Novel Collective Autoionization Process Observed in Electron Spectra of He Clusters

Y. Ovcharenko,[1,*] V. Lyamayev,[2] R. Katzy,[2] M. Devetta,[3] A. LaForge,[2] P. O'Keeffe,[4] O. Plekan,[5] P. Finetti,[5] M. Di Fraia,[5,6] M. Mudrich,[2] M. Krikunova,[1] P. Piseri,[3] M. Coreno,[4,5] N. B. Brauer,[7] T. Mazza,[8] S. Stranges,[9,10] C. Grazioli,[5,10,11] R. Richter,[5] K. C. Prince,[5,10] M. Drabbels,[7] C. Callegari,[5] F. Stienkemeier,[2] and T. Möller[1,†]

[1]*Institut für Optik und Atomare Physik, TU Berlin, 10623 Berlin, Germany*
[2]*Physikalisches Institut, Universität Freiburg, 79104 Freiburg, Germany*
[3]*CIMAINA and Dipartimento di Fisica, Università degli Studi di Milano, 20133 Milano, Italy*
[4]*CNR Istituto di Metodologie Inorganiche e dei Plasmi, 00016 Monterotondo Scalo, Italy*
[5]*Elettra-Sincrotrone Trieste, Basovizza, 34149 Trieste, Italy*
[6]*Department of Physics, University of Trieste, 34128 Trieste, Italy*
[7]*Laboratoire de Chimie Physique Moléculaire, Ecole Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland*
[8]*European XFEL GmbH, 22607 Hamburg, Germany*
[9]*Dipartimento di Chimica e Tecnologie del Farmaco, Università La Sapienza, 00185 Rome, Italy*
[10]*IOM-CNR TASC Laboratory, Basovizza, 34149 Trieste, Italy*
[11]*Department of Chemical and Pharmaceutical Sciences, University of Trieste, 34128 Trieste, Italy*

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The ionization dynamics of He nanodroplets irradiated with intense femtosecond extreme ultraviolet pulses of up to 10^{13} W/cm^2 power density have been investigated by photoelectron spectroscopy. Helium droplets were resonantly excited to atomiclike $2p$ states with a photon energy of 21.4 eV, below the ionization potential (I_p), and directly into the ionization continuum with 42.8 eV photons. While electron emission following direct ionization above I_p is well explained within a model based on a sequence of direct electron emission events, the resonant excitation provides evidence of a new, collective ionization mechanism involving many excited atomiclike $2p$ states. With increasing power density the direct photoline due to an interatomic Coulombic decay disappears. It indicates that ionization occurs due to energy exchange between at least three excited atoms proceeding on a femtosecond time scale. In agreement with recent theoretical work the novel ionization process is very efficient and it is expected to be important for many other systems.

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With the advent of short-wavelength free-electron lasers (FELs) the interaction between intense, high-energy light pulses and matter has become a very active field of research [1–3] and one of the most exciting topics in atomic and molecular science. Key questions are related to ionization dynamics on an atomic level, answers to which will help to develop an understanding of processes in more complex systems. In pioneering experiments and theoretical studies, various new phenomena such as absorption enhancement [1,4], bleaching [3,5,6], as well as modification [7] and suppression [8] of electron emission were discovered.

At high power densities a nanoscale sample, such as a large molecule or cluster, can absorb a large number of photons and the system undergoes a transition to a highly excited, nonequilibrium state. Ionization in this case is strongly interlinked with correlated electron dynamics, either due to multielectron collisions with energy exchange [7] or by novel types of autoionization processes related to interatomic Coulombic decay (ICD), as predicted recently [9]. According to this work, clusters resonantly irradiated by intense light pulses with photon energies insufficient to ionize the atoms by single photon absorption are efficiently autoionized due to the energy exchange between two excited electrons [Fig. 1(a)]. As a result, an unusual form of a collectively excited, plasmalike state may be formed which is expected to autoionize on a fs–ps time scale [9]. Initial evidence for such an ionization process in Ne clusters has been reported recently [10,11].

