Formation of Xe 4*d* double-core-hole states in intense EUV-FEL fields studied by multielectron-ion coincidence spectroscopy

The nonlinear optical response of materials in the extreme ultraviolet (EUV) and X-ray regions has attracted a great deal of attention for its importance in various applications of intense ultrashort free-electron lasers (FELs). Atoms and molecules in intense FEL fields have been studied as a benchmark for clarifying the underlying processes, which revealed that they typically undergo multiple ionization by multiphoton absorption [1].

In the multiple ionization process involving inner-shell electrons, Auger electron emission processes associated with the decay of the inner-shell hole compete with the subsequent multiphoton absorption process, resulting in the emission of many electrons as well as charged ions depending on the ionization pathway. To understand the nonlinear ionization mechanism involving such multiple pathways in detail, it is necessary to clarify the electronic states involved in each ionization process.

Electron spectroscopy is a powerful technique for this purpose since it allows the measurement of the energy of electrons emitted during ionization, from which intermediate and/or final electronic states can be identified. It has been applied to nonlinear ionization involving doubly excited states [2] and double-core-hole (DCH) states [3], but nonlinear signals are usually weak such that they are often smeared out by signals originating from strong one-photon (linear) processes.

In EUV and X-ray intense laser fields, highly charged ions tend to be generated in high-order nonlinear processes where a large number of photons are absorbed. This means that the ions can be used as "tags" for separating electron signals associated with a target nonlinear process from other dominant signals mainly produced by one-photon processes (Fig. 1). In this work, we introduced multielectron-ion coincidence spectroscopy to tag electrons with the counterpart ion produced by the ionization of a single atom. We incorporated this idea in the multiphoton ionization of Xe by EUV-FEL irradiation as a benchmark system. By relating electron signals to Xe^{4+} ions generated by the two-photon process, we successfully captured electron signals that are associated with the two-photon DCH formation of Xe 4*d* inner-shell states [4].

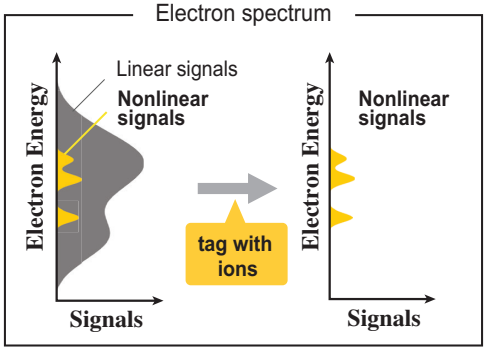

Fig.1. Schematics of electron spectra obtained by multielectron-ion coincidence spectroscopy.

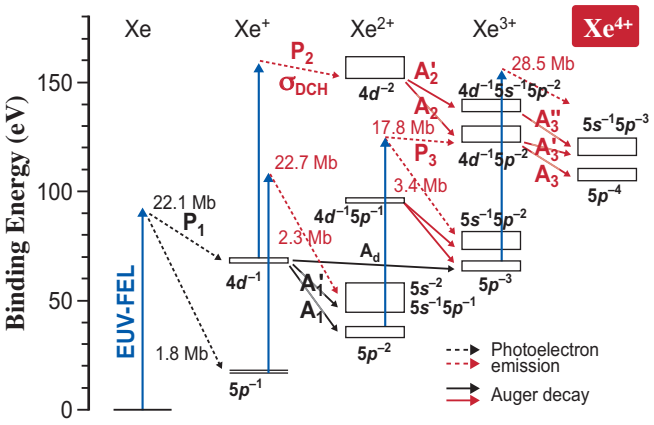

Fig.2. Energy diagram of relevant electronic states of neutral and ionic Xe atoms [4]. P and A stand for electron emissions by photoionization and Auger decays, respectively.

Experiments were conducted at the soft X-ray beamline, SACLA **BL1**. Intense EUV laser pulses were focused by a Kirkpatrick-Baez mirror onto the diffusive Xe gas introduced into the interaction region of a magnetic bottle-type electron spectrometer equipped with an ion detection unit. Electrons produced in the interaction region were guided to a microchannel plate (MCP) detector placed in one end of a time-of-flight (TOF) tube by magnetic fields formed by a permanent magnet and a solenoid coil, while the counterpart ions were introduced into the TOF tube by pulsed electric fields and detected with the same MCP. The chamber was kept under an ultrahigh-vacuum condition ($<5\times10^{-10}$ Torr), and coincidence measurements were carried out at a typical event rate of 0.25 events/shot to suppress false coincidence events to less than 20% of the total events.

Irradiation with EUV-FEL pulses (91 eV, 30 fs, 60 Hz, 1.6×10^{12} W/cm^2) produced Xe^{Z+} ions ($Z \leq 4$).

