X-ray two-photon absorption

Two-photon absorption (TPA) is one of the most fundamental nonlinear optical phenomena. Although it is widely used for microscopy and spectroscopy in the visible region, it has yet to be observed in the hard X-ray region. In the TPA process, the two photons are absorbed simultaneously, because there is no real intermediate state. When we consider TPA near the threshold, i.e., the pump photon energy is just above the half of the absorption edge, the lifetime of the virtual intermediate state can be approximated by $1/\omega$, where ω is the pump frequency, and the TPA cross section may be written as [1]:

$$\sigma_{TPA} = \sigma \frac{1}{\omega} \sigma'$$

where σ and σ' are the cross sections for the one-photon absorption (OPA). Since TPA consists of two OPA processes, the selection rule is expected to be different from OPA. The OPA process is allowed between states with different parities, e.g., 1*s* and 4*p*, while TPA is between states with the same parity, e.g., 1*s* and 3*d*. This unique nature of X-ray TPA should realize a new kind of X-ray spectroscopy, namely, X-ray TPA spectroscopy.

Here, we roughly estimate σ_{TPA} in the X-ray region. The OPA cross-sections and the frequency are typically $\sigma, \sigma' \sim 10^{-20}$ cm^2 and $\omega \sim 10^{-19}$ 1/s, resulting in a very small TPA cross-section of $\sigma_{TPA} \sim 10^{-59}$ cm^4/s. The TPA process is comparable to the OPA process, i.e., $\sigma \sim I\sigma_{TPA}$, when the peak intensity reaches $I \sim 10^{39}$ photons/cm^{2}s. Such a high intensity can be realized by an X-ray pulse with a flux of 10^{14} photons and 1-fs pulse duration focused down to the 100-nm size. Even if we use a state-of-the-art X-ray free-electron laser and focusing technique, the observation of X-ray TPA is still very challenging.

To observe X-ray TPA, we used the 50-nm focusing system installed in the experimental station 5 at beamline **BL3** of SACLA [2]. The sample was a thin germanium plate. The photon energy was 5.6 keV, which is just above half of the *K*-shell binding energy at 11.1 keV. The measured focus size was 110(H)×140(V) nm, and the average pulse energy was 13 μJ. Using a pulse duration of 2.5 fs (full width at half maximum) estimated from the double core-hole experiment [3], the estimated peak intensity is 3.4×10^{19} W/cm^2 (3.7×10^{34} photons/cm^{2}s). We measured X-ray fluorescence by TPA [4] because the contribution of TPA to the total absorption is too small to measure directly. X-rays at the fluorescence photon energy were selected using a bent Si(111) crystal in the Johansson geometry, which was followed by an MPCCD (multi-port CCD) detector. The spectrometer suppresses the elastically and inelastically scattered X-rays, allowing the very weak signal of TPA fluorescence to be measured.

Figure 1 shows the histogram of the readout counts from each pixel of the MPCCD during the experiment. The large peak centered at the origin is the null event. Because the probability of measuring an X-ray photon in a particular pixel of MPCCD is less than 10^{-5}, the readout count is proportional to the photon energy of a single photon. Thus, the histogram can be regarded as the spectrum. The conversion coefficient between the readout count and the photon energy was determined

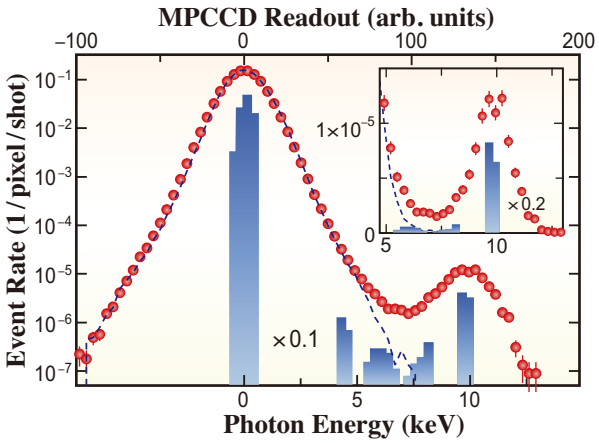

Fig. 1. X-ray fluorescence spectrum of germanium by two-photon absorption [3]. Circles and dashed line denote the measured data and read-out noise spectrum, respectively. Vertical bars indicate the deconvoluted spectrum from the noise, showing a clear fluorescence peak at 10 keV. Inset shows an enlarged spectrum around 10 keV.

