Sequential multiphoton multiple ionization of xenon atoms by intense X-ray free-electron laser pulses from SACLA

In early 2012, a new XFEL facility, the SPring-8 Angstrom Compact free electron LAser (SACLA) [1], started user operation. One of the first experiments at SACLA was to detect anomalous signals of naturally occurring sulfur atoms in a protein (lysozyme microcrystal) at a photon energy of 7.3 keV, set far from the sulfur *K*-edge (~2.5 keV) to suppress electronic damage [2]. Although the attempt to clarify the anomalous substructure failed, the results demonstrated that anomalous data can indeed be obtained by serial femtosecond crystallography (SFX). As a next step, we have investigated dynamical behaviors, i.e., deep inner-shell multiphoton ionization and cascade decay, of heavy Xe atoms exposed to high-intensity X-ray pulses at 5 and 5.5 keV [3,4].

Multiphoton processes are well-known phenomena in the optical regime and have been investigated for decades. The advent of extreme ultraviolet (EUV) FELs with femtosecond pulse widths has led to renewed interest in multiphoton ionization processes in the EUV regime. The objective of these studies was mainly to reveal the pathways of multiphoton multiple ionization newly opened up by these light sources. Multiphoton processes at higher photon energies discussed in the present work are of particular importance because of their direct relevance to electronic damage in high-resolution X-ray imaging measurements.

The experiment was carried out at the experimental hutch 3 (EH3) of beamline 3 (BL3) of SACLA [5]. The XFEL beam was focused by a Kirkpatrick-Baez mirror system to a focal diameter of ~1 μm (FWHM). Xe gas was introduced as a pulsed supersonic gas jet to the focal point of the XFEL pulses in an ultrahigh-vacuum reaction chamber. The XFEL pulse energies were measured by a beam-position monitor located upstream of the beamline. The relative X-ray pulse energy passing through the interaction point was also measured shot-by-shot by a PIN photodiode.

Ions produced in the source volume were extracted towards an ion time-of-flight (TOF) spectrometer equipped with microchannel plates (MCP) and a delay-line anode (Roentdek HEX80). Signals from the delay-line anode and MCP were recorded by a digitizer and analyzed by a software discriminator. The arrival time and arrival position of each ion were determined. The position information was used to compensate the TOF, which varied with the departure position perpendicular to the spectrometer axis [4]. Figure 1 depicts the TOF spectrum for Xe ions measured at a photon energy of 5.5 keV after TOF compensation. We can clearly see ions with charge states of up to +26 and well-resolved isotopes at different charge states.

Figure 2 depicts the charge state distribution of Xe at photon energies of 5 and 5.5 keV. The peak fluence of the XFEL pulse determined by calibration using Ar [3,4] is 47 μJ/μm^2 for both photon energies. The charge state distribution varies with the peak fluence. The peak fluence dependence of the ion yield for each charge state indicates the contribution of multiphoton processes. Charge states of up to +22 are oserved at the photon energy of 5 keV, whereas charge states of up to +26 are observed at the photon energy of 5.5 keV. The binding energies of 2*s*, $2p_{1/2}$, and $2p_{3/2}$ of neutral Xe are 5.5, 5.1, and 4.8 keV, respectively. According to the calculated results [3,4], the 2*p* ionization thresholds become larger than 5 keV beyond the charge state of +11; thus, the sequential one-photon ionization ends at the charge state of +11 for the photon energy of 5 keV. On the other hand, the photon energy of 5.5 keV is above the ionization thresholds for charge states of up to +23. Thus, one-photon ionization is always induced at the charge states of up to +23 for the photon energy of 5.5 keV. Therefore, the maximum charge state at 5 keV is lower than that at 5.5 keV.

Theoretical charge state distributions [3,4] are also shown in Fig. 2. In the theoretical model, relativistic effects and shake-off are not included.

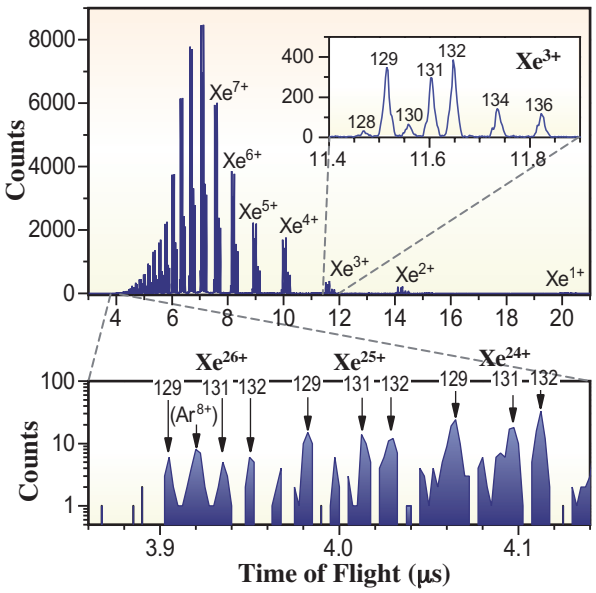

Fig. 1. Ion time-of-flight spectrum of Xe recorded at the photon energy of 5.5 keV [3].

