reviews [8−11]. Various versions of 2PPE have been developed for applications in different surface related studies. Fauster and co-workers employed this technique to study the structure and dynamics of image potential states on metal surfaces [12, 13]. This method has also been used for the study of hot electron dynamics of metals [14] and semiconductors [15], and to probe the electronically excited states and the dynamics of atoms and molecules adsorbed metal surfaces [16−23]. In recent years, 2PPE has been applied to investigate the surface electron dynamics of molecular adsorbed metal oxide surfaces [24, 25]. These developments clearly show that 2PPE is a uniquely powerful tool in studying the excited electron dynamics of various materials. However, the ability of this technique to study surface chemical reaction kinetics has not been realized thoroughly.

The key for the surface 2PPE technique is the application of the high peak-power and high repetition rate ultrafast Ti:Sappire oscillator. This laser gives a sufficiently high two-photon excitation probability and low single pulse energy which would avoid the damage of the surface samples and space charge effect. In addition, considerable technological progress has been made for the electron energy analyzers. It is now possible to measure simultaneously the energy and angular distributions of the photoelectrons from surfaces using an electron imaging detector [26]. Such photoelectron imaging technique enables us to measure surface photoemission spectrum changes due to surface chemical or photochemical reactions in real time. More recently, a time-of-flight spectrometer has also been developed for angle and energy resolved photoelectron measurements using a microchannel plate stack in coupling with a position sensitive delay-line detector [27].

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[*] Author to whom correspondence should be addressed. E-mail: xmyang@dicp.ac.cn.

[†] Who made similar contribution to this work.

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In this report, we describe a femtosecond two-photon surface photoemission spectrometer recently constructed in our laboratory for studies of excited surface electron dynamics using a Mach-Zehnder interferometer [28] and surface photochemical kinetics for metal and metal oxides surfaces dosed with various molecules. This report first describes the structure and basic functions of the instrument. Preliminary results from Cu(111) and $C_2H_5OH/TiO_2(110)$ surfaces are then presented in order to demonstrate the ability of the instrument to measure the surface photoelectron spectroscopy, excited electron dynamics and surface photochemical kinetics. The combination of interferometric and time-dependent 2PPE (TD-2PPE) measurements is demonstrated for investigating surface photochemical processes and the ultrafast dynamics of photoinduced surface excited states. Finally, possible applications in future surface reaction kinetics studies using 2PPE are discussed.

II. DESCRIPTION OF THE EXPERIMENTAL APPARATUS

Figure 1 shows a schematic diagram of the femtosecond 2PPE spectrometer. The 2PPE experimental apparatus is comprised of an ultrahigh vacuum system, which includes a sample preparation and characterization chamber and a main probing chamber with a hemispherical electron energy analyzer, as well as a Ti:Sapphire femtosecond laser system with a frequency doubling setup and a home built Mach-Zehnder interferometer that allows for ultrafast excited electron dynamics studies. In the following sections, the vacuum system, the detection system and the laser optical system will be described respectively in details.

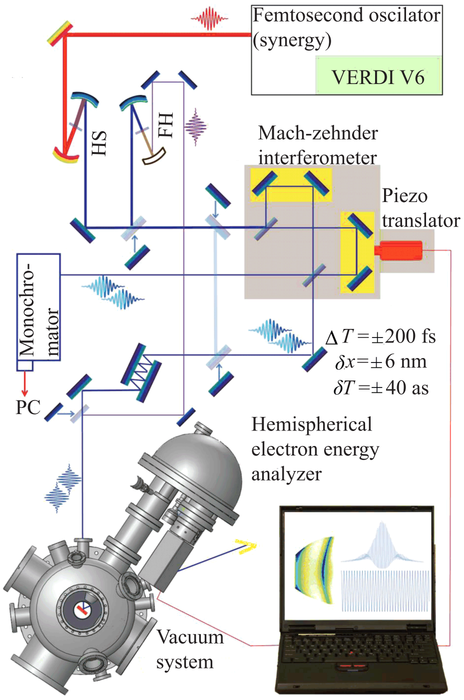

FIG. 1 The schematic diagram of the femtosecond two-photon surface photoemission spectrometer.