experimentally. The width of the peak at the origin represents the photon energy resolution of 1.8 keV. The photon energy of the weaker peak is 10 keV, which corresponds to the germanium fluorescence by TPA.

The germanium fluorescence increases quadratically with the pulse energy (Fig. 2), indicating a two-photon process. However, the fluorescence counts deviate downwards from the quadratic dependence at higher pulse energies. The deviation can be explained as follows. Intense X-rays excite germanium mainly by the OPA process in the *L*-shell. When a core hole is created in the *L*-shell, the *K*-shell binding energy becomes deeper than twice the X-ray photon energy, i.e., 11.2 keV, due to a reduction in the screening effect. Thus, atoms with an *L*-shell core-hole cannot contribute to TPA. The *L*-shell hole decays immediately, leaving two holes in the *M*-shell. Interestingly, an atom with two *M*-shell holes is subject to TPA because the *K*-shell binding energy is less than the TPA threshold.

Since there are many different decay channels, a self-consistent simulation is needed to estimate how many atoms can participate in the TPA process. We solved numerically the coupled rate equations, and simulated the population dynamics of the electronic configurations of interest [5]. The temporal shape of the X-ray pulse is assumed to be Gaussian, and the spiky time structure is ignored because the lifetimes of the excited states are much longer than the spike duration. The pulse-energy dependence of the TPA fluorescence was calculated based on the time-dependent population dynamics. The unknown parameter in the simulation is the TPA cross section, which is determined by fitting the calculated pulse-energy dependence to the measured data. The best fit is obtained with σ_{TPA} = 6.4×10^{-60} cm^4/s, which is comparable to the rough estimation above.

In conclusion, we successfully observed X-ray TPA for the first time and estimate the TPA cross section. The different selection rule for TPA from the conventional XAS would be useful for studying the 3*d* orbitals of transition metal compounds. However, the intense X-rays change the electronic structure of the sample within the pulse duration, and the ground-state property is difficult to measure. A more efficient detecting system would allow TPA measurements under moderate peak intensities, enabling X-ray TPA spectroscopy to reveal the ground-state property of a sample.

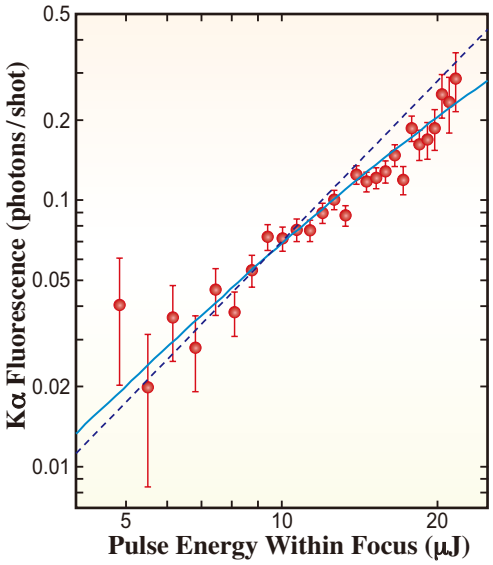

Fig. 2. Pulse-energy dependence of X-ray fluorescence [3]. Circles and vertical bars indicate the measured data and statistical error, respectively. Dashed line shows a simple quadratic dependence with a slope of two, while the solid line is the best fit of the simulation result with the fitting parameter of the TPA cross section.

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References

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