In high-intensity laser light, matter can be ionized by direct multiphoton absorption even at photon energies below the ionization threshold. However on tuning the laser to the lowest resonant transition, the system becomes multiply excited, and more efficient, indirect ionization pathways become operative. These mechanisms are known as interatomic Coulombic decay (ICD), where one of the species de-excites to its ground state, transferring its energy to ionize another excited species. Here we show that on tuning to a higher resonant transition, a previously unknown type of interatomic Coulombic decay, intra-Rydberg ICD occurs. In it, de-excitation of an atom to a close-lying Rydberg state leads to electron emission from another neighbouring Rydberg atom. Moreover, systems multiply excited to higher Rydberg states will decay by a cascade of such processes, producing even more ions. The intra-Rydberg ICD and cascades are expected to be ubiquitous in weakly-bound systems exposed to high-intensity resonant radiation.
When an inner-valence ionized atom or molecule is surrounded by other atoms or molecules, the energy released via the electronic relaxation of the ionized species can be transferred to a neighbouring atom or molecule, which uses the released energy to emit one of its electrons. This process is called interatomic/intermolecular Coulombic decay (ICD). Since the first prediction in 1997 (ref. 1), ICD has been extensively studied both theoretically and experimentally in a variety of weakly bound systems (for recent reviews, see refs 2,3). It is worth noting that ICD has also been observed in molecular water clusters, suggesting that ICD may also occur in water-abundant biological systems4,5 and be an important source of genotoxic low-energy electrons and radical cations.

Intriguingly it has been shown theoretically and verified experimentally that ICD is not an isolated phenomenon, but might be part of complex cascade relaxation mechanisms, occurring for instance following an Auger decay process6-14. To understand relaxation mechanisms, it is necessary to be aware of all possible channels and determine their significance, and in the present work, we investigated this subject.

In the regime of high-intensity radiation, Kuleff et al.15 proposed an ICD mechanism in which two neighbouring species are resonantly photo-excited to low-lying excited states, and the de-excitation of one of them leads to the ionization of the other via an ultrafast energy transfer. It was argued that this process could be an additional important ion-production mechanism in clusters exposed to intense resonant light, largely dominating the direct multi-photon ionization of clusters' constituents at moderate intensities. Recent experimental studies of large helium droplets excited to low-lying states further supported the high efficiency of this variant of the decay processes16,17.

What happens when the cluster constituents are brought to higher excited states?

In this article, we show that in this case different relaxation dynamics take place. We report the observation of a new type of ICD, as well as of a cascade of ICD processes. For ease of analysis and interpretation, we chose to study neon clusters. Ne clusters containing about 5,000 atoms were irradiated by free electron laser (FEL) pulses of 61 nm wavelength, corresponding to the 2p6 → 2p3 3d atomic-like transition in the cluster18. The FEL pulse produces a multiply excited cluster which can relax either via ICD in which one of the excited 3d electrons recombines with the 2p hole, as shown in Fig. 1a, or with a much slower rate, by fluorescence. The present experiment, however, clearly demonstrated that this 'direct' ICD channel is significantly suppressed and instead, ICD transitions that lead to the final state 2p3 3s (see Fig. 1b) are dominant. Hereafter, we will refer to these transitions as ‘intra-Rydberg’ ICD. We have also observed secondary ICD processes (ICD cascades) resulting from the intermediate excited states such as 2p3 3s populated by the primary ICD processes (see Fig. 1c). We note that similar processes have been studied in a completely different regime and form of matter, namely Rydberg gases, and shown to be responsible for the so-called avalanche ionization phenomenon.