A. Vacuum and detection system

The vacuum system consists of a main chamber for 2PPE measurement, a sample preparation and characterization chamber and a load-lock system. A schematic of the vacuum system is shown in Fig.2. The load-lock system is used for loading samples under atmospheric conditions onto the sample holder without breaking the ultrahigh vacuum condition, which makes the replacement of the samples very easy. A gate valve separates the load-lock system pumped by a 60 L/s turbo pump (Pfeiffer) from the upper chamber. The whole Ultrahigh vacuum (UHV) chamber is pumped by a 1200 L/s turbo pump (Pfeiffer), a 500 L/s ion pump (Varian) and a titanium sublimation pump (Varian). The base pressure of the whole vacuum system is maintained at 5 nPa.

The upper chamber is designed for sample preparation and characterization. It is equipped with an Argon ion gun (IQE 11/35, SPECS) for sample cleaning and a LEED detector (ErLEED 150, SPECS) for LEED pattern check to ensure that samples are contamination free and well ordered before experimental measurements. A residual gas analyzer (RGA200, SRS Systems) is also mounted on this chamber for residual gas analysis, adsorbate purity check, and leak test. The sample holder has the capability of moving the sample in x, y, and z directions, as well as rotating it around the z-axis and the surface normal. Sample temperature can be varied between 100 and 1200 K.

The main measurement chamber is below the preparation and characterization chamber. The key element of this apparatus is the hemispherical electron energy

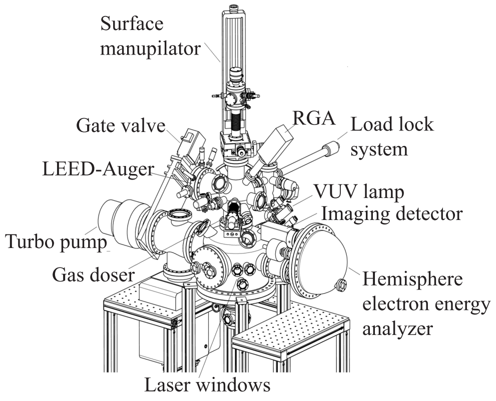

FIG. 2 The vacuum system of the 2PPE apparatus. The upper chamber is the sample preparation and characterization chamber, while the lower one is the measurement chamber.

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analyzer (PHOIBOS 100, SPECS, Ultimate analyzer resolution 2.8 meV) for low energy photoelectron detection from the sample surface. A μ-metal shield was mounted inside the main vacuum chamber, which shields the earth magnetic field. This allows to measure the surface photoelectrons at energy well below 1 eV without applying a small voltage on the surface. It is important to do that in studies of surface photochemistry because adding a voltage could alter the dynamics of charged carriers on the surface. At the end of the hemispherical electron energy analyzer, a two dimensional electron imaging detector is utilized for simultaneous detection of the kinetic energy and angular distributions of the photoelectrons. An experimental scheme is also developed using the imaging detector for time-dependent 2PPE measurement over the energy range from the work function edge to twice of the photon energy relative to the Fermi level. The electron signal received was amplified by Chevron microchannel plate (MCP) detector. The amplified electrons are accelerated to a phosphor screen detector. The 2D imaging signals on the phosphor screen are then recorded by a CCD camera system. Because of the high repetition rate of the femtosecond laser system (75 MHz), the CCD camera has to be used in a "long time exposure mode", which also continuously counts background. Therefore, it is crucial to use a cooled semiconductor CCD camera (SensiCam, PCO), which is cooled down to −12 °C reducing the background noise to a very low level. The signal-to-noise ratio of the present setup can reach about 1500, which is sufficiently high for most 2PPE studies. A minor disadvantage of the electron imaging detector is that the data readout time is considerably slower than the delay-line detector [27]. Electron imaging detector is, however, ideal for 2PPE measurement using very high repetition rate laser (∼80 MHz); while delay-line detector with TOF measurement can only work with lower repetition rate laser (several hundred kHz). An electron gun (EQ 22/35, SPECS) is also mounted on this chamber for Auger spectroscopy using the hemispherical electron analyzer detector.

