Two-Photon Excitation and Relaxation of the 3*d*-4*d* Resonance in Atomic Kr

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Two-photon excitation of a single-photon forbidden Auger resonance has been observed and investigated using the intense extreme ultraviolet radiation from the free electron laser in Hamburg. At the wavelength 26.9 nm (46 eV) two photons promoted a 3*d* core electron to the outer 4*d* shell. The subsequent Auger decay, as well as several nonlinear above threshold ionization processes, were studied by electron spectroscopy. The experimental data are in excellent agreement with theoretical predictions and analysis of the underlying multiphoton processes.

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The chief manifestation of the coupling of electrons bound in atoms or molecules to electromagnetic radiation of high intensity is the onset of nonlinear processes, a feature that could in fact be viewed as the definition of a strong field. Phenomena such as multiphoton multiple ionization, above threshold ionization (ATI), and high order harmonic generation span the broad field of strong field physics that has until recently been restricted to interactions with infrared and optical radiation [1]. Because of the small photon energy, only the outermost electrons are ionized and multiple ionization is obtained via successive stripping of the outer subshell. In contrast, short-wavelength radiation couples predominantly to electrons in lower, more strongly bound shells, producing core-hole states, which decay primarily by ultrafast Auger decay. The opportunity to study the underlying multiphoton dynamics arises only now with the availability of free electron lasers (FELs) in the extreme ultraviolet (XUV) to hard-x-ray wavelength regime [2,3].

The investigation of nonlinear interactions using FELs started recently and has already highlighted several phenomena, such as, e.g., the formation of very high charged states [4,5] and two-photon double ionization [6,7], that could not be anticipated on the basis of the existing linear experience. A unique access to explore the interaction between matter and strong XUV fields is given by resonant two-photon inner-shell processes. Firstly, two-photon processes enable the study of a class of resonances, which are inaccessible in a single-photon process from the ground state. Secondly, inner-shell resonances are characterized by a dramatic increase of the photoionization cross section and provide, for example, chemical (i.e., atomic) selectivity in the photoionization process of molecules or clusters. The lifetime of a core hole of the order of several femtoseconds is determined by Auger processes, and the excitation in strong XUV fields of similar durations will inevitably result in the competition between sequential ionization and Auger decay. This new phenomenon, which will be present in all processes involving the interaction between intense XUV light and matter, can be addressed only due to the short pulse durations. It is the nonlinear behavior of such interactions that presents a new frontier, with multiphoton excitation and/or ionization of subvalence electrons representing the backbone of the underlying physics.

Given the novelty of the sources and the hitherto largely unexplored radiation-matter territory at XUV and x-ray photon energies, certain benchmark experimental studies are necessary in order to provide a first assessment of their feasibility as well as the predictive potential of relevant theoretical and computational approaches (e.g., [8,9]). It is important to recall that the so-called single active electron approximation, often adopted in the long-wavelength regime, is not valid in the short-wavelength regime. Instead, a fairly detailed input of atomic structure combined with the time-dependent dynamics will be necessary. It is the purpose of this Letter to present the first experimental results, together with their theoretical interpretation, on one of the most basic nonlinear processes involving inner-shell transitions, namely, the two-photon excitation of an Auger resonance.

In this work, we applied electron spectroscopy to explore the dynamics of interconnected multiphoton processes and to further unravel their complex ionization pathways. The intense XUV pulses from FLASH were used to induce a two-photon excitation of the strongly bound 3*d* core electrons in atomic Kr (Fig. 1). The photon energy of the FEL radiation chosen for this study was