In this Letter we report a study of electron emission from He clusters irradiated by intense pulses from the new seeded-FEL FERMI [12] at power densities where such collective autoionization (CAI) processes are expected to occur [13]. He droplets were either resonantly excited to the $2p$ atomiclike state [14], which is well below the ionization potential (I_p), or excited into the continuum. The electron spectra recorded following excitation to the $2p$ state provide evidence for a new ionization mechanism.

The experiment was performed at the low density matter beam line [15], at the FERMI FEL [12]. FEL pulses with photon energies of 21.4 and 42.8 eV having a wide range of pulse energies (0.5–60 μJ) were focused by a Kirkpatrick-Baez optical system [16] to a spot size of around 75 μm (FWHM) diameter. The FEL polarization was chosen to be linear and the axis to be perpendicular with respect to a

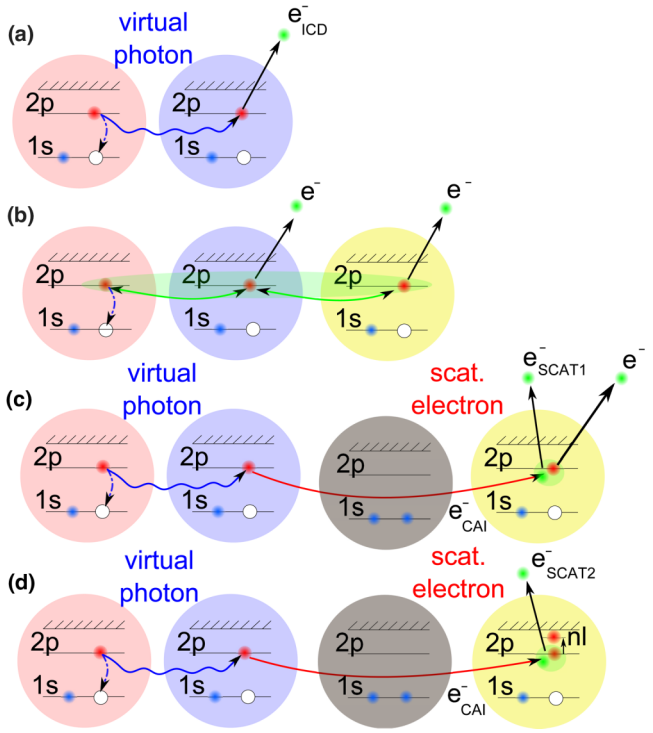

FIG. 1 (color online). Schematic diagrams of (a) ICD [9], (b) CAI type process involving three excited atoms, and (c),(d) CAI with electron scattering on a third neighboring excited atom (for details see text).

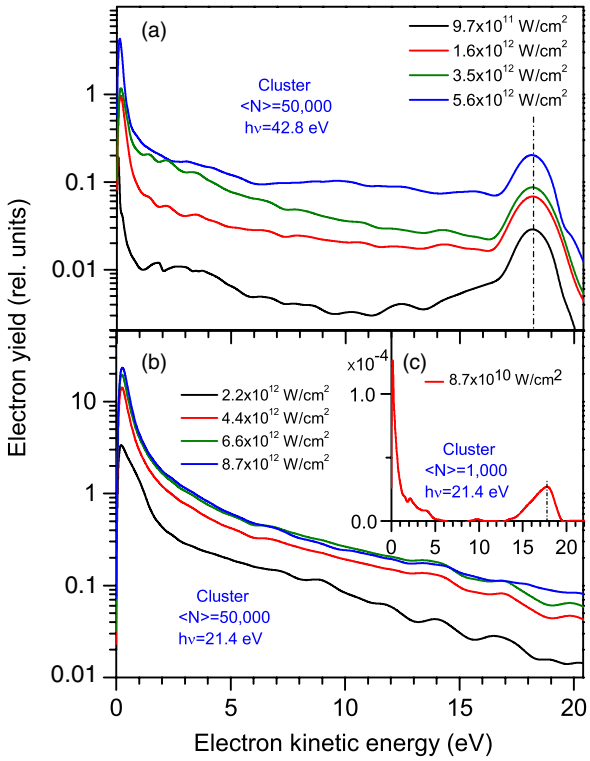

FIG. 2 (color online). Comparison of the photoelectron spectra of nanodroplets ($N \approx 50\,000$) irradiated at 42.8 (a) and at 21.4 eV (b) photon energy for different power densities. The inset (c) depicts photoelectron spectrum of small nanodroplets ($N \approx 1000$) at 21.4 eV for low power density.