B. Laser and optical system

The laser system used in the 2PPE system is a Ti:Sapphire femtosecond oscillator (Synergy PRO, FEMTOLASERS), pumped by a Verdi V6 diode laser (Coherent Co.). The center wavelength of the femtosecond laser is near 800 nm. The whole laser system is stationed in a clean room with temperature control. The temperature of the clean room is maintained at 20 °C with an error of ±0.2 °C. The repetition rate of the laser is 75 MHz, while the laser pulse width is about 10 fs. The short pulse width of the femtosecond laser is crucial for measuring the ultrafast excited electron dynamics on surfaces and interfaces. The 800 nm output light was frequency doubled to 400 nm using a thin β-barium borate (BBO) crystal (10 mm×3 mm×0.1 mm, CASTECH). The 800 nm light was focused to the BBO crystal using a concave mirror with a focal length of 25 mm (Fig.3). The 400 nm light was then sent to a Mach-Zehnder interferometer (MZI). The output beam of the MZI was directed to a pair of chirp compensation mirrors before it was reflected and focused onto the sample surface in the vacuum chamber through a lens window, which is differentially pumped. Chirp compensation can be made using various passive and active compensators [29]. Prism pairs are often used for chirp compensation because they can generate a small amount of negative group velocity dispersion (GVD) dependent on the wavelength, while a pair of chirp compensation mirrors produce nearly constant negative GVD over a wide spectral range required to achieve ultra short pulses. With this optical setup, we have performed interferometric autocorrelation of the 400 nm excitation pulses on a polycrystalline molybdenum surface. The pulse width was extracted to be 28 fs using a fitting process developed previously [30]. The interferometric autocorrelation trace serves as an excellent diagnostic method of the 400 nm laser pulses.

Figure 4 shows the picture of the home built MZI. The doubled light at 400 nm first passes through a beam splitter (50:50), and the two split beams go through two separate arms that have two reflection mirrors and recombine on another beam splitter. One of the beam path lengths is fixed, the other beam path length is varied by a preloaded closed-loop piezo translator

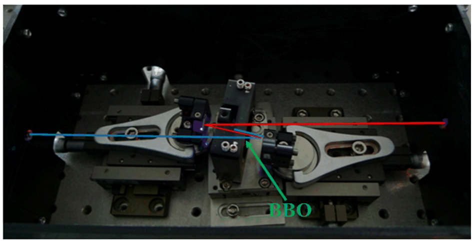

FIG. 3 The frequency doubling setup using a thin BBO crystal.

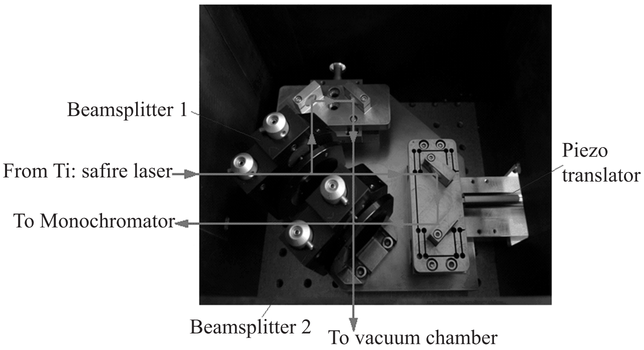

FIG. 4 The home built Mach-Zehnder interferometer in the 2PPE apparatus.

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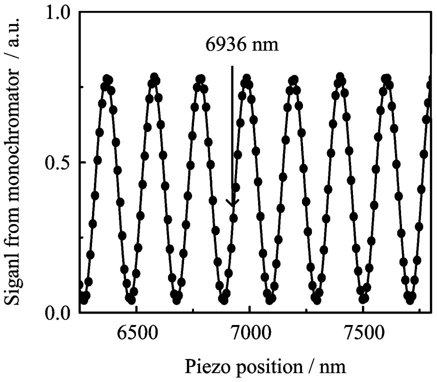

FIG. 5 The optical interference signal of the 400 nm light at the exit of monochromator when scanning the piezo translator position.