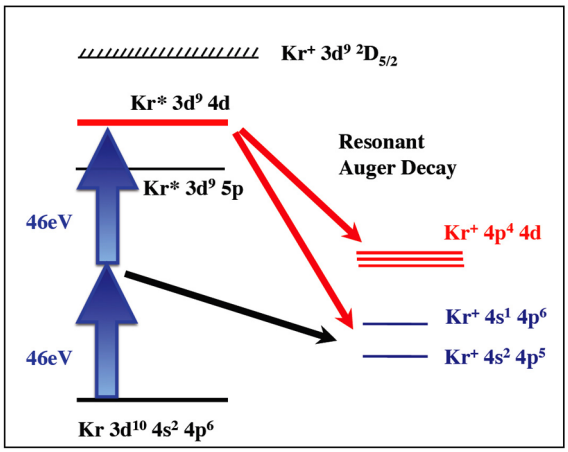

FIG. 1 (color online). Energy level diagram and excitation scheme for atomic Kr.

around 46 eV, so that the energy of two photons (92 eV) is on resonance with the transition to the Kr* $3d^9(^2D_{5/2})4s^24p^64d$ ($J = 0, 2$) core excited states [10]. With two-photon excitations, a new class of resonances with the same parity as the initial state and $\Delta J = 0, 2$ can be investigated that cannot be reached by one-photon processes. Moreover, the analysis shows clear evidence for sequential processes, i.e., one-photon and two-photon ionization of singly charged Kr ions.

Given the pulsed nature of the source and the substantial bandwidth ($\approx$0.45 eV), as well as the ac Stark shifts of atomic states exposed to intense radiation, the resonance condition represents a dynamic situation, which requires the formulation and solution of the appropriate density matrix equations. In addition to a reasonable model for the time-dependent field, the formulation of the theory requires realistic dipole matrix elements coupling the states entering the description, as well as the relevant Auger decay rates of the hole states created by the promotion of an inner $3d$ electron to the $4d$ orbital. Moreover, quantitative predictions about the expected photoelectron energy spectra are necessary for the documentation of the observations. The peak intensities reached in the experiment were at most 10^{15} W/cm^2. At the photon energy of 46 eV, even at such intensities, the ponderomotive energy, which represents the cycle-averaged kinetic energy of free or quasifree electrons in the field as well as the shift of the Rydberg states, is much smaller than the photon energy. In planning the experiment, the shift of the $4d$ resonance, which turns out to be of the same magnitude as the laser bandwidth, needed to be taken into account, so that the maximum shift during the pulse brings the $4d$ state on resonance at the peak of the intensity, thus maximizing the two-photon transition.

The experiments were performed on beam line BL2 at FLASH using an experimental setup for electron spectroscopy similar to that described earlier [11]. The FEL was operated in single-bunch mode at a 5 Hz repetition rate and fundamental wavelengths of 26.9 nm (46 eV) with a mean pulse energy of 10–15 μJ as measured on line for each pulse using a gas-monitor detector [12]. In this wavelength region the temporal width of the pulses is of the order of 30 fs [13]. The FEL beam was focussed to a diameter of about 5 μm in the acceptance volume of a magnetic bottle electron spectrometer (MBES). Focusing was obtained by a spherical Mo/Si multilayer mirror (reflectivity of about 40%) mounted in the rear of the vacuum chamber. By introducing a small angle (5°) between incoming (unfocused) and reflected beams, only the focused beam passed through the interaction volume. Taking into account the reflectivity of the mirror, an intensity of more than 5×10^{14} W/cm^2 was obtained at the focus. The spectral bandwidth of the non-Fourier-transform-limited FEL pulses was measured to about 0.25 nm (0.43 eV) and was therefore larger than the natural width of the Kr* $3d^{-1}$ hole state (about 120 meV). Because of the fluctuation of the spectral profile, a strong FEL pulse does not always lead to a strong resonant excitation. For this reason, the electron spectra were recorded by averaging over many FEL pulses and normalized to the average intensity. The pressure in the chamber was below 10^{-8} mbar without and about 3×10^{-7} mbar with Kr gas.