**Figure 1 | Schematic diagram of Interatomic Coulombic Decay transitions from resonant excited states.** (a) Schematic diagram of the direct Interatomic Coulombic Decay (ICD) process: Ne*(2p3 3d) + Ne*(2p3 3d) → Ne+(2p6) + Ne(2p5) + eICD, which can be abbreviated as 3d + 3d → 2p + eICD. Here one excited neon atom, Ne*(2p3 3d), returns to its ground state (Ne(2p6)) and the other neon atom is ionized by using the energy transferred by a virtual photon exchange. (b) Intra-Rydberg ICD: 3d + 3d → 3s + eICD. In this process, one Ne*(2p5 3d) undergoes a transition to a lower excited state, Ne*(2p3 3s), and the other one is ionized. Note that excited neon atoms remain in the neon cluster after intra-Rydberg ICD. (c) ICD cascade: after an intra-Rydberg ICD, the excited species thus produced continue to decay by secondary ICD processes either among themselves, or with other neighbouring excited species. Note that such an ICD cascade produces more ions compared with the case when the multiply-excited cluster would have decayed only by direct ICD processes.
and the creation of ultracold plasma\textsuperscript{19–22}. In Rydberg gases, however, collisions are recognized as a prerequisite for the ionizing mechanism, while in the van der Waals clusters studied by us the energy transfer between excited atoms is so efficient, due to the much smaller interatomic distances, that collisions (although not excluded) are not necessary for producing electrons and ions. Our study on clusters complements that on Rydberg gases and makes clear the importance of cascades in condensed matter.

Results

Experimental approach. The experiments were performed at the SPring-8 Compact SASE Source test accelerator in Japan\textsuperscript{23}. Intense EUV-FEL pulses at 20.3 eV photon energy (bandwidth of 0.3 eV full-width at half-maximum (FWHM)) and of 30 fs duration were focused on a Ne cluster beam. The kinetic energy distribution of the emitted electrons was measured with a velocity map imaging (VMI) spectrometer (see Fig. 2a, Methods and ref. 24). Electron velocity map images for Ne clusters and atoms are shown in Fig. 2. The photon energy of 20.3 eV corresponds to the resonant excitation energy in a cluster of ground-state Ne atoms to the \(2p^5 3d^1\) states. Despite the high FEL intensity, it is evident from Fig. 2 that the FEL pulse does not cause any significant electron emission from isolated atoms despite its high intensity (\(\sim 5.3 \times 10^{12} \text{ W cm}^{-2}\)). The situation changes dramatically for clusters, where a strong electron signal is produced already at moderate FEL intensities (\(\sim 4.5 \times 10^{11} \text{ W cm}^{-2}\)) due to the ICD processes.

Electron emission spectra of neon clusters and assignment. Electron spectra from Ne clusters are shown in Fig. 3. On top of the well-known exponential thermal distribution of the electrons\textsuperscript{25}, stemming from the increase of the cluster potential by charge accumulation and nanoplasma formation, we also observe distinct structures at about 1.8 and 11 eV that become more pronounced with increasing FEL intensity. Before assigning the observed structures, let us first consider the possible ICD transitions in Ne clusters under the present conditions, using the atomic energy level data for Ne (ref. 26). Table 1 summarizes all energetically allowed transitions. Apart from the \(3d\) to \(2p\) transition, the \(3d\) to \(3s\) transition in one Ne atom is able to eject a \(3d\) electron from a neighbouring excited atom. This intra-Rydberg ICD process can be viewed as a 'super Coster-Kronig' transition since all participating electrons occupy \(n=3\) shells and, as we will see, dominates the other ICD.
Theoretical modelling of the ICD transition rates. To validate our interpretation of the measured electron spectra, we performed numerical simulations based on a system of rate equations. The system of equations describes the time evolution of the population of the excited atoms, which can decay pair-wise via an energetically allowed ICD transition with the corresponding rate. To obtain the rate of each possible ICD transition, we made use of the asymptotic formula for the ICD width \( \Gamma \) (derived in ref. 15) which involves the oscillator strength \( f \) of the de-excitation transition in one of the atoms in the pair, and the cross-section \( \sigma \) to ionize the other excited electron in the other atom with the energy \( \omega \) released by the de-excitation transition:

\[
\Gamma(R) = \frac{3c}{\pi\hbar^2} \frac{f \sigma}{R^6}.
\]  

In the above expression, given in atomic units, \( c \) denotes the speed of light and \( R \) is the distance between the excited atoms. For all possible ICD transitions, the required atomic quantities (oscillator strengths and ionization cross-sections) were computed at the Hartree-Fock level.