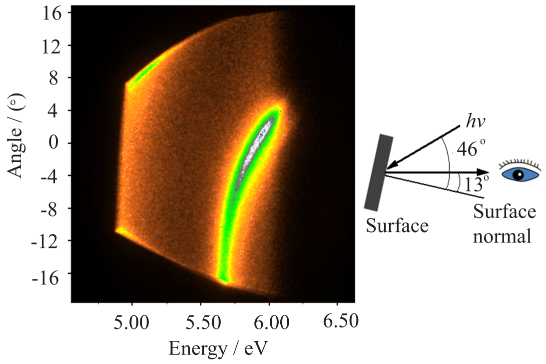

FIG. 6 The two photon photoelectron image from the Cu(111) surface at the center wavelength of 400 nm with angle and energy resolved. The horizontal axis is the energy of the photoelectrons relative to the Fermi level, while the vertical axis is the electron scattering angle.

(P841.40, Physik Instrumente GmbH). The maximum displacement of the piezo translator is smaller than 60 μm. Since optical path length change is twice the piezo translator movement, this would cause a maximum 400 fs time difference between the two split pulses.

The stability of the interferometer is crucial for the measurement of the surface electron interference spectroscopy. The movement of 150 nm by the piezo translator will cause a difference of time of 1 fs. Such instability will cause difficulties in measuring the interference pattern of the photoelectrons. Therefore a stable base plate is essential. We have used Invar steel as the base plate that has a very low thermal expansion coefficient, $<1\times10^{-6}$ K^{-1} and is about one tenth of that of normal steel. The base plate used for the MZI is 4 cm thick. The two optical arms of the MZI were also made symmetric relative to the fixing point, so the thermal induced change between the two optical paths cancel one another. The two beam splitters are mounted on vertically driven Gimbal optical mounts (VGM-1BHC, Newport). In order to increase the stability, the MZI setup is covered by an anodized aluminum box during operation.

For stability testing, the output of the MZI was sent to a monochromator for optical interference signal measurement first. Figure 5 shows the interference pattern with the monochromator set at 400 nm when the piezo translator position is scanned. The optical interference signal easily shows a peak-to-peak time difference of an individual optical cycle at 400 nm, corresponding to a time duration of 1.33 fs. And then the piezo position was set to the middle position where the interference signal gradient is the biggest (arrow position in Fig.5). The result shows that the optical path length difference between the two optical arms of the MZI is stable within ±12 nm over a 20 min period. This corresponds to a time delay stability of ±40 as between the two split pulses.

III. PRELIMINARY RESULTS

A. Normal 2PPE and TR-2PPE Study on Cu(111) surface

2PPE from a clean Cu(111) surface were detected using the 2PPE system described above, with the center wavelength of the frequency doubled Ti:Sapphire femtosecond laser tuned to 400 nm, which has a bandwidth of about 16 nm (FWHM). Figure 6 shows a typical image measured at an angle of about 13° from the surface normal with a collection angle of ±13°, which was arranged to detect the Fermi edge structure of the Cu(111) surface state. This image was measured with one beam path in the MZI blocked, which was considered to be a normal 2PPE measurement. Such measurement is exactly the same as that with a zero time-delay between the two optical paths in the MZI. The incident angle of the femtosecond laser beam is about 46°, relative to the surface normal. A normal 2PPE spectrum can thus be obtained by integrating the imaging signals over a certain angle-range at different energies. In such measurements, the spectrum of the 400 nm doubled output of the femtosecond laser was monitored to ensure its Gaussian distribution around the center wavelength. The 2PPE image for Cu(111) clearly shows a single feature, which comes from the Cu(111) surface state (n=0).