Figure 2 shows a typical photoelectron spectrum of atomic Kr recorded under the above conditions. This spectrum is dominated by the strong photoline at 32 eV kinetic energy due to single-photon ionization of the $4p$ electron leading to the Kr^+4p^5 final ionic state. The two spin-orbit components $^2P_{3/2}$ and $^2P_{1/2}$, being separated by only 0.66 eV, are not resolved in the present experiment. The small feature at about 20 eV arises from ionization of the $4s$ shell, as well as from a contribution of sequential two-photon ionization of a second $4p$ electron from the Kr^+ ion. The cross section of Kr($4s$) ionization at 46 eV is more than 2 orders of magnitude smaller than that of Kr^+ ($4p$), and, therefore, most of the intensity at 20 eV can be attributed to the ionization of the Kr^+ ion. Spectra recorded

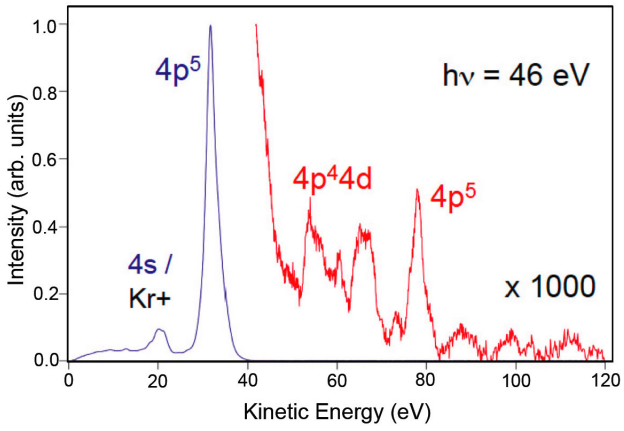

FIG. 2 (color online). Electron spectrum of atomic Kr upon excitation by intense FEL radiation of 46 eV photon energy recorded by integrating the signal over 500 FEL pulses.

with increased spectral resolution show clearly the three components ^1S, ^1D, and ^3P of the final $Kr^{2+}4p^4$ ionic configuration. In the region of high kinetic energies ($\geq$46 eV), where electrons are released by two-photon ionization processes, very small structures are observed, visible only after the intensity scale has been magnified by 3 orders of magnitude. The line at the highest kinetic energy (78 eV) results from two-photon ionization of the Kr($4p$) shell, which is an ATI process. This simultaneous absorption of two photons by the $4p$ electron is, in accordance with theoretical estimates, about 500 times smaller than the corresponding one-photon absorption at the used FEL intensities of 5×10^{14} W/cm^2. The broad structure between 50 and 60 eV is attributed to the resonant Auger decay $Kr^*3d^94s^24p^64d \rightarrow Kr^+3d^{10}4s^24p^44d^{2,4}L_J$. Only very few of these Kr^+ multiplet lines have been observed in the past, as small satellites in conventional photoelectron spectroscopy experiments [14], and it is, in that case, their resonantly enhanced intensity which allows for a detailed investigation of the multiplet structure. On the basis of energy considerations, the structure at 65 eV kinetic energy is assigned to the $4p$ ATI of the Kr^+ ion.

To exclude any influence of the second harmonic of the FEL (typically of the order of 0.1%–0.5% [15]), complementary measurements were performed. A 100 nm Al filter was introduced in the path of the FEL, which reduced the intensity of the FEL at the fundamental wavelength (26.9 nm) to 70% and of the second order harmonic signal (13.45 nm) to 5%. The electron signal dropped only to 50%, indicating that contributions from the second harmonics were negligibly small. In addition, the nearly quadratic dependence of the electron signal on the intensity of the incoming FEL light, i.e., $(0.7)^2 \approx 0.5$, is a clear signature of a two-photon process. As further evidence, the structure below 60 eV disappeared when the wavelength of the FEL was slightly detuned to 26.5 nm (46.8 eV), i.e., out of resonance for the two-photon process, whereas the lines at 65 and 78 eV were still relatively strong.