The rate equations were solved for the number of electrons emitted in all possible ICD channels along the cascade (see Methods). The results are shown as a histogram in Fig. 4 together with the experimental data. The model cannot predict absolute intensities, but only relative ones, assuming all excited pairs have decayed and all emitted electrons have reached the detector with their initial energies. The model is also not sensitive to the initial concentration of Ne*\((2p^53s)\) and, therefore, to the FEL pulse intensity. That is why, to compare with the experimental spectrum, an exponential function accounting for the thermal distribution of the electron emission has been extracted from the experimental curve and added to the theoretical results, and the resulting data have been normalized to the intensity of the measured peak at \( \sim 11.6 \text{ eV} \). We see that despite the simplicity of the model, it correctly describes the experimental observations: two strong peaks at \( \sim 2 \text{ and } \sim 11.6 \text{ eV} \) are predicted with an intensity ratio of approximately 2:1, while the transitions at \( \sim 15.1 \text{ and } \sim 18.6 \text{ eV} \) have very low rates and are thus not observed experimentally. The high-intensity of the line at \( \sim 2 \text{ eV} \) is due to the high decay rate of the \( 3d^3 \rightarrow 3s + e_{\text{ICD}} \) transition which nearly completely suppresses the 'direct' \( 3d^3 \rightarrow 2p + e_{\text{ICD}} \) process (see column 6 in Table 1). According to our calculations, the \( 3s + 3s \rightarrow 2p + e_{\text{ICD}} \) transition is also much more efficient compared with the other secondary ICD transitions and, therefore, is the dominant decay mode in the second stage of the decay giving rise to the peak at \( \sim 11.6 \text{ eV} \). We note that relaxing via a two-step ICD cascade produces up to 1.5 times more ions compared with the direct ICD transition, the upper limit corresponding to the case when all atoms that have relaxed to their \( 3s \) excited state in the first ICD step decay pairwise in a second ICD transition.

Discussion

Let us discuss the intensity and the shape of the peak at around \( 11.6 \text{ eV} \). We see that the peak becomes more prominent at higher FEL intensities, has an asymmetric shape, and a developing

| Label | Primary ICD Process (Intra-Rydberg ICD) | Secondary ICD Process (Cascade ICD) | Estimated ICD electron energy | Observed ICD electron energy | Estimated ICD lifetime |
|-------|----------------------------------------|------------------------------------|------------------------------|-----------------------------|------------------------|
| 1     | \( 3d + 3d \rightarrow 2p + e_{\text{ICD}} \) |                                    | 18.6 eV                      | -                           | 87.8 ns                |
| 2     | \( 3d + 3d \rightarrow 3s + e_{\text{ICD}} \) |                                    | 2 eV                         | 1.8 eV                      | 9.2 fs                 |
| 3     | \( 3s + 3s \rightarrow 2p + e_{\text{ICD}} \) |                                    | 11.6 eV                      | 11 eV                       | 18.3 ps                |
| 4     | \( 3s + 3d \rightarrow 2p + e_{\text{ICD}} \) |                                    | 15.1 eV                      | -                           | 0.5 ns                 |

Table 1 | Electron energies of possible transitions.

Note that relaxing via a two-step ICD cascade produces up to 1.5 times more ions compared with the direct ICD transition, the upper limit corresponding to the case when all atoms that have relaxed to their \( 3s \) excited state in the first ICD step decay pairwise in a second ICD transition.
plateau on the low-energy side. Bostedt et al.\textsuperscript{27} reported a similar feature in the photoelectron spectra of small argon clusters recorded at 38.7 eV. They suggested a multi-step ionization model, where sequential 1-photon–1-electron photionization is assumed, and the plateau is attributed to the deceleration of the electrons by the developing attractive Coulomb potential of the cluster ion. In the present experiment, the $3s + 3s \rightarrow 2p + e_{\text{ICD}}$ process can take place after at least two primary ICD transitions have produced two positive charges in the cluster. Therefore, in the multi-step ICD process one can expect a deceleration of the ICD electrons by the accumulation of positive ions along the $3d \rightarrow 3s \rightarrow 2p$ cascade, shifting the energies of the emitted ICD-electrons and thus forming a plateau in the electron spectrum. In addition, the increase of the cluster potential by charge accumulation would result in trapping the low-energy ICD electrons and thus nanoplasma formation. The intensity ratio of thermal electrons to ICD electrons increases with the increase in ICD-electrons and thus forming a plateau in the electron spectrum.