Xe^{Z+} ions with lower charge (Z=1–3) can be generated by single-photon ionization, while for the formation of Xe^{4+} ions, the absorption of more than two photons is required because of the FEL photon energy used (see Fig. 2).

Figure 3(a) shows a two-dimensional correlation map of electrons that are simultaneously detected with Xe^{2+} ions. The observed features are formed by electrons generated by the photoionization of Xe 4*d* inner-shell levels (4*d* photoelectron; P_1) and the ultrafast Auger decay to Xe^{2+} (Auger electron; A_1, A_1') [5]. These features are also identified in the electron map for Xe^{4+} ions (Fig. 3(b)), indicating that Xe^{4+} can be produced via the Xe^{2+} states by the absorption of another EUV photon. On the other hand, broad electron distributions that are not explained by the sequential photoionization process mentioned above are observed in the energy region of 26–38 eV. These electron energies agree well with the kinetic energies of Auger electrons (A_2) associated with the decay of $Xe^{2+}(4d^{-2})$ into $Xe^{3+}(4d^{-1}5p^{-2})$, suggesting that the two-photon formation of Xe 4*d* DCH states is involved in the generation of Xe^{4+} ions.

A quantitative analysis of the Auger electron intensities associated with these two pathways, (A_1, A_1') and (A_2, A_2'), revealed that the contribution of the Xe 4*d* DCH pathway is comparable to that of the sequential one [4]. This result indicates that the Xe 4*d* DCH states are efficiently formed from the transient $Xe^{+}(4d^{-1})$ states (lifetime of ~6 fs) even though the EUV-FEL pulses employed here have a rather long pulse duration of 30 fs. A numerical simulation based on coupled rate equations for two-photon absorption processes showed that the efficient two-photon formation of the Xe 4*d* DCH states becomes possible when the ionization cross section σ_{DCH} of $Xe^{+}(4d^{-1})$ states, $Xe^{+}(4d^{-1}) + h\nu \rightarrow Xe^{2+}(4d^{-2}) + e^{-}$, falls in the range between 27 and 64 Mb. The obtained results suggest that σ_{DCH} is considerably larger than the normal 4*d* cross sections (~20 Mb), which could be attributed to the resonance excitation from the $4d^{-1}$ to $4p^{-1}$ states in Xe [4].

The present work clearly demonstrates the power of multielectron-ion coincidence spectroscopy for gaining a deeper understanding of nonlinear phenomena induced by intense EUV and X-ray laser fields. This coincidence technique can be extended to molecular systems in which core holes can be created in different atomic sites. Since such DCH states are known to sensitively reflect the local environment of core-hole sites within a molecule [3], the present approach is expected to become a key technique for uncovering nonlinear reaction pathways for a novel X-ray chemical analysis.

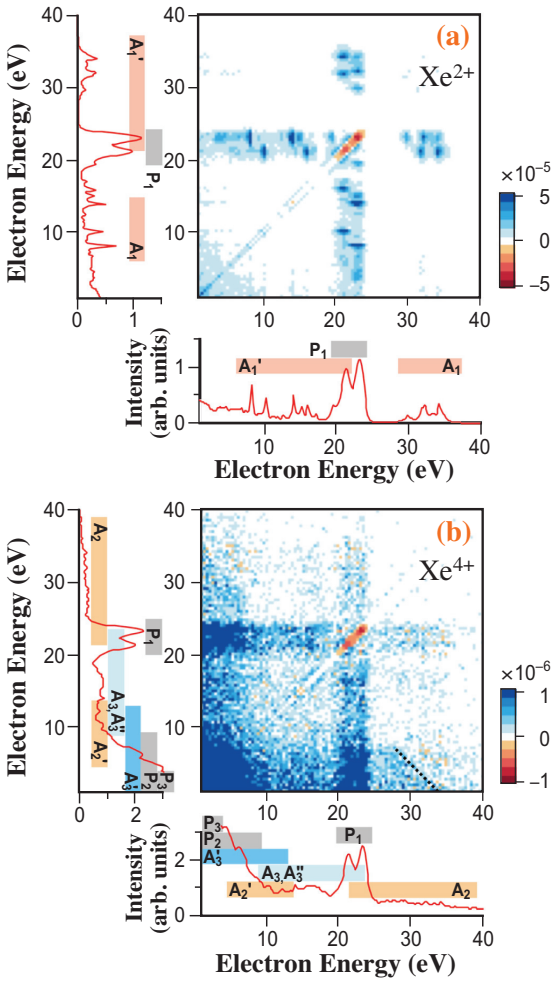

Fig.3. Two-dimensional map of electrons detected in coincidence with **(a)** Xe^{2+} and **(b)** Xe^{4+} ions, obtained by triple covariance analysis [4]. Electron energy regions observed in each process are indicated by color bars.

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