To predict and then interpret the observed structures, a thorough theoretical analysis was undertaken. The results are compared in Fig. 3 with a high-resolution electron spectrum, recorded by applying a retardation potential of -41 V to the entrance aperture of the MBES. In modeling the spectrum, the two-photon resonant excitation of krypton atoms from the ground to the $Kr^*3d^9_{5/2}4d$ autoionizing states (with total angular momentum $J = 0$ and 2) was calculated. At 46 eV photon energy, this two-photon transition does not involve any near resonances to intermediate atomic states, as the nearest allowed single-photon transition to $3d^9_{5/2}5p$ is detuned by more than 40 eV. Nevertheless, the two-photon coupling $3d \rightarrow 4d$ involves a summation over a number of nonresonant intermediate states adequate for convergence. In the formulation, they are adiabatically eliminated, entering into the two-photon matrix element only via their dipole matrix elements to the initial and final states and their energy difference denominators [16]. In the quantitative calculations, these matrix elements were obtained through the GRASP Dirac-Fock code, and sensitivity to the gauge has been evaluated. The $3d^94d$ states form two groups of states separated by about 1.2 eV. The lower- and higher-lying groups are characterized by the coupling of the $3d$ electrons to the total angular momentum $J_c = 5/2$ and $3/2$, respectively. In the following, we concentrate only on the $J_c = 5/2$ states, observed in the experiment.

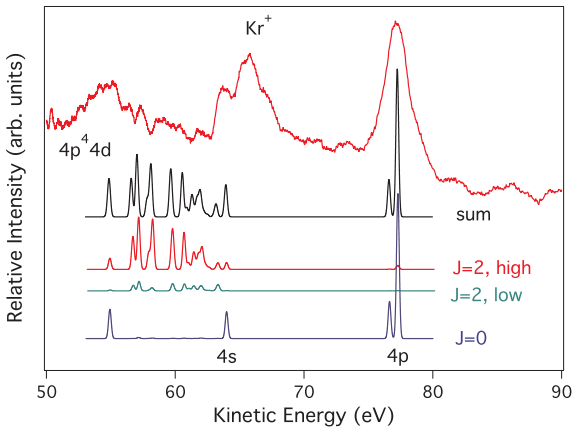

FIG. 3 (color online). High-resolution electron spectrum of atomic Kr compared to a theoretical spectrum taking into account the relative probabilities for the excitation of different $3d^{-1}4d$, $J = 0, 2$ resonances and their decay rates to the $Kr^+4p^44d^{2,4}L_J$ final ionic states. To compare with the experiment, the theoretical results have been convoluted with a Gaussian profile of 0.25 eV FWHM.

Owing to the strong intensity of the FEL (more than 10^{14} W/cm^2), in addition to the two-photon excitation of the Kr $3d^9_{5/2}4d$ resonance, a number of other ionization processes take place, all of which are monitored through the observation of the electron spectra. These are single-photon ionization of the neutral, as well as single-photon and two-photon (ATI) ionization of Kr^+, which is produced and ionized during the pulse. For identification of all observed photoelectron signals, their contributions must also be calculated. This is achieved through a set of kinetic equations governing the evolution of all relevant species during the pulse. The corresponding single- and two-photon cross sections have been calculated. To describe the autoionization of the Kr $3d^9_{5/2}4d$ hole states, multiconfiguration Dirac-Fock computations were performed on the level structure and transition amplitudes of the neutral excited and the Kr^+4p^44d ionic states. These computations utilize the wave functions from the GRASP92 code [17] to evaluate the Auger (electron) energies and intensities from the decay of the $J = 0$ and 2 resonances to all final states by using the RATIP program [18]. The intensities are strongly affected by the configuration mixing in the final states. For the computation of the Auger amplitudes, the continuum spinors are solved within a spherical but state-dependent potential of the final ion and including the