detector axis, while the estimated pulse length is 100 fs (FWHM). The power density is calculated to be in the 10^{10}–10^{13} W/cm^2 range. He nanodroplets containing on average up to 50 000 atoms were produced in a supersonic expansion of He gas at 50 bar stagnation pressure through a conical nozzle (100 μm diameter, half-opening angle of 45°) cooled to 17 ± 0.1 K. The kinetic energy distribution of emitted electrons was determined using a velocity map imaging (VMI) spectrometer with an energy resolution of 4%. The kinetic energy distributions were reconstructed using a standard Abel based inversion method [17], taking into account the calibration curve of the VMI spectrometer. The uncertainty of kinetic energy distribution may be larger than the statistical noise since background subtraction was applied.

Photoelectron spectra for direct ionization at 42.8 eV (above I_p) and for resonant excitation below the I_p to the $2p$ cluster state at the absorption maximum around 21.4 eV [14] are presented in Figs. 2(a) and 2(b), respectively. Note that the total energy deposited into the system by two 21.4 eV photons and one 42.8 eV photon is the same. While these photoelectron spectra have some similarities, there is an important difference: for resonant excitation the direct photoline expected at ~18 eV [assuming a resonant two-photon ionization process or an autoionization process according to Fig. 1(a), see below] is only observed in measurements for small clusters [average $N = 1000$ atoms, see Fig. 2(c)].

The photoelectron spectra following direct ionization [Fig. 2(a)] reveal similar characteristics to those found for Ar clusters [8]. This has been explained with a sequence of direct electron emission events in the developing Coulomb field. While the cluster absorbs many photons, electrons are ejected one after the other leading to a charging of the cluster. As a result, electrons emitted at later stages need to overcome the Coulomb potential of the charged cluster and lose energy [8,18]. At the highest power densities a nanoplasma is formed, where ionization is frustrated due to the deep cluster potential. This leads to evaporative electron emission, which is characterized by a thermal tail in the photoelectron spectrum with an exponential distribution. This behavior is also observed for He nanodroplets excited at 42.8 eV photon energy. For the highest power densities there are two prominent maxima (~0 and ~18 eV) with tails in opposite directions, due to both the sequence of direct electron emission events and the electron evaporation from the nanoplasma.

For the resonant excitation case [Fig. 2(b)] a clear photoline is observed only for the small clusters [Fig. 2(c)]. It can be explained as either due to nonsequential resonant two-photon ionization, which is an instantaneous process, or due to the ICD type process

mentioned above and illustrated in Fig. 1(a). This peak corresponds to a line observed at even lower power density with synchrotron radiation [19]. Since its relative intensity at high power density is rather low [20], we can conclude that this is due to the ICD type decay, as we will show below. For bigger clusters the photoline is completely absent providing evidence of CAI involving several—we propose at least three—electronically excited atoms. Furthermore, inelastic electron-electron collisions are expected to play an important role [7]. In the following we present a phenomenological explanation of our observations. For a correct interpretation, sophisticated modeling is needed, taking into account band formation, excitation transfer, decay rates, e.g., in a Fano-Stieltjes approach [21], as well as multielectron [7] and ion dynamics. All these processes are highly density dependent and modeling is beyond the scope of this Letter.