We have also performed time-resolved 2PPE measurements for the Cu(111) surface using MZI. By integrating the image signals at different time delays between the two optical paths in the MZI over different angles and different electron energies, TR-2PPE spectrum can be acquired for the Cu(111) surface state feature. Figure 7(a) shows the TR-2PPE spectrum for the Cu(111) surface, which has two small bumps at about ±50 fs time-delay in the spectrum. This is due to a slightly chirped pulse that is not fully compensated by the chirp compensation mirrors at this wavelength. The shape of the TR-2PPE spectrum contains important

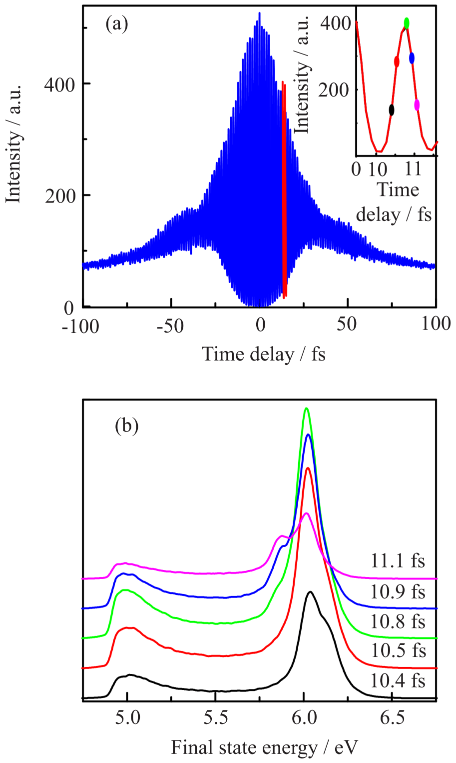

FIG. 7 (a) Time resolved scan of the photoelectron signal of the Cu(111) surface state in Fig.6 using the Mach Zehnder interferometer. The signal shown in this figure was integrated from 12° to 14° in the imaging signal. (b) The 2PPE spectra at five different time delays between two beams in the MZI.

information about the excited electron dynamics (excited state lifetime, dephasing time *etc.*) that can be extracted using model simulations [9]. Such dynamics measurements are valid for static surface excited states.

Figure 7(b) shows photoelectron spectra at five different time-delays between the two laser beam paths in the MZI. The optical spectrum was monitored using a monochromator at these time-delays. The changes in the photoelectron spectra at different time delays are attributed to changes in the optical spectrum of the combined laser beams from the MZI. This demonstrates that the MZI can be used to control the optical spectra of the femtosecond laser in a convenient way. Since the MZI combines two coherent femtosecond laser pulses into one with a controllable time-delay, this can be regarded as a simple pulse shaping method to control the time-structure and thus optical spectra of the femtosecond laser pulse (two equal pulses with a variable delay).

B. 2PPE spectroscopic study on the ethanol/TiO_2(110) Surface

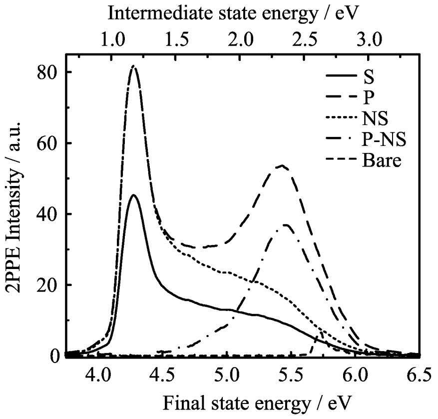

FIG. 8 2PPE spectra for the bare and CH_3CH_2OH adsorbed TiO_2(110) surface. For the ethanol adsorbed surface, 2PPE spectra were measured for the both P-polarization (P) and S-polarizations (S) after the surface was illuminated by the P-polarized femtosecond probing laser for more than 15 min. The excited resonance spectrum (P-NS) peaked at 5.5 eV is obtained by subtracting the normalized S-polarization (NS) data from the P-polarization (P) data. The spectra were obtained by integrating the image signals between $-5°$ and $+5°$. The lower x-axis indicates the final energy of the electron emitted to the vacuum relative to the Fermi level. The upper x-axis shows the intermediate state energy before another photon was absorbed.

