Attosecond X-ray interaction with core-hole atoms

We assume implicitly that X-rays interact with atoms in their ground state when we analyze data obtained by X-ray diffractometry or spectroscopy. Now, the success of X-ray free-electron lasers (XFEL) challenges this "common sense." A femtosecond flush of XFEL provides X-ray photons comparable to those generated by SPring-8 undulator beamlines over one second. Such high intensity X-rays may be able to excite most atoms in the beam section several times. Furthermore, the interval of the successive excitations may be shorter than the lifetime of the core-hole states. Since the X-ray property in the core-hole states differs considerably from that in the ground state, the X-ray interaction with the core-hole atoms is very important for the analysis of XFEL experiments as well as the basic interest in the field of X-ray nonlinear optics.

To investigate the X-ray interaction with the core-hole states, we measured X-ray fluorescence from krypton gas illuminated by focused XFEL beam of SACLA [1]. When X-rays photoionize an atom, the $K\alpha$ fluorescence is emitted from the atom with a core hole in the K shell. When X-rays photoionize the single core-hole (SCH) atom again before the fluorescence decay, it becomes a double core-hole (DCH) state. The fluorescence from the DCH state is called the hypersatellite $K^h\alpha$, giving evidence of X-ray interaction with SCH atoms. The incident photon energy of 15 keV is sufficiently high to create the DCH state by sequential photoionization, and is considerable lower than the threshold of the shake-off process of around 29 keV. A Kirkpatrick-Baez mirror system [2] focused X-rays down to 1.2 × 1.3 μm^2, increasing the peak intensity.

Figure 1 shows the fluorescence spectrum with clear hypersatellite peaks on the higher photon energy side [3]. Both $K\alpha$ and $K^h\alpha$ are doublets because of splitting of the L shell into the L_2 and L_3 subshells. We emphasize that the lifetime of the SCH state is only 170 attoseconds. Nevertheless, the focused XFEL beam photoionizes the SCH atom again to create the DCH atom, providing evidence of the attosecond X-ray interaction with SCH atoms.

Since the DCH creation is a two-photon process, the $K^h\alpha$ yield is expected to depend quadratically on the pulse energy. However, the measured dependence appears to be just superlinear (Fig. 2). The milder dependence is due to the linear contribution from the $K\alpha$ tail. The measured dependence can be fitted by a sum of linear and quadratic terms.

Now, we discuss a possible application of the DCH creation. The different pulse-energy dependence between the $K\alpha$ and the $K^h\alpha$ fluorescence yields allows us to estimate the pulse duration. Such estimation is not straightforward because of the temporal pulse shape. First, the DCH creation is a sequential process; thus, its efficiency depends on the pulse duration. For example, it is suppressed as the pulse duration approaches the SCH lifetime. Fortunately, the SCH lifetime of 170 attoseconds is considered to be much shorter than the expected pulse duration. Accordingly, the pulsed effect is

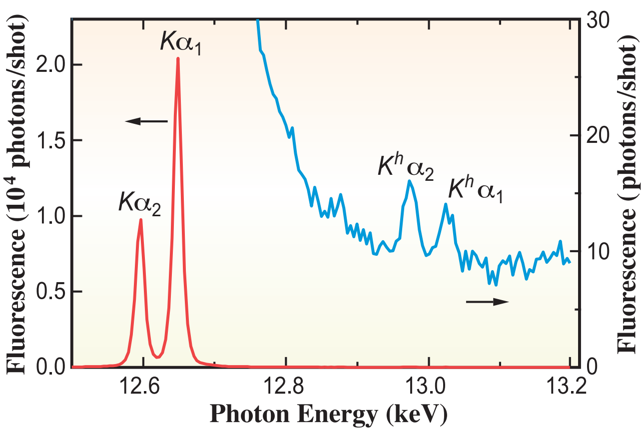

Fig. 1. X-ray fluorescence spectrum of krypton. Hypersatellite peaks $K^h\alpha$ are observed on the higher photon-energy tail of the $K\alpha$ lines.

not important in the present case. Second, the spiky temporal structure due to the self-amplified spontaneous-emission operation can increase the rate of DCH creation, because the instantaneous intensity is higher than that expected from an averaged smooth profile. The effect can be included statistically in the estimation as the degree of second-order coherence, $g^{(2)}(\tau)$.

At present, there is no experimental technique that can be used to determine $g^{(2)}(\tau)$. Thus, we employ an XFEL simulation code, SIMPLEX [4]. The parameters, such as emittance and peak current of the electron beam, are determined from the measured FEL gain curve. Then, we refine these parameters so that the degree of the first-order coherence, $g^{(1)}(\tau)$, calculated from the simulation results agrees with that determined from measured single-shot spectra. Using the calculated $g^{(2)}(\tau)$ and assuming a Gaussian pulse shape, we analyze the ratio between the $K\alpha$ and the $K^h\alpha$ fluorescence, and determine the pulse duration to be 2.5-2.8 fs (FWHM). Our estimation is found to be consistent with the electron bunch length deduced from the measured FEL gain length.

In conclusion, we successfully observed, for the first time, the DCH creation by sequential X-ray two-photon ionization and showed that intense X-rays can interact with atoms in the core-hole states. Here, we briefly discuss the impact on the structural analysis using an XFEL. When an atom becomes the SCH state, the absorption edge shifts to higher photon energies, and the anomalous scattering factor changes drastically. Since the anomalous phasing method widely used in protein crystallography relies on the physical property at the *K* edge of atoms in the ground state, it would be important to know how much X-rays are scattered by the SCH atoms. We also show that the DCH creation is useful for determining the pulse duration in the sub-10-femtosecond range. Compared with other two-photon processes, such as two-photon absorption and second-harmonic generation, we consider that the DCH creation is more efficient and suitable for XFEL beam characterization. Combined with X-ray optical delay, one will be able to construct an X-ray autocorrelator with a femtosecond resolution.

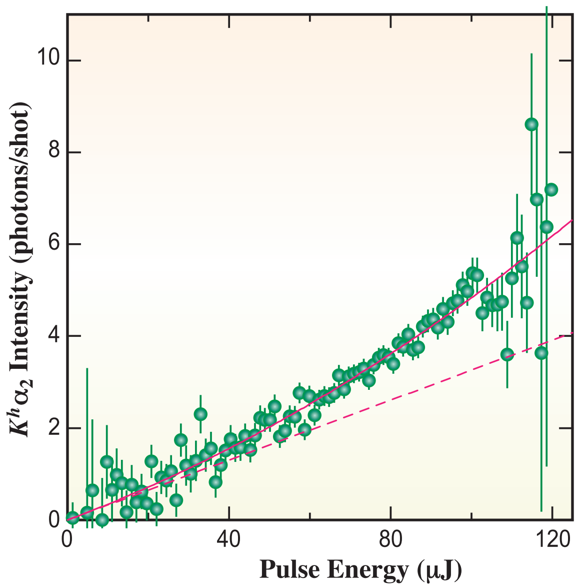

Fig. 2. Pulse-energy dependence of the $K^h\alpha_2$ fluorescence. Circles indicate the measured fluorescence intensity. Vertical bars indicate the standard error of the mean. Solid line shows the fitting with a sum of linear (dashed line) and quadratic terms.

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