Time-resolved hard X-ray photoelectron spectroscopy using SACLA: Investigation of space-charge effects induced with optical pump and X-ray probe pulses

Hard X-ray photoelectron spectroscopy (HAXPES) is well known as a powerful method to study the bulk electronic structure of condensed matter owing to its intrinsic advantages, e.g., element and atomic-site specificity and its large probing depth. In order to extend its capability for investigating the transient electronic states excited in the bulk material, we have established a time-resolved HAXPES (trHAXPES) technique and successfully demonstrated its feasibility at the X-ray free-electron laser (XFEL) facility SACLA [1-3]. In general, time-resolved PES (trPES) is achieved by a pump-probe method, i.e., a target material is photoexcited by an intense pump pulse and the temporal evolution of the transient electronic structure is subsequently probed by a second ultrashort photon pulse.

The use of ultrashort pump and probe pulses with high peak intensities implies a fundamental limitation for trPES: vacuum space-charge effects. Whenever the absorption of a photon pulse leads to the emission of more than one electron into the vacuum, the mutual Coulomb repulsion between the photoelectrons on their passage to the spectrometer may result in distortions of the detected photoelectron spectra, i.e., shifts in the initial kinetic energy and spectral broadenings [4]. Such distortions are essentially unavoidable in pump-probe type PES at high photon energies due to the notoriously low photoionization cross sections and the low repetition rates of the ultrashort-pulsed hard X-ray FEL sources currently available. However, we have found that space-charge effects can be easily moderated by adjusting the experimental conditions. In order to understand the probe and pump pulse-induced space-charge effects, we have carried out systematic studies using the micro-focused and non-focused XFEL beam from SACLA.

In the left panel of Fig. 1, we show typical Ti 1*s* core-level photoemission spectra of $SrTiO_3$, as a function of pulse energy, excited by the micro-focused 8 keV XFEL beam [1]. As can be seen in the figure, the Ti 1*s* HAXPES spectra show drastic spectral changes due to strong space-charge effects with increasing pulse energy. This can be qualitatively understood by N-body numerical simulations [4] shown in the right panel of Fig. 1. Although the peak position of the spectrum simulated for the highest pulse energy (red open triangles) shows a deviation from the measured one, the tendency of the spectral evolution as a function of the pulse energy is explained fairly well. The deviation between measurement and simulation may be attributed to deviations and uncertainties of the used parameters, in particular in the diameter of the XFEL beam. The sharpest spectrum (black curve) at the lowest pulse energy demonstrates that HAXPES using the micro-focused XFEL beam is almost close to being practical because the acquisition time of the spectrum is approximately 40 min at a repetition rate of only 30 Hz.

We have also studied pump pulse-induced space-charge effects, as shown in Fig. 2, by conducting a real pump-probe trHAXPES measurement at a fixed pump-probe delay of –80 ps (probe pulse before pump pulse). A $SrTiO_3$ and a VO_2 sample were excited with optical pump pulses of two different photon energies ($h\nu$ = 1.55 eV and 3.10 eV) with pulse energies in the range of 40-550 μJ corresponding to incident fluences of about 1.6-22.5 mJ/cm^2 (beam diameter ~700 μm), whereas the average XFEL pulse energy was set to about 0.9 μJ/pulse to minimize the space-charge effects induced with the probe pulse. Such strong optical excitation generally leads to the nonlinear emission of a dense disk-like cloud of "slow" photoelectrons, with up to 1.3×10^6 particles in the present case [2], that will interact with the "fast" photoelectron cloud emitted by the non-focused XFEL probe pulse with a spot diameter of approximately 700 μm. Figure 2 demonstrates that the "fast" photoelectron cloud is continuously broadened and shifted toward higher kinetic energies when the pump pulse energy is increased. Energy shifts up to 2 eV are observed. The energy shift induced by space charge is expected to be proportional to the number of pump electrons. This number, however, will depend nonlinearly on the absorbed pump pulse energy because two or more photons have to be absorbed simultaneously for the emission of a photoelectron, i.e.,

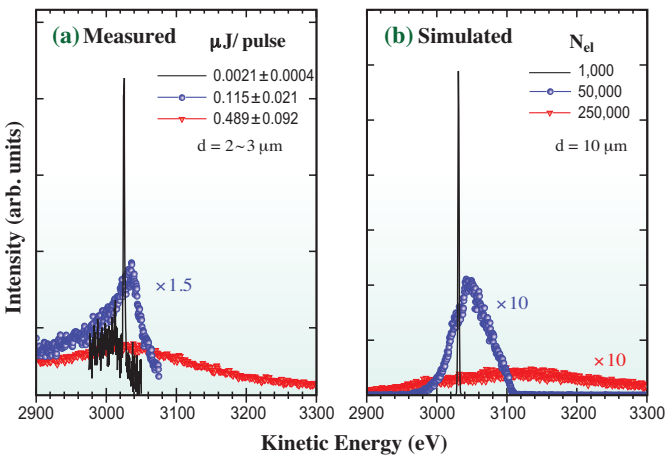

Fig. 1. Measured **(a)** and simulated **(b)** Ti 1*s* HAXPES spectra of $SrTiO_3$ as a function of the micro-focused XFEL pulse energy. N_{el} : Number of electrons in the cloud.

nonlinear multi-photon electron emission has to take place, when the pump photon energy ($h\nu$ = 1.55 eV and 3.10 eV) is lower than the work function of the target material, e.g., 4.0 ± 0.2 eV for $SrTiO_3$. We have found that the power law dependencies of the pump laser-induced energy shift on the pump pulse energy can be interpreted by regarding the close relationship between the multiphoton electron emission induced by intense pump pulses and the work functions of target materials. Details are described in Ref. 2.