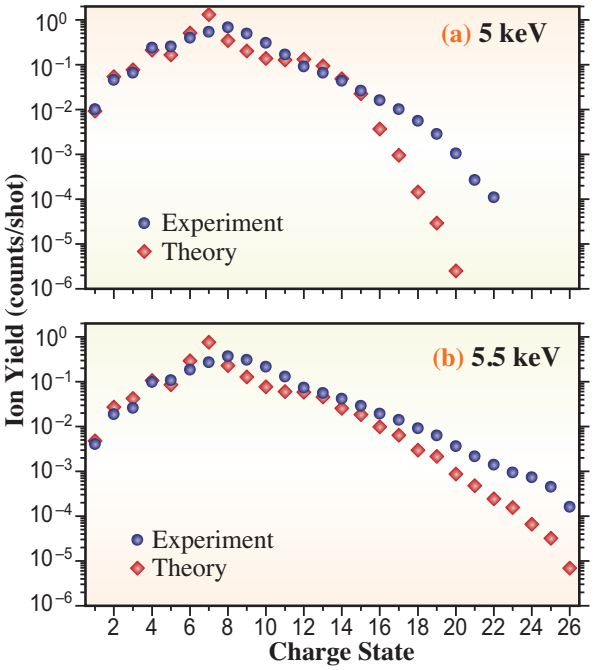

Fig. 2. Experimental and theoretical charge state distributions of Xe at the photon energies of 5 keV **(a)** [4] and 5.5 keV **(b)** [3]. The peak fluence is 47 μJ/μm^2 for both photon energies.

In spite of these limitations, the experimental and theoretical results are in reasonable agreement at 5.5 keV, at least semiquantitatively. In the charge state distribution at 5 keV, notable discrepancies between experimental and theoretical results appear above the charge state of +16 and increase with the charge state. The discrepancies, namely, significantly higher ion yields for high charge states and the highest charge state of +22 in the experiment, are interpreted on the basis of the resonant-enabled X-ray multiple ionization mechanism, where transient resonant excitation enhances the ionization process beyond the limit expected by the sequential ionization model. This feature is not shown at 5.5 keV, because 5.5 keV is above each ionization threshold.

Let us consider the pathways of multiphoton multiple ionization observed in this study. Figure 3 depicts one typical pathway yielding Xe^{24+} obtained by theoretical calculation [3]. The plot illustrates that the total energy of the system varies in the course of ionization. After L-shell photoionization, the energetically excited core-hole state relaxes via a series of Auger and Coster-Kronig decays and/or fluorescences. Note that another photoionization occurs before the atom fully relaxes to the ground configuration. For each photoionization, the deep single-core vacancy is rapidly filled up within sub-fs, and the time scale of the accompanying Auger and Coster-Kronig decay cascade ranges from a few fs to tens of fs. The time scale of fluorescences at the highest charge state is about 0.7 ps. In the present calculations, the pulse shape is assumed to be a Gaussian with an FWHM of 30 fs. In the case of sequential multiphoton absorption, the results are not sensitive to the pulse shape or spikiness of individual pulses, unless the pulse duration is much shorter than the decay time scale.

In conclusion, we have clarified that the ionization of heavy atoms irradiated by intense XFEL pulses rapidly progresses with the repetition of inner-shell photoionization and following Auger/Coster-Kronig decay within the XFEL pulse duration. Understanding the ionization dynamics of heavy atoms exposed to high-intensity hard-X-ray beams will provide useful input for future molecular imaging experiments using XFELs.

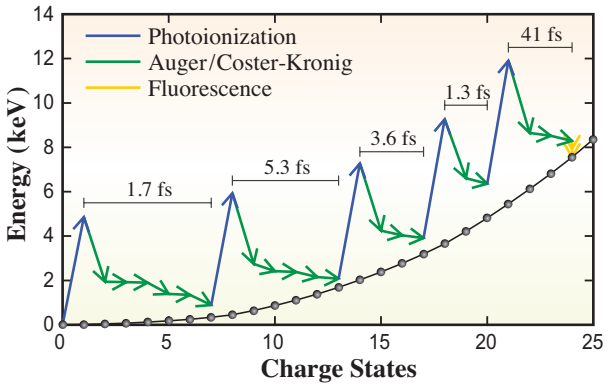

Fig. 3. Exemplar pathway of multiphoton multiple ionization of Xe at 5.5 keV [3]. The black solid line with dots indicates the ground-configuration energy for the given charge states, and the energy of neutral Xe is set to zero.

Hironobu Fukuzawa[a,b,*], Koji Motomura[a] and Kiyoshi Ueda[a,b]

[a] Institute of Multidisciplinary Research for Advanced Materials, Tohoku University
[b] SPring-8/RIKEN

*E-mail: fukuzawa@tagen.tohoku.ac.jp

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