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SUPPLEMENTARY INFORMATION
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Supplementary Online Material

In order to further elucidate the role of transient resonances in the production of the unexpectedly high charge states in Xe at 1500 eV, a more detailed description of the ionization steps involved is given in the following.

The ground-state electron configuration of xenon is $1s^2\ 2s^2p^6\ 3s^2p^6d^{10}\ 4s^2p^6d^{10}5s^2p^6$. At 1500 eV (2000 eV) photon energy, the 3d shell exhibits the largest photoionization cross section with 0.49 Mb (0.22 Mb), followed by 3p with 0.22 Mb (0.14 Mb), 4d with 0.06 Mb (0.03 Mb), and 3s with 0.05 Mb (0.03 Mb), according to our calculation. Any of these photoionizations will result in a series of Auger decays (see Supplementary Fig. 2), with the Auger cascade being longest if the photoelectron originated from the 3s shell. Thus, absorption of a single photon with subsequent Auger decays can yield up to Xe^{8+} as synchrotron studies [21] have shown. With increasing charge state Xe^{q+}, the n = 5 and n = 4 shells become depleted, leaving less electrons for Auger decay, such that the Auger cascades after the sequential 3p or 3d ionizations quickly shrink to the point where an M-shell ionization is accompanied by only one or two Auger relaxations. For charge states beyond Xe^{20+}, direct 3p photoionization is no longer possible with a single 1500-eV photon. From Xe^{25+} on, the Auger lifetime of the 3d hole exceeds the inverse 3d photoionization rate at the experimental X-ray fluence (see Supplementary Fig. 1) such that 3d electrons are faster ionized than 3d vacancies are filled through Auger decay and hollow-atom states are increasingly produced. Direct one-photon photoionization of the 3d-shell can proceed until Xe^{26+} and, with multiple 3d holes, Auger relaxation can lead up to Xe^{27+}, as our calculations show in Fig 1(b). The time-evolution of these processes and the resulting time-dependent population of Xe charge states according to our model is shown in Supplementary Fig. 3. According to these simulations, the highest charge state produced is Xe^{27+}, and we conclude that at 1.5 keV, higher charge states can only be reached via resonant excitation from the M-shell. Resonant photoabsorption cross sections for selected resonances around 1500 eV in

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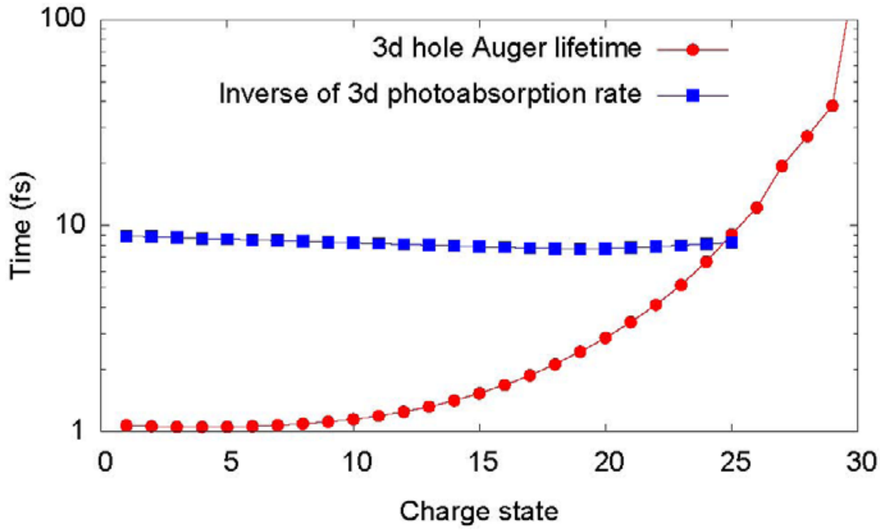
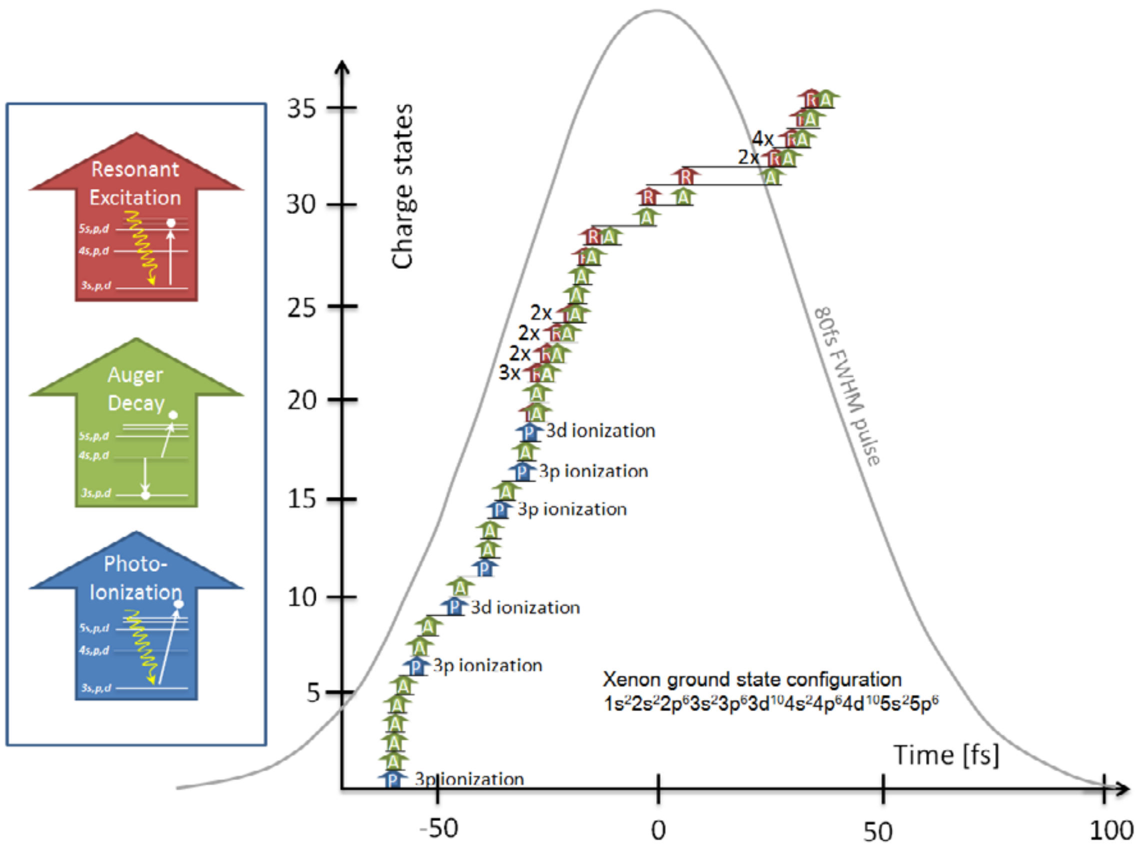
charge states Xe^{q+}, q>21 are shown in Fig. 3(b). It is important to note that the single-shot bandwidth of the FEL radiation at LCLS is on the order of +/-0.5% (i.e. about +/-7.5 eV for 1500 eV photon energy), such that resonances within a 15 eV energy range can be excited by a single LCLS pulse. Additionally, the shot-by-shot variations of the photon energy are on the order of +/-1%, such that different resonant pathways can be excited in different shots.