For the purpose of understanding the ionization dynamics in such a complex system involving many different processes, we will restrict our description to a three-atom model. If more excited atoms are involved, the processes are expected to be rather similar. Three electronically excited atoms in direct contact can exchange energy by a virtual photon as electrons in two different atoms do [9]. In addition, these excited atoms can be considered as a triply excited state of a trimer, surrounded by a shell of ground state atoms. Since the width of the $2p$ excitation in big He clusters is very large (FWHM more than 0.5 eV, [14]), a simple model as depicted in Fig. 1(b) can be applied which neglects the effect of Coulomb blockade [22]. In the simplest approach approximately 3×21.4 eV energy is stored in the triply excited trimer which is sufficient for double ionization of a He dimer (~ 52 eV [23]) and thus also for the He trimer. The process can proceed either in one step,

$$\begin{aligned} &\mathrm{He}^*(1s2p)\mathrm{He}^*(1s2p)\mathrm{He}^*(1s2p) \rightarrow \\ &\mathrm{He}(1s^2)\mathrm{He}^+(1s)\mathrm{He}^+(1s) + 2e^-, \end{aligned} \tag{1}$$

or in two steps

$$\begin{aligned} &\mathrm{He}^*(1s2p)\mathrm{He}^*(1s2p)\mathrm{He}^*(1s2p) \rightarrow \\ &\mathrm{He}(1s^2)\mathrm{He}^+(1s)\mathrm{He}^*(1s2p) + e^-_{\mathrm{CAI}} \rightarrow \\ &\mathrm{He}(1s^2)\mathrm{He}^+(1s)\mathrm{He}^+(1s) + e^-_{\mathrm{SCAT}_1} + e^-, \\ &\text{or} \quad \mathrm{He}(1s^2)\mathrm{He}^+(1s)\mathrm{He}^*(1snl) + e^-_{\mathrm{SCAT}_2}. \end{aligned} \tag{2}$$

In the first case, the nonsequential process (1), the coupling between the three $2p$ electrons is even stronger and thus an excess energy of ~ 15 eV can be shared between the two electrons either by the shake-up or shake-off processes in resonantly, multiply excited atoms [24,25]. This can result in a broad continuum as seen in our experiment [Fig. 2(b)]. Single ionization resulting in the emission of one electron with ~ 39 eV kinetic energy is expected to be less likely since the overlap between the wave function of the free, high energy electron and that of the $2p$ electrons is very small.

In the second case (2), the situation is similar to the process involving two excited atoms [see Fig. 1(a)] [9], but after autoionization the free electron either ionizes the third excited atom [Fig. 1(c)] or promotes the excited electron to higher Rydberg states [Fig. 1(d)]. The cross sections for such inelastic processes are very large (2000–3000 Mb [26]); thus, we assume that they take place with close to unit probability. As a result, an almost continuous electron distribution is expected since the primary electron can lose energy due to inelastic collisions as depicted in Figs. 1(c) and 1(d).

In the case when three excited atoms are in direct contact [Fig. 1(b)], inelastic collisions are expected to be even more efficient and dominant. In addition, the interaction and subsequent autoionization of two neighboring electronically excited atoms can be affected by He ions nearby which may lead to autoionization of one of the excited atoms.

In general, the decay rate for processes (1) and (2) depends sensitively on the interatomic distance of excited atoms and the number of participating neighbors [21]. Therefore, we expect that once the interatomic separation decreases and at the same time the number of $2p$ excited atoms increases the ionization rate will be dramatically enhanced. Before discussing this aspect in detail we point out that under our experimental conditions (power density of 10^{13} W/cm^2) a large population of $2p$ states can be created within a few fs. Using the estimated value of $2p$ excitation cross section of 25 Mb [19] we expect that $\sim 50\%$ of the atoms are in $2p$ excited states within 20 fs. In other words, a very unusual plasma is formed during the duration of the light pulse. Thus, within a few fs, $2p$ excited atoms are formed in direct contact allowing ionization to take place.