We have also performed a preliminary 2PPE study on the ethanol/TiO_2(110) surface using the instrument described above. The experiments on ethanol/TiO_2(110) described here were carried out on a TiO_2(110) surface, which was prepared by several cycles of Argon ion sputtering and annealing with 10 μPa of oxygen at 850 K for 60 min [24]. The surface quality was confirmed by Auger electron spectroscopy (AES) and low energy electron diffraction (LEED). This procedure allows us to prepare a nearly stoichiometric TiO_2(110) surface with a work function of 5.5−5.8 eV. On such surface, few bridge bonded oxygen defects are present. For the study of the ethanol/TiO_2(110) surface, we have prepared one monolayer of ethanol molecules on this nearly stoichiometric TiO_2 surface.

Normal 2PPE spectra for the bare TiO_2(110) surface and the ethanol adsorbed surface prepared using the above procedure were taken and are shown in Fig.8. The 2PPE spectrum for the bare TiO_2(110) surface is also shown in Fig.8. The spectrum on the bare TiO_2(110) surface is helpful in qualitatively characterizing the presence (or absence) of bridge-bonded oxygen vacancies. The signal from the bare surface is considerably smaller than that from a surface with an ethanol adlayer. The small 2PPE signal along with the apparent high work function from the 2PPE spectrum shows that the bare TiO_2(110) surface prepared here is nearly stoichiometric [24].

2PPE spectra of the ethanol adsorbed TiO_2(110) surface were measured with both P-polarized and S-polarized light, which approach the surface with an in-

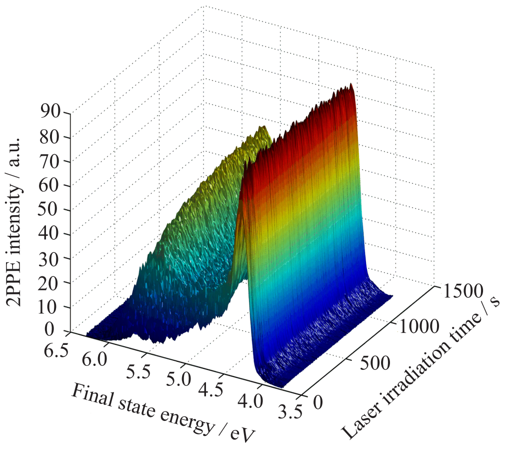

FIG. 9 The TD-2PPE spectra were measured for the ethanol adsorbed stoichiometric $TiO_2(110)$ surface after it had been exposed for different time durations. This plot shows the time evolution of the 2PPE spectra after the surface was exposed to the 400 nm light. The exited resonance feature is clearly not present initially and rises as the laser illumination time increases.

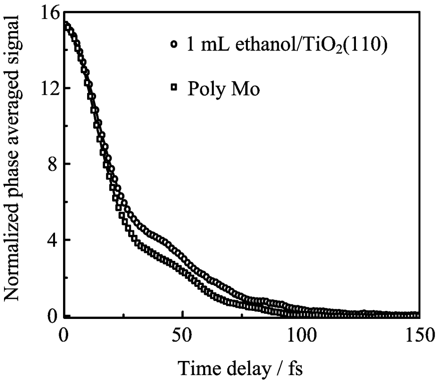

FIG. 10 Phase averaged TR-2PPE result for the photoinduced excited resonance on the ethanol/$TiO_2(110)$ surface after it had been exposed for 15 min, and the interferometric autocorrelation trace of the excitation pulses on the polycrystalline molybdenum surface.

cidence angle of 33° relative to the surface normal, after the surface had been exposed to P-polarized femtosecond light for more than 15 min. These two spectra are clearly polarization dependent. In the P-polarized 2PPE spectrum, there is an additional feature at 5.5 eV in comparison to that obtained with S-polarization. This feature arises from an electronically excited surface state, present only when ethanol is adsorbed on $TiO_2(110)$, which can only be observed using P-polarized light. This implies that the excited state has symmetry along the surface normal [31].