Figures:



Supplementary Figure 1. Multiple-core-hole formation. Comparison between the 3d single-core-hole Auger lifetime and the inverse of the 3d photoabsorption rate in xenon ions as a function of charge state q calculated at 1500 eV for an X-ray fluence of 50 μJ/μm². Multiple-core-hole formation in the 3d-shell becomes significant when the 3d single-core-hole Auger lifetime becomes comparable to or exceeds the inverse of the 3d photoabsorption rate.



Supplementary Figure 2. Diagram of an exemplary pathway leading to Xe^{36+}. X-rays with a photon energy of 1500 eV primarily photoionize Xe 3p,d-shell electrons (P, blue arrows), followed by a cascade of Auger decays (A, green arrows). Each of these processes increases the charge state of the Xe ion (vertical axis) by one. Within an X-ray pulse with FWHM of 80 fs (pulse profile shown in grey) and a fluence of 50 $\mu J/\mu m^2$, a sequence of photoionizations and Auger decays quickly leads to charge state Xe^{19+}, where the first resonant excitation (R, red arrows) occurs in the exemplary pathway shown here. The resonant excitations themselves do not increase the charge state, but they are followed by Auger decays which do increase the charge state. In some instances, more than one Auger decay can follow a resonant excitation or several excitations happen before an Auger decay (or autoionization) occurs. If multiple resonant excitations occur at a single charge state, the number of excitations is indicated above.

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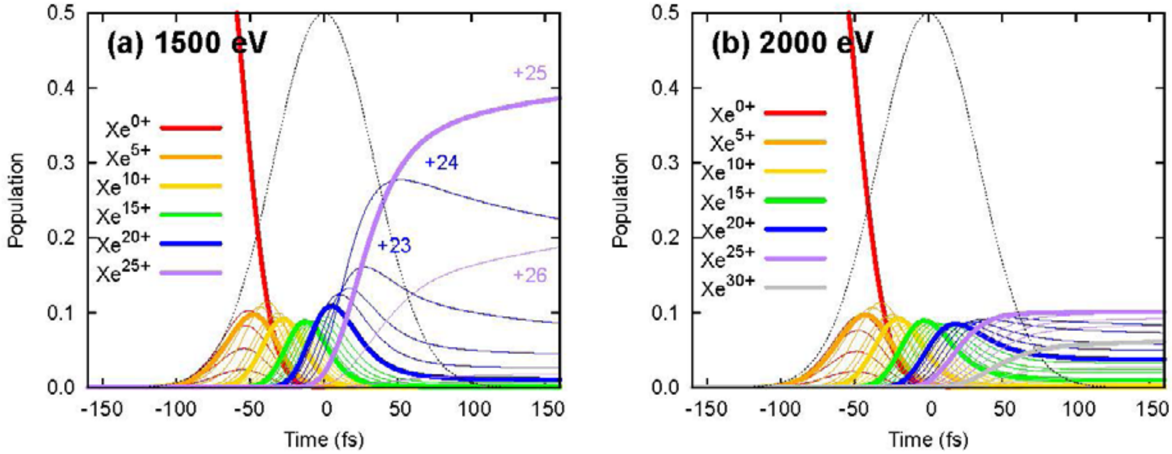

Supplementary Figure 3. Population of xenon charge states as a function of time during an 80-fs X-ray pulse. The time-dependent populations are calculated at (a) 1500 eV and (b) 2000 eV for an X-ray peak fluence of 44 and 86 μJ/μm², respectively, without inclusion of resonances. The temporal profile of the X-ray pulse is shown as grey dotted line. The calculations show that charge states Xe^{q+} with $q > 20$, for which transient resonances can occur at 1500 eV, are produced in significant abundance already close to the maximum of the X-ray pulse, such that they can be further ionized very efficiently via resonant processes. In contrast, highly charged ions, especially those with charge states Xe^{q+} with $q > 28$, for which transient resonances can occur at 2000 eV, are produced significantly less and later within the X-ray pulse at this higher photon energy due to the smaller absorption cross sections at 2000 eV. Therefore, the influence of REXMI at 2000 eV is very small for the given X-ray fluence in our experiment.