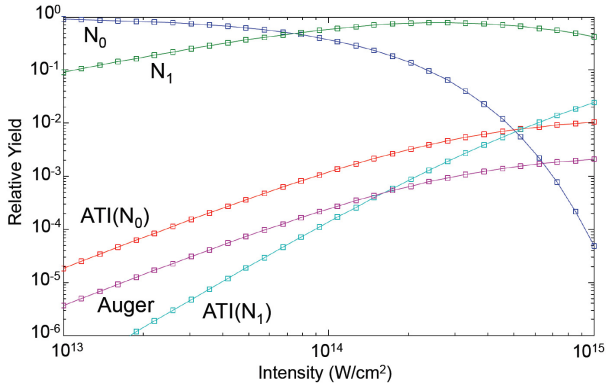

FIG. 4 (color online). Power dependence of the population of the neutral (N_0, Kr $3d^{10}4s^24p^6$) and ionic (N_1, $Kr^+3d^{10}4s^24p^5$) species after the end of the FEL pulse. The relative yields of electrons produced in the ATI from neutral (N_0) and ionic (N_1) krypton and in the resonant Auger process are also given.

exchange interaction of the emitted electron with the bound state density.

In Fig. 3 the results of the calculations are compared to the experiment. The energy scale of both spectra has been calibrated via the strong $4p$ ATI line at 78 eV. The contributions from the different excited states ($J = 0, 2$) are given independently. The $3d^9_{5/2}4d$, $J = 0$ resonance provides most of the intensity for the $4p$ and $4s$ lines as well as to the subsequent decay to the $4p^4(^1D)4d\,^2S_{1/2}$ level from the $4p^44d$ multiplet at 55 eV kinetic energy. The latter is strongly mixed with the $4s$ line. Most of the intensity for the resonant Auger lines is therefore attributed to the decay of the higher-lying $J = 2$ resonance. In general, the intensity ratios of most peaks, especially between the $4p$ line and the resonant Auger lines, is well reproduced. However, the kinetic energies of the Auger lines to the $Kr^+4p^44d\,^{2,4}L_J$ final states are higher than the experimental values by about 2 eV, which most likely arises from the strong coupling of the $3d^9_{5/2}4d$ resonances to the continuum [19] and a slightly unbalanced treatment of correlation effects in the neutral and singly ionized Kr. The calculated overall intensity for the two-photon processes corresponds well to the experimental values. Theoretically the two-photon processes are calculated to be about 10^3 times smaller than the one-photon processes at intensities of some 10^{14} W/cm^2.

The calculation strongly supports the assignment of the line at 65 eV to a two-photon process, namely, the $4p$ ATI process in the Kr^+ ion. Because of the strong one-photon process (see the strong line at 32 eV in Fig. 2), a large portion of the target atoms has already been ionized when the center of the XUV radiation pulse passes through the interaction volume. This is quantified in Fig. 4 where the populations of the neutral and ionic species, which are produced at the end of the FEL pulse, are given as function of the intensity of the FEL radiation. Starting at 1×10^{14} W/cm^2 the population of Kr^+ ions in the Kr^+4p^5 ground state becomes higher than the population of the neutral ground state. In the experiment, the signal of Kr^+ (line at 65 eV) was estimated to be 1.5 times more intense than the $4p$ ATI line from the neutral (line at 78 eV). Given that the experiment averages over many pulses with varying intensity and integrates over an extended source volume, where only in the center the 5×10^{14} W/cm^2 peak intensity is reached, the experimental value number is consistent with the theoretical prediction.

Beyond its significance as the first observation of a two-photon excitation of an Auger resonance, this work highlights a number of issues in the study of nonlinear processes in this novel context. Owing to the high intensity of the FEL pulse, necessary for the observation of a specific nonlinear process, other nonlinear processes have been shown to play a significant role that must be evaluated. And this is a general feature of nonlinear interactions. Finally, the strength of the transitions in this case can serve as a point of calibration and extrapolation to the study of analogous nonlinear processes at much shorter wavelengths and deeper shells [20].

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