Now it is necessary to explain why for the resonant $2p$ excitation the clear photoline at ~ 18 eV is present only for small clusters at rather low power density. There are two reasons for this: first, ionization from the plasmalike state with three or more excited atoms in direct contact is substantially faster than the autoionization due to the energy exchange between two excited atoms [9]; second, the isolated doubly excited dimers are only present in the first few fs, while the estimated decay time is much longer, presumably in the ps time regime (see below). In other words, the decay channel of two isolated excited atoms giving rise to a photoline is quenched long before it has time to occur. In addition, in a small cluster most of the free electrons are created near the surface, which suppresses further inelastic collisions. Based on the $2p$ photoexcitation and the $2p$ photoionization cross sections of 25 [19] and 0.02 Mb [27], respectively, we obtain an ionization fraction of 0.6% due to resonant two-photon ionization at the end of

the 100 fs FEL pulse with power density of 10^{13} W/cm^2. If the photoline [Fig. 2(c)] had resulted from a nonsequential resonant two-photon ionization process, the intensity ratio of the photoline to thermal electrons would increase with power density, in striking contrast to our results. If it is due to the ICD type ionization process we have a natural explanation why it disappears with increasing power density. The characteristic time constant of the autoionization process involving two $2p$ excited atoms can be estimated by the virtual photon model [9,21]

$$\Gamma(R) = \frac{3cf\sigma}{\pi\omega^2} \times \frac{1}{R^6}, \tag{3}$$

where f is the oscillator strength of the excitation transition, σ is the ionization cross section from the excited state, ω is the virtual-photon energy, and R is the internuclear distance. Using atomic data, i.e. the oscillator strength for the $1s \rightarrow 2p$ transition in He of $f = 0.29$ [28], photoionization cross section of $He^*(1s2p)$ excited state of 0.02 Mb [27], and equilibrium distance of 3.58 Å [29], we find a decay lifetime for the process of about 52 ps. However, the virtual photon model considerably underestimates the decay rate due to neglect of the orbital overlap [9,21]. More reliable results are expected from *ab initio* methods, by means of which the doubly excited Ne dimer was predicted to undergo an enhancement of the decay width by a factor of 20 [9]. Thus, assuming a similar enhancement for the He dimer, the decay time is expected to be ~2.5 ps. For the three or more excited atoms case [Fig. 1(b)], we expect that the process can be even faster. Since the rate is expected to be proportional to the number of neighbors [21] by going from two to three atoms the gain increases by a factor of 2.

The second important aspect is that according to our estimates, at high power densities isolated, doubly excited dimers are expected to be present only in the first few fs of the light pulse. The populations of electronically excited dimers, trimers, and higher oligomers n_s (s is the number of atoms in the oligomer) embedded in the droplets can be derived with percolation theory [30]. Here we give some estimates. At very low power density the population n_s is a function of excitation probability p and follows a simple power law $n_s = p^s$. If the excitation probability approaches a critical value p_c electronically excited atoms build a "continuous network"; thus, a plasma is formed with more than 4 nearest neighbors in a liquid with average coordination number of 12 [30]. Therefore, we expect that as soon as 3 or 4 excited atoms are formed in direct contact, one can see a plasma type, broad continuous electron emission. This critical number p_c is rather small. If 12% of atoms within a nanodroplet are excited such a network will be formed at the expense of dimers, trimers, and larger isolated oligomers [30]. At 10^{13} W/cm^2 12% of atoms are excited within less than 3 fs. This is almost 1000 times shorter than the characteristic ICD type autoionization decay rate estimation (~2.5 ps, see above) of an *isolated* doubly excited dimer. In other words, the probability to decay via this channel is only 10^{-3}, which is in line with our findings that at high power densities ($> 10^{12}$ W/cm^2) the photoline is absent.

While rigorous calculations are necessary to verify these conclusions, the model based on multiply excited trimers and larger oligomers does give a natural explanation as to why the photoline is absent at high power densities.

