



## Ultrafast soft X-ray emission spectroscopy of surface adsorbates using an X-ray free electron laser



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### ABSTRACT

We report on an experimental system designed to probe chemical reactions on solid surfaces on a sub-picosecond timescale using soft X-ray emission spectroscopy at the Linac Coherent Light Source (LCLS) free electron laser (FEL) at the SLAC National Accelerator Laboratory. We analyzed the O 1s X-ray emission spectra recorded from atomic oxygen adsorbed on a Ru(0001) surface at a synchrotron beamline (SSRL, BL13-2) and an FEL beamline (LCLS, SXR). We have demonstrated conditions that provide negligible amount of FEL induced damage of the sample. In addition we show that the setup is capable of tracking the temporal evolution of electronic structure during a surface reaction of submonolayer quantities of CO molecules desorbing from the surface.

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### 1. Introduction

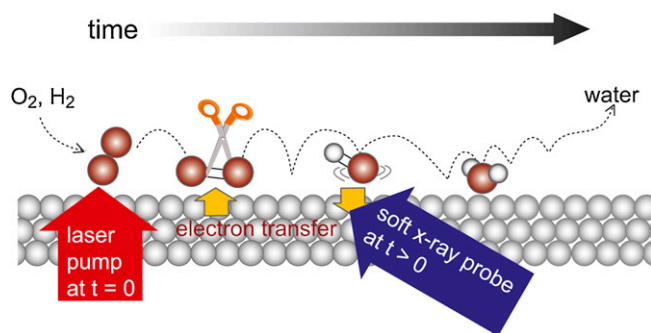
The fundamental understanding of heterogeneous catalysis requires a detailed knowledge of the dynamics of elementary processes on the atomic scale, such as adsorption, surface reactions involving different intermediates, and desorption, as schematically shown in Fig. 1. During a surface reaction there are important electron and energy transfer processes between the different adsorbates and the catalytic substrates, which determine many of the important reaction steps [1]. The ultimate goal here is to understand on a fundamental level, i.e. microscopic, how chemical bonds are broken and reformed during catalytic reactions. Specifically, we would like to obtain a molecular-level understanding of reactivity, visualize how electrons are transferred and how different molecular states are rearranged during the course of surface events. Such knowledge provides the basis for the understanding of

chemical trends and predicting chemical reactivity for many different catalytic surfaces.

The elementary steps of surface chemical reactions typically take place on picosecond or sub-picosecond time-scales and the lifetime of transient intermediate states can be very short. Therefore the equilibrium concentration of these intermediate states is often low and it becomes a challenge to observe these under steady-state conditions. One way to overcome this issue is to perform pump-probe experiments where a reaction is initiated via an ultrashort laser pulse at a well-defined point in time and monitored by another ultrashort laser pulse after a well-defined time span [2]. Such experiments have been performed for surface reactions, where the adsorbate dynamics have been followed in real-time during the course of reactions [3,4]. For this purpose, ultrafast optical laser based techniques have been used, which is ideal to monitor nuclear dynamics [5,6] and hot-electron dynamics [7]. In order to dynamically follow the transient evolution of the electronic structure of adsorbates in sub-monolayer quantities, one has to overcome problems with a small signal-to-background ratio. Ultimately it is desirable to extend such studies to use element-specific

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**Fig. 1.** Schematic figure showing the elementary steps in a catalytic reaction involving molecular oxygen and hydrogen. The reaction can be stimulated by laser pump and probed with XES using the FEL soft X-ray pulse.

and/or site-specific electronic structure probes of the electronic structure that can monitor the chemical bonding changes in real time and follow how molecules are transformed around the center where the interesting chemistry takes place. Ultrafast X-ray pulses from an X-ray FEL have allowed such a dream to now become a step closer to reality by using core level X-ray absorption and emission spectroscopies [8] as probes of chemical reactions on surfaces at FEL facilities.

X-ray Emission Spectroscopy (XES) has the unique ability to provide an *atom-specific probe of the electronic structure*. The atomic sensitivity arises from the creation of a core hole on an atom during the X-ray absorption process, which can only be filled by valence electrons in close proximity to the excited atom. The final state of the X-ray emission process is single valence hole state similar to that in valence band photoemission but here the valence electronic structure is projected onto a specific atom [9,10], thus eliminating the background from a metallic substrate. Accessing the 1s core levels of C, N and O in the soft X-ray regime with spectroscopy opens up new possibilities to study time-resolved changes in the electronic structure of surface reactions and catalysis for chemically important species. Due to the electronic transition dipole selection rule, XES observes the partial density of states for *p*-components of occupied valence orbital projected onto the selected atom. Thus we can experimentally probe the hybridized orbitals of the adsorbate–substrate bonding by the atomic-site-specific projection similar to the linear combination of atomic orbital (LCAO) approach [9,10]. In addition XES can be used as a mean to obtain fluorescence-detected X-ray absorption spectra (XAS), providing a complementary atom-by-atom electronic structure probe of the unoccupied density of states. Furthermore, many spectroscopic techniques such as photoelectron spectroscopy are based on electron detection that will have severe limitations for ultrafast studies where the large peak intensity will build up space charge on the surface [11–16]. In XES and XAS both the excitation source and the detected signal are photons so the spectra will not be distorted due to the development of space charge.

