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# Ultrafast surface dynamics probed with time resolved photoemission

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ABSTRACT

Time resolved core level photoemission (trXPS) allows real-time atom-specific investigation of ultrafast surface dynamics. Core levels contain information on the chemical state and the structure of the surface as well as the local charge distribution around specific atoms. Monitoring their evolution after optically exciting the surface, can give valuable information on the electronic (few picosecond time scale) and lattice dynamics (several picosecond timescale). We have performed a trXPS experiment at the free-electron laser FLASH at DESY in Hamburg on a clean Ir(111) surface measuring the temporal evolution of the 4f core levels of Ir(111) after optically exciting the sample. The spectral changes due to X-ray and optical laser induced space charge effects which occur in trXPS experiments with high fluence pump and probe pulses have been fully characterized and controlled during the measurements. At early time scales after the optical excitation we observe time-dependent energy shifts and intensity changes which can be partially attributed to the formation of sidebands. Furthermore, we can clearly identify contributions which result from a change in the surface electron density which then relaxes on a time scale on the order of 2 ps.



## 1. Introduction

Surface femtochemistry, i.e. the study of laser-induced chemical reactions at metal surfaces, has widely developed in the last decade with the aim of achieving control on the transition states active in relevant chemical reactions [1,2]. An important progress has been recently achieved with optical pump-X-ray probe experiments at free electron laser sources. In fact it has been possible to follow the dynamical changes of the electronic structure of the transition state in simple catalytically important reactions, i.e. CO desorption [3] and CO oxidation [4] on a ruthenium catalyst.

The theoretical treatment of photo-induced chemical reactions on metal surfaces is commonly based on the two temperature model [5,6] under the assumption that the optical excitation is exclusively absorbed in the metal substrate. In this model the response of the metal to an ultrafast optical excitation is described using two coupled subsystems: the electrons and the lattice. The optical pulse leads initially to a non-equilibrium electron distribution which relaxes on a few femtosecond time scale due to electron–electron scattering. Since the specific heat of the electronic system is low, the electronic subsystem is heated very fast (femtosecond time scale) to very high temperatures while the lattice still remains relatively cold. Subsequently, thermalization between the electronic subsystem and the lattice takes place via electron-phonon coupling, that occurs on a picosecond timescale. The non-equilibrium condition between the electron and the lattice subsystems in the first picoseconds after excitation is responsible for electronically driven chemical reactions of adsorbates [1]. It is therefore crucial to gain a detailed knowledge of the relaxation processes taking place on the clean metal surface without adsorbates, to improve the described modeling.

Time resolved photoemission (PES) is a powerful tool to investigate non equilibrium dynamics: it offers the possibility to follow the temporal evolution of the electronic structure after the optical pulse impinged on the sample. Up to now most of the time resolved PES experiments on clean metals have studied the valence band dynamics due to the limited photon energy range available [7,8]. However the study of core levels, thanks to their sensitivity to chemical state, electronic and geometric structure of the surface, can give valuable information on the electron and lattice dynamics. By using femtosecond soft X-ray pulses from the free electron laser FLASH synchronized with a femtosecond optical laser, we have performed a time resolved core level photoemission study of a clean Ir(111) surface. Iridium surfaces are relevant for several femtochemistry experiments [2] and the Ir 4f core levels present a bulk and a surface component separated by 550 meV [9], offering therefore the possibility to distinguish among surface and bulk effects. When analyzing time resolved core level PES measurements the changes due to the laser-assisted photoelectric effect (LAPE) [10] have to be considered

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together with changes due to the thermalization dynamics described above. The intense IR laser field causes a dressing of the photoemitted electrons that determines the appearance of sidebands on the spectra [8,10–13] whose temporal duration is given by the cross correlation of the pump and probe pulses. In the time resolved measurements of the Ir 4f core levels here presented, we not only observe the appearance of sidebands in the first picosecond after the optical excitation but we also observe a contribution from the surface electron density relaxation.

## 2. Materials and methods

### 2.1. Experimental setup and sample preparation

The optical pump-X-ray probe experiment has been performed at the PG2 beamline [14–16] of the free electron laser FLASH [17]. The experimental setup is described in Fig. 1.

A $10 \times 10$ mm$^2$ commercial Ir(111) single-crystal (Matek, Germany) was cleaned in ultrahigh vacuum by $Ar^+$ sputtering (T = 300 K, E = 1.7 keV) and repeated cycles of oxygen treatment at 1000–1200 K ($p_{O2} = 1 \times 10^{-7}$ mbar) [9]. The cleanliness of the sample was confirmed by X-ray photoelectron spectroscopy and by measuring a sharp LEED ($1 \times 1$) pattern. To eliminate the influence of contaminants during the measurements, the sample was annealed to 800–900 K every 30 min.

X-ray photons (probe) of ~6.3 nm wavelength were delivered by FLASH in pulse trains of 30 pulses at 250 kHz repetition rate. Each pulse train was repeated at 10 Hz with an average single pulse energy of about 12 μJ. By considering the beamline transmission (second order of the PG2 monochromator, hv = 198 eV) [15,16] and the transmission through a 320 nm Al foil inserted into the beampath, the average energy per probe pulse on the sample was estimated to ~2 nJ (corresponding to about $10^7$ photons per pulse).