Our interpretation of the ionization process is further supported by the measured electron yields. The total electron yields versus FEL intensity at 21.4 and 42.8 eV are depicted in Fig. 3. Experimental points are obtained by integrating the single-shot VMI images and binning them (5 μJ/step) according to the incoming pulse energies. The experimental results demonstrate that the electron yield of resonant $2p$ excitation (dots) is much higher than that of *direct* excitation into the continuum above the I_p (triangles). Such behavior is expected in view of the results recently predicted for the ICD of Ne clusters [9]. The yield for the direct photoionization process (42.8 eV, DPI in Fig. 3) is lower than the electron emission rate at 21.4 eV (ICD), calculated for the ICD process with two excited atoms involved. In these calculations it is assumed that all atoms in the cluster can be excited and that after the pulse

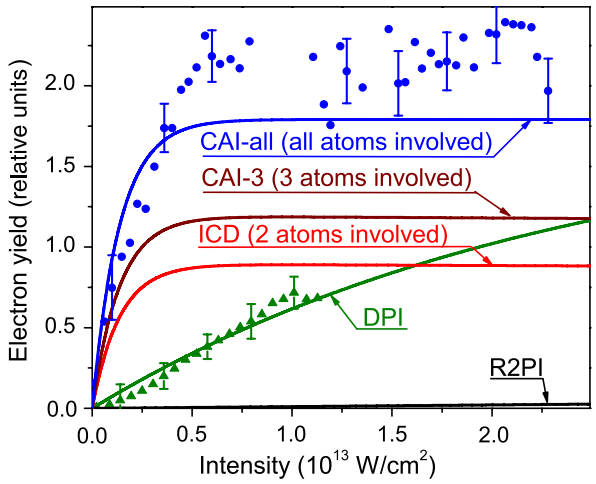

FIG. 3 (color online). Total electron yield vs FEL intensity for two different photon energies. Dots and triangles represent the experimental data at 21.4 and 42.8 eV, respectively. R2PI and ICD indicate theoretical electron yields for the resonant two-photon ionization process and ICD process at 21.4 eV, respectively. CAI-3 and CAI-all represent the theoretical yield for the CAI process where three and all excited atoms are involved, respectively. DPI shows the rate for the direct photoionization process at 42.8 eV ($\sigma_i \approx 2.89$ Mb [31]). The theoretical electron yields are normalized to the experimental data through the DPI process.

all excited atoms decay by the ICD process. Although the details of autoionization involving two, three (CAI-3), or many excited atoms (CAI-all) are different, the total electron yield is expected to be rather similar since it is only governed by the large single photoabsorption cross section of the He $1s \rightarrow 2p$ transition, at least at high power density. Since the CAI process is very efficient, one would expect that after the pulse, every excited $He^*(1s2p^1P_o^1)$ atom in the droplet will undergo CAI, producing a number N_{CAI} of He ions. N_{CAI} is estimated as the number of excited atoms multiplied by 2/3 and 21.4/24.6 (all deposited energy is used for ionization) in the three and many excited atom models, respectively. The discrepancy between the experimental data and rate estimation at the 21.4 eV photon energy is reasonable since the estimation takes into account neither the power density dependence of the absorption cross sections nor secondary processes depicted in Fig. 1(c) nor the charging up of the cluster [8]. All in all, our results confirm work on ion yields [13]. In that work [13] discrepancies between calculation and the measured data were attributed differently, namely, to uncertainties of the power density and atomic cross sections.

In conclusion, we have studied electron dynamics of He clusters excited resonantly by intense femtosecond extreme ultraviolet radiation pulses to $2p$ excited states below the ionization potential as well as directly to the ionization continuum. While the photoelectron spectra recorded by excitation into the ionization continuum can be well explained by the sequential single ionization concept [8], ionization following the resonant excitation exhibits clear evidence of a novel, collective ionization process. The electron spectra reveal that in this case a high density plasma with a very large number of electrons in bound excited states is formed. The novel ionization mechanism is characterized by fast energy exchange and subsequent autoionization of at least three electrons in excited states. The process is of quite general character and is expected to be important for many other systems, such as weakly bound clusters and nonmetallic nanoparticles, especially considering the fact that it is extremely efficient.

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*Corresponding author.
yevheniy.ovcharenko@physik.tu-berlin.de
†Corresponding author.
thomas.moeller@physik.tu-berlin.de

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