C. Time-dependent 2PPE of photochemical kinetics on ethanol/$TiO_2(110)$

The 2PPE spectra on the ethanol/$TiO_2(110)$ surface in this work were seen to change slowly over a period of seconds to several minutes due to laser illumination. This suggests that 2PPE can be used to monitor changes in the electronic structure of the surface in real time, which requires 2PPE images to be measured in a very short time window (~1 s or less). This time-dependent 2PPE (TD-2PPE) measurement requires rather highly sensitive 2PPE detection. On this apparatus, we have developed a data acquisition program for 2PPE imaging with a real time measurement window of 0.1 s. This means that 2PPE spectra can be obtained in less than 0.1 s. The TD-2PPE technique allows us to measure kinetics of surface photochemical and chemical reactions that induce considerable excited electronic structure changes. The TD-2PPE technique developed clearly has sub-monolayer detection sensitivity.

The TD-2PPE method has been applied to study the photochemistry of ethanol on $TiO_2(110)$. Figure 9 shows a series of 2PPE spectra—using P-polarized light—in 1 s steps over a period of several minutes. One can clearly see that the resonance feature at 5.5 eV grows to a maximum over a period of ~1000 s. Moreover, the 2PPE spectra in Fig.9 show that the 5.5 eV excited resonance feature is initially absent, when the 400 nm probing laser start to illuminate the surface. This feature is obviously due to a photoinduced electronically excited state. Such measurements can certainly provide detailed kinetic information on the photoinduced surface chemical reactions.

In order to understand the nature of the photoinduced excited resonance on ethanol/TiO_2, TR-2PPE measurement for the surface excited resonance can also be carried out using the MZI. Since the surface excited resonance is photoinduced, it is crucial that the TR-2PPE measurement is made when the excited resonance signal is not rising or changing significantly anymore. If one is not aware of the rising or changing of the excited resonance signal, the TR-2PPE measurement result would be definitely seriously flawed. Therefore, in studying the surface photochemical kinetics, it is important to combine the TR-2PPE measurement with the TD-2PPE measurement. The apparatus described in this work offers this unique feature. Figure 10 shows the phase averaged TR-2PPE result for the photoinduced excited resonance on ethanol/TiO_2 and the interferometric autocorrelation trace of the 400 nm excitation pulses on the polycrystalline molybdenum surface. The lifetime of the photoinduced excited resonance state can be extracted from such measurement using the model described previously [32]. Such measurement could provide crucial information on the surface excited state.

The exact nature of the photoinduced surface resonance, however, is not immediately clear at this point and requires further detailed experimental and theo-

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retical studies. Nevertheless, the combined measurements using both TR-2PPE and TD-2PPE techniques can provide a unique way to investigate the kinetics of photochemical reactions on chemisorbed surfaces. This method can also be used to probe kinetics of gas-surface reactions, since such reactions can also induce substantial excited surface state changes.

IV. CONCLUSION

In this report, we have described a multifunctional, surface femtosecond two-photon photoemission spectrometer that has been constructed in our laboratory for the study of ultrafast excited electron dynamics and time-dependent surface kinetics of photoinduced processes. This apparatus utilized the frequency doubled output of a high repetition rate femtosecond laser for surface two-photon photoemission study. Ultrafast TR-2PPE study using a Mach-Zehnder interferometer has been demonstrated on the Cu(111) surface and the ethanol/TiO_2 surface. This method for ultrafast electron dynamics studies can achieve a time resolution of about ten femtoseconds. In addition, TD-2PPE technique is also developed for kinetics studies of photoinduced surface chemistry. The method has been demonstrated on the study of photochemistry on the ethanol/TiO_2(110) system. It is important to note that the combination of TR-2PPE and TD-2PPE measurements are very crucial for studying the ultrafast dynamics of photoinduced excited surface resonances as well as the photoinduced surface chemical kinetics, since photoinduced excited state population could change during the TR-2PPE measurement. The combination of TR-2PPE and TD-2PPE techniques can also be potentially applied to investigate kinetics of surface catalytic processes.

V. ACKNOWLEDGMENTS

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