The 800 nm Ti:Sa optical pump laser (p-pol) (pulse duration: 120 fs) was synchronized with the X-rays [18]. The two beams have been coupled and collinearly propagated to the sample, in grazing incidence at 7°. The estimated X-ray spot size on the sample was $(300 \times 300)$ μm$^2$. The measurements have been performed at two optical pump fluences on the sample, 1 mJ/cm$^2$ and 2 mJ/cm$^2$ , respectively. At low pump fluence the optical laser repetition rate was 500 kHz and at high pump fluence 250 kHz. This implies that at low fluence each optical pulse train was consisting of 60 pulses, but the X-rays were probing only every second pulse. The temporal resolution during the experiment, evaluated by means of a cross correlation measurement on a $Si_3N_4$ sample [19,20], was 1.1 ± 0.1 ps at 1 mJ/cm$^2$ and 1.2 ± 0.1 ps at 2 mJ/cm$^2$ pump fluence.

It included the pulse stretching due to the monochromator and the temporal jitter and drift over the bunch train [19] which was not corrected in the experiment. The photoemitted electrons from the Ir(111) sample have been measured at 30° emission by an hemispherical electron analyzer (VG Scienta SES 2002) using a charge coupled device (CCD) detection scheme consisting of a stack of MCPs, a phosphor screen and a Basler 102 F CCD camera readout at 10 Hz. The pump-probe measurements have been acquired with analyzer pass energy 200 eV. With this setting an energy window of ~12.3 eV is covered on the detector with the central kinetic energy set to 136 eV so that the Ir-4f levels are included in the detection window.

### 2.2. Fitting parameters

Fig. 2 shows the Ir 4f $_{7/2}$ and Ir 4f $_{5/2}$ XPS lines measured without optical pump and at higher resolution than in the pump-probe experiment with analyzer pass energy 100 eV (overall resolution 300 meV, hv = 198 eV). The splitting of the 4f core levels due to the surface core level shift (SCLS) of 550 meV in the photoemission from bulk and surface [9] can be inferred from the experimental data (dots). Each peak has been fitted according to [9] with two Doniach–Sunjich (DS) functions by using the software IGOR Pro 6.3. The distance between the surface and bulk DS functions and the overall Gaussian resolution were the only constrained parameters in the fit. The background is assumed to be constant. The parameters resulting from the best fit are: Lorentzian width $\Gamma_{bulk} = 200$ meV and $\Gamma_{surface} = 400$ meV, Anderson singularity asymmetry parameter $\alpha_{bulk} = 0.13$ and $\alpha_{surface} = 0.22$, convoluted with Gaussians of width $G_{bulk} = 200$ meV and $G_{surface} = 100$ meV. The resulting parameters are in good agreement with [9]. Γ, α and G of the DS functions employed in the fit of the pump-probe data have then been kept fixed to the values determined from the high resolution measurement. However $\alpha_{surface}$ had to be varied and fixed to 0.1 for all measurements to allow fit convergence. This could be explained as an effect of the optical pump changing the contribution of the many electron effects to the lineshape that is included in α. Due to the detector inhomogeneity, the spin–orbit ratio in the pump-probe data was optimized at a value of 0.6 and an integral background had to be employed for the high fluence measurement. The optimized integral background at a delay of −4 ps has subsequently been adopted at all time delays. Finally at both pump fluences a convolution with a Gaussian profile to account for space charge effects and the instrumental resolution has been used (see below). The Gaussian FWHM was optimized and fixed at 1.2 eV for 2 mJ/cm$^2$ and at 1.1 eV for 1 mJ/cm$^2$.

### 2.3. Space charge analysis

In time-resolved photoemission experiments with high intensity laser sources one has to control space charge effects [11,21–23]. For our experiment we have analyzed these effects in detail. The photoemission spectrum from one X-ray pulse train consists of 40 to ~200 detected electrons ("blobs"). In fact the electrons emitted by the sample for each X-ray pulse train are energy-selected by the analyzer. A fraction of them proportional to the analyzer transmission hits the MCPs and are converted into a fluorescent signal on the phosphor screen. We operate in an X-ray fluence regime where each electron hitting the MCPs is imaged as a "blob" by the CCD, i.e. as a hit comprising few pixels. Each blob

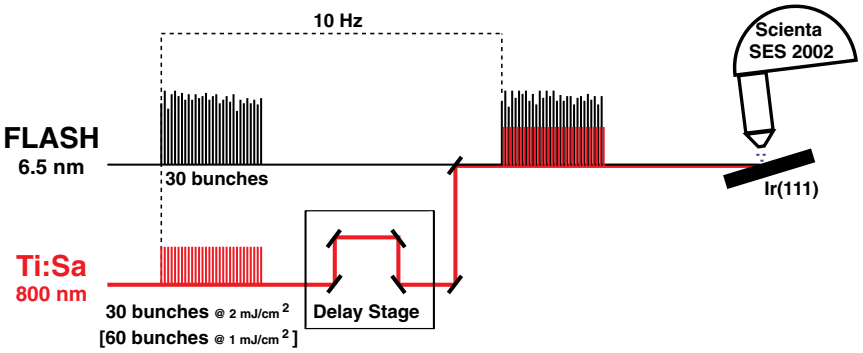


**Fig. 1.** Experimental setup as described in detail in the text.