Ultrafast quantum control of ionization dynamics in krypton

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Ultrafast spectroscopy with attosecond resolution has enabled the real time observation of ultrafast electron dynamics in atoms, molecules and solids. These experiments employ attosecond pulses or pulse trains and explore dynamical processes in a pump-probe scheme that is selectively sensitive to electronic state of matter via photoelectron or XUV absorption spectroscopy or that includes changes of the ionic state detected via photo-ion mass spectrometry. Here, we demonstrate how the implementation of combined photo-ion and absorption spectroscopy with attosecond resolution enables tracking the complex multi-dimensional excitation and decay cascade of an Auger auto-ionization process of a few femtoseconds in highly excited krypton. In tandem with theory, our study reveals the role of intermediate electronic states in the formation of multiply charged ions. Amplitude tuning of a dressing laser field addresses different groups of decay channels and allows exerting temporal and quantitative control over the ionization dynamics in rare gas atoms.
n the last decade, time-resolved spectroscopy with attosecond resolution has revolutionized our understanding of electron dynamics by capturing ultrafast processes in atoms, molecules and solids in real time. While the first photoelectron studies with attosecond resolution could, for example, track a few-femtosecond Auger process, meanwhile ultrafast metrology became so advanced that unexpected delays in photoemission from atoms were discovered, most recently down to sub-attosecond precision. Attosecond time-resolved mass spectroscopy provided the first time-domain observation of field-induced tunnel ionization manifesting itself in a step-like rise in the ion yield. More recently, attosecond transient absorption detection could launch and detect valence electron wavepackets in atoms, examine their interference with continuum states and enabled studying tunnel ionization in solids.

Photoelectron detection techniques generally suffer from electron backgrounds produced by strong laser fields or secondary electrons that do not carry any information about the dynamics under inspection. The detection of the correspondingly produced ions, however, is background-free. Nevertheless, both methods require the release of photoelectrons and thus are suitable only for the study of ionizing events. Transient absorption spectroscopy (TAS) in contrast is not limited to phenomena liberating electrons and is the method of choice for investigating bound–bound transitions. Instead of measuring the yield of generated charge carriers, TAS measures the spectrally resolved absorption of an attosecond extreme ultraviolet (XUV) pulse in a medium that has been coherently excited by an XUV pulse or dressed by an intense, time-delayed near-infrared (NIR) few-cycle laser pulse. This method typically provides a higher resolution in energy ($\Delta E/E \sim 10^{-3}$) than ion or electron detection ($\Delta E/E \sim 10^{-2}$ at best). However, it generally lacks the dynamic range to simultaneously detect the characteristic absorption signals of different co-existing ionic charge states due to insufficient spectral bandwidth or due to the absorption cross-sections and abundances of the different ionization states that typically vary by several orders of magnitude. TAS experiments have been successful in recording auto-ionizing state lifetimes in xenon and other species. However, even a detailed theoretical investigation could not explain whether the interrogating ultrashort and intense NIR laser pulse couples the auto-ionizing states to neighboring resonances or to which extent excited electrons are promoted into the ionization continuum by the laser field. In contrast, the ion detection that enabled the first observation of tunneling electrons in neon and xenon could track the change in ion yield of different charge states. However, mass spectroscopic studies to this date cannot resolve individual shake up satellites.

To overcome the limitations of single observable experiments and in order to draw a complete picture of the co-evolving excitation/ionization dynamics, in this article we demonstrate the benefit of combining ion spectroscopy and transient absorption with attosecond temporal resolution. Merging these detection methods provides complementary insight into the excitation/decay mechanism as the transient absorption maps the initiating resonant excitation and the ion detection sensitively records the subsequent branching into intermediate and final states. The combination of transient absorption with ion spectroscopy compensates the limits in the simultaneous detection of several ionic states that absorption spectroscopy typically brings along. The prerequisite is that the pump–probe experiment can be performed twice under identical experimental conditions except for differing target densities optimized for the two detection methods. Adjusting the laser electric field amplitude allows selectively addressing different intermediate states of the auto-ionization cascades that follow the XUV excitation resulting in different apparent lifetimes. With that, the experimentalist...
For all isotopes similarly, the Kr$^{3+}$ ion yield rises shortly before XUV/NIR pulse overlap and decays with a slower time constant when compared to the almost to its original value, with an exponential time constant corresponding to the state lifetimes. The absorbance at the resonances transiently decreases at XUV/NIR pulse overlap and subsequently recovers for positive times on the delay axis. The absorbance at the resonances transiently decreases at XUV/NIR pulse overlap and subsequently recovers.

Delay $t_R$

Supplementary Note 1 for details. Figure 1c shows the transmission spectrum scanning the arrival time difference between XUV and laser pulse.

Obtains control of the temporal evolution and the absolute yield of the ionization dynamics by accessing different level groups in the cascade with different NIR intensities. The accompanying absorption measurement enables the determination of the instrument response function, the lifetimes of resonantly excited states involved in the process and proves that the overall conditions of the experiment (resonant excitation and ionization) remain unchanged for a large range of NIR intensities.