As a first major step to apply trHAXPES to the study of intrinsic material dynamics, we have carried out systematic studies of time-dependent pump laser-induced space-charge effects on core-level photoelectron spectra at SACLA [2,3]. The experimental results of the trHAXPES measurements are plotted in the left panel of Fig. 3 together with the best fits using Voigt profiles. The zero of the horizontal axis is defined by the position of the Ti 1*s* photoemission peak at a blocked pump beam. When pump and probe pulses overlap in time (at zero delay), the maximum spectral shift and broadening are observed. In the right panel of Fig. 3, the extracted time dependence of the Ti 1*s* spectral shift is shown together with the calculations which are obtained from a series of simple mean-field models [2]. In the simplest form of the model, the radial and longitudinal broadening of the charged disk are neglected ('1D model'). In two successive extensions of the model, the radial expansion of the disk is taken into account ('2D model') and the kinetic energy spread of the pump electrons is further incorporated ('Ext. 2D model'). We found that the more realistic model, i.e., extended 2D model, explains the experimental results fairly well. Furthermore, we also found that the sharp peaking of the spectral shift that occurs when pump and probe pulses overlap in time can be used to determine the experimental time zero with a precision of better than ±10 ps.

As we have shown here, our systematic experimental investigation of space-charge effects in trHAXPES, along with N-body numerical simulations and simple analytic models, has laid the basis for a novel sub-picosecond time-resolved solid-state spectroscopy technique. This technique will become fully practical as soon as the repetition rates of XFELs enter the kHz range.

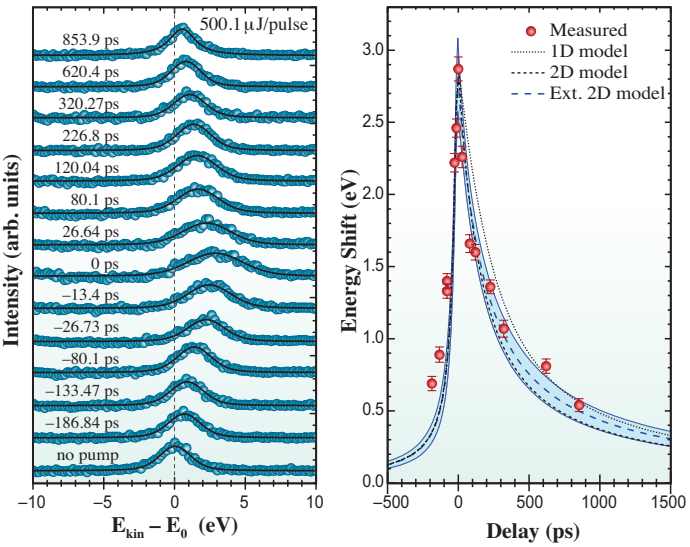

Fig. 3. **(a)** Temporal evolution of Ti 1*s* HAXPES spectra of $SrTiO_3$ as a function of pump-probe delay. The vertical dashed-line shows the peak position for a blocked pump beam (E_0=3030.97±0.3 eV). **(b)** Spectral shift of Ti 1*s* emission as a function of pump-probe delay. The red-filled circles are experimental data. The lines are from different analytic models. For the "extended 2D model", 68.3% confidence bands are also indicated.

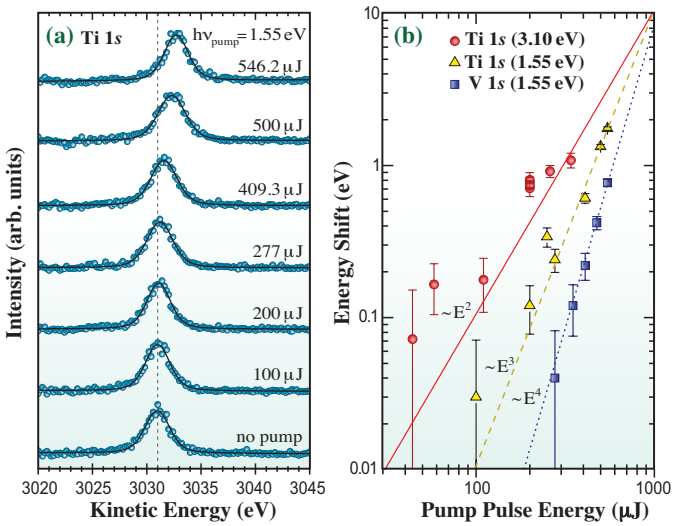

Fig. 2. **(a)** Evolution of Ti 1*s* HAXPES spectra of $SrTiO_3$ as a function of the pump pulse energy. The vertical dashed-line indicates the peak position for a blocked pump beam. **(b)** Spectral shifts of Ti 1*s* emission from $SrTiO_3$ and V 1*s* emission from VO_2 as a function of the pump pulse energy in a log-log plot. The red-filled circles, yellow-filled triangles, and blue-filled squares are experimental data from different experimental runs. The lines indicate fits to the experimental results with the assumption of power law dependences on the pump pulse energy.

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