In the present paper we describe the implementation of an experimental system for the ultrafast studies of surface reactions using free-electron laser based XES and XAS. One of the essential questions that needs to be addressed is if the ultrashort FEL pulse will modify the spectroscopic signature due to nonlinear phenomena. Here we show that the same spectroscopic signatures are obtained for the adsorbate systems O/Ru(0001) and CO/Ru(0001) at the FEL as with conventional synchrotron radiation based XES.

## 2. End station

The ultrafast soft X-ray surface science experimental end station (see Fig. 2) consists of preparation and analysis vacuum chambers

with an operating pressure of  $1 \times 10^{-10}$  Torr or lower. The preparation chamber is equipped with an electron beam heater and an ion-gun for sample cleaning, as well as gas dosers for sample preparation. The analysis chamber is equipped with a grating spectrometer for X-ray emission spectroscopy measurements and an electron energy analyzer (VG-Scienta, R3000) for photoelectron spectroscopy measurements, which is mounted perpendicular to the beam propagation direction at a  $45^\circ$  angle with respect to the horizontal, which is also the fixed direction of the electric field vector of the incoming light at LCLS. The experimental station is mounted on an optical table (Advanced Design Consulting USA, Inc., OPT-1000-6) that can be translated longitudinally, laterally and vertically with respect to the axis of the incoming beam. The pitch, roll, and yaw can also be adjusted (see Fig. 2).

The Ru(0001)-*p*( $2 \times 1$ )-O phase [17] was prepared on a  $10 \text{ mm} \times 10 \text{ mm}$  commercial Ru(0001) single-crystal (Matek, Germany) by exposing the surface to  $5 \times 10^{-8}$  Torr of molecular oxygen while cooling from 900 K to 400 K, which corresponded to 15 Langmuir. The CO saturated Ru(0001) phase was prepared by exposing the clean surface to  $1 \times 10^{-8}$  Torr of CO for  $>3$  Langmuir at room temperature. During the data acquisition, CO was re-dosed through a variable leak valve with an attached tube (5 mm ID outlet) directed toward the surface.

The X-ray emission spectrum is recorded by the slit-less grating spectrometer based on an elliptically shaped grating ( $40 \text{ mm} \times 100 \text{ mm}$ ) optimized in negative diffraction order (see Fig. 2 inset). The grating is coated with Ni to enhance the reflectivity at less grazing incidence angles. Since the entrance slit is removed, then the incident beam on the sample becomes the source point. Energy resolution in the X-ray emission spectrometer is defined by the source size as well as grating aberrations, slope errors and image errors. The spectrometer is based on a Rowland grating setup, which images the source vertically onto a 2D-detector. Although various setups are used today [18] they are all subject to the relations given by the Rowland condition. This condition gives a simple spherical focusing term and minimized coma aberration with unit magnification and constant wavelength dispersion both in negative and positive order. For first order diffraction, the reciprocal wavelength dispersion is given by  $\Delta\lambda/\lambda = d/R$ , where  $d$  is the grating period, which is equal to the inverse of the grating line density, and  $R$  is the spherical radius of the grating. Large deviations from these values are associated with efficiency loss, either by grating efficiency or solid angle acceptance. We optimized the performance of the spectrometer to obtain the source size limited energy resolution by optimizing the line density and spherical radius of grating. For the photon energy of the oxygen K-edge, line densities of 1100 lines/mm and  $R$  about 5000 mm give a typical dispersion about  $0.02 \text{ \AA}/\mu\text{m}$  or  $40 \text{ meV}/\mu\text{m}$ . By replacing the spherical shape with an elliptical shape, the illuminated section of the grating can be made a few times longer without blowing up the image error contribution. A high collection angle of 1 milliradian is achieved with a grating illumination length of 100 mm at an incident angle of  $5^\circ$  from the grating surface. The 2D-detector assembly is based on multichannel plates (MCP) coated with CsI for enhanced efficiency [19] with a negatively biased electrode placed in front of the MCP. Digital cameras, Allied Vision Technology Dolphin F-145C for measurements at SSRL and Adimec OPAL-1000 for measurements at LCLS, are used to record the image from a phosphor screen behind the MCP.

The soft X-ray beam can be focused down to  $50 \mu$  along the horizontal direction and less than  $10 \mu$  along the vertical direction using a Kirkpatrick-Baez pair of focusing mirrors at both the synchrotron beamline (SSRL, BL13-2) [20] and the FEL beamline (LCLS, SXR) [21–23], which is required to obtain good energy resolution, yielding a typical resolving power of about 1000.

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