The results on helium droplets at the resonance derived from the same excitation of neon clusters\textsuperscript{24} may be more closely related to the present work. In the present experiment, the nanoplasma formation was significantly reduced by removing the same electron with a 19 eV photon (corresponding to the $3d \rightarrow 3p$ transition). In addition, the decay rate depends as $1/t_{\text{ICD}}$ on the virtual-photon energy, which also largely favours the $3d + 3d \rightarrow 3s + e_{\text{ICD}}$ transition. The ionization cross-section for removing a 3d electron with a 2 eV photon (corresponding to the $3d \rightarrow 3s$ transition) is about 3 orders of magnitude larger than the cross-section for removing the same electron with a 19 eV photon (corresponding to the $3d \rightarrow 2p$ transition). In addition, the decay rate depends as $1/t_{\text{ICD}}$ on the virtual-photon energy.

We note also that since the model does not take the cluster dynamics into account and assumes that all excited pairs have decayed by ICD to produce electrons with the respective energies, it is not sensitive to the initial population of $Ne^+(2p^3d)$ in the cluster and, therefore, to the FEL intensity.

Theoretical modelling. The present calculations were performed by solving a system of coupled rate equations that describes the population of the excited atoms decaying pair-wise by a cascade of ICD processes. For extracting the rate constant for the intra- and inter-shell ( comunidad) ICD transition in a Ne cluster was approximated as a centered cubic system with a lattice constant of 4.4 Å (corresponding to a nearest-neighbor distance of 3.1 Å) filling a sphere with a radius of 29.6 Å, resulting in a cluster of 5,017 neon atoms. Assuming that the FEL pulse can excite about 10% of the atoms in the cluster, the total decay rate (width) of each transition was obtained as the sum of the partial ICD widths, $\Gamma$, of all possible pairs of 500 randomly-distributed excited atoms estimated via equation (1). The latter was derived by expanding the Coulomb transition matrix element between the ICD initial and final electronic states of the dimer in a multipole series, and keeping only the dipole–dipole term.\textsuperscript{5,6} In this asymptotic approximation, the ICD width is the product of the transition probabilities for the radiative de-excitation in one of the atoms and for the photoionization of the other one. Those transitions are characterized by the excitation oscillator strength $f$ and by the photoionization cross-section $\sigma$ which were computed at the Hartree-Fock level. We note that although within this approximation the radiative transition $3d \rightarrow 3s$ is dipole-forbidden, the ICD process $3d + 3d \rightarrow 3s + e_{\text{ICD}}$ is allowed, since the outgoing electron carries the angular momentum required for the conservation of the total momentum in the Coulomb matrix element.

Moreover, in a large cluster the orbital momentum is no longer a good quantum number as the atomic orbitals overlap locally to form mixed states. Thus, a strict distinction between $p$ and $d$, and so on. Rydberg state is nearly impossible. The important difference is between intra- and inter-shell transitions. That is why, in order to estimate the ICD width for $3d + 3d \rightarrow 3s + e_{\text{ICD}}$ transition on the same level of theory, the oscillator strength of the atomic dipole-allowed $3d \rightarrow 3p$ transition was utilized in equation (1). This is a rough assumption, but the model is not very sensitive to the exact value of the oscillator strength. It can be a few orders of magnitude smaller than that estimated by the FEL process. This is a result of the other quantities entering in equation (1), the ionization cross-section $\sigma$ and the virtual photon energy $\omega$, which also largely favour the $3d + 3d \rightarrow 3s + e_{\text{ICD}}$ transition. The ionization cross-section for removing a 3d electron with a 2 eV photon (corresponding to the $3d \rightarrow 3s$ transition) is about 3 orders of magnitude larger than the cross-section for removing the same electron with a 19 eV photon (corresponding to the $3d \rightarrow 2p$ transition). In addition, the decay rate depends as $1/t_{\text{ICD}}$ on the virtual-photon energy.

Data availability. The data that support the findings of this study are available from the corresponding author on reasonable request.

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Author contributions

The experiment was conceived by K.N., A.I.K., M.Yao and K.U. The experiment was prepared and carried out by K.N., K.Ma, H.F., K.Mo, T.N., T.S., T.T., S.M., S.W., K.C.P., A.I.K. acknowledge the financial support of ERC under AdG no 227597 and partially of DFG Research Unit 1789. P.V.D. acknowledges financial support from the LOEWE focus-project ELCH.

Additional information

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