Results

Experiment. To explore the decay dynamics of highly excited krypton (see Fig. 1a), a phase-stabilized Ti:Sapphire few-cycle laser$^{14,16,17}$ is used to produce isolated attosecond pulses (cp. Supplementary Fig. 1) via high harmonic generation in a pump–probe scheme united with a reflectron-type ion spectrometer and an XUV grating spectrometer (see Fig. 1b and Supplementary Note 1 for details). Figure 1c shows the transmission spectrum without (violet) and with (green) krypton gas sample with the NIR pulse preceding the XUV pulse by 150 fs. For the same time delay, Fig. 1d depicts the corresponding ion spectrum with singly, doubly and triply charged krypton ions. For the time-resolved studies, we measured the krypton transmission and ion spectrum scanning the arrival time difference between XUV and laser pulse.

Merging ultrafast absorption and ion mass spectroscopy. Figure 2a shows the spectrally resolved change in absorbance (optical density $\Delta OD = -\log_{10}(I(\Delta t)/I_0)$ states function of the XUV/NIR time delay, while Fig. 2b depicts the isotope-resolved Kr$^{3+}$ ion yield change. The absorbance starts to transiently decrease at XUV/NIR pulse synchrony while the Kr$^{3+}$ ion yield short time rises, however, with a slightly retarded response with respect to the absorption change.

Ionization dynamics in krypton. To reveal further details of the ionization dynamics, Fig. 3 presents the absorbance $\Delta OD$ at 91.23 eV (corresponding to the 3$d^{10}\,5p$ resonance) relative to the OD measured at $\Delta t = -30$ fs and the Kr$^{3+}$ ion yield added up over the four most abundant krypton isotopes for two different NIR intensities: Fig. 3a for low NIR intensity of $(8.6 \pm 1) \times 10^{13}$ W cm$^{-2}$ and Fig. 3b for high NIR intensity of $(2.9 \pm 0.5) \times 10^{14}$ W cm$^{-2}$. For both cases, the absorbance decreases on a quick (<10 fs) time scale before it recovers almost to its original value. The time constant of the fast $\Delta OD$ decrease reflects the
Control of krypton ionization dynamics. Figure 4 shows for three different NIR intensities that the observed decay time increases for higher NIR intensities due to a second set of decay channels (3d$^{10}$np $\rightarrow$ 4s$^{2}$4p$^{-2}$np$\rightarrow$4p$^{-1}$4p$^{-3}$4d$\rightarrow$ 4p$^{-2}$). This second set (indicated by B in Fig. 1a) has a much longer effective lifetime as it was already speculated$^{17}$. A double exponential decay fit gives rise to a second decay time of 60 ± 28 fs, if we apply 9.3 fs as the first decay time that has been found for the lowest intensity. At higher NIR intensity, channel B results in an increase of the amplitude ratio B/A. Amplitude A corresponds to the Auger cascade emerging at low NIR intensities. The results of our theoretical calculations of the effective lifetimes with 6 fs for the 4s$^{-2}$np levels and 49 fs for the 4s$^{-1}$4p$^{-1}$np/4p$^{-3}$4d levels agree very well with the measurements.

There occurs a transient drop in the Kr$^{3+}$ ion production shortly before pulse overlap (approximately at −5 fs) that depends on the NIR intensity but appears independent of the carrier envelope phase (strongest dip at high NIR intensities, best visible in Fig. 3b). This dip has been observed previously$^{17}$, and its origin is not yet understood. It could result from a transient population transfer$^{28}$ but may arise also as a Fano-type resonance$^{29}$ that is embedded into the K$^{2+}$ continuum.

Discussion

While a control of the end configuration in the dissociative ionization process of deuterium by tuning the carrier envelope phase has been already demonstrated$^{30}$, we have shown here that combined attosecond transient absorption and mass spectrometry allows the observation and control of the XUV-induced ionization dynamics in rare gas atoms. The study reveals the role of intermediate electronic and ionic states and highlights how laser-induced state coupling can be used to control the post-excitation decay dynamics. The experiment simultaneously determines the instrument response function, the effective lifetimes of the resonantly excited states and confirms that the initiating resonant excitation is not affected by the dressing laser field amplitude while the evolution of the post-excitation decay can be dynamically and quantitatively manipulated.
Data availability. The data that support the findings of this study are available from the corresponding author upon request.

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Author contributions

Experimental studies and analysis of experimental and theoretical signatures were carried out by K.H., M.M., V.S. and B.B. Theory and modeling were performed by S.O.S. and R.B., supervised by S.F. Customized XUV optics were provided by A.G. J.R., A.D., R.H., M.S.W. and R.K. contributed to the experimental setup and measurement. The manuscript was written by N.M.K. and B.B. All authors discussed the results and commented on the paper.

Additional information

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