Ionization of Clusters in Strong X-Ray Laser Pulses

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The effect of intense x-ray laser interaction on argon clusters is studied theoretically with a mixed quantum/classical approach. In comparison to a single atom we find that ionization of the cluster is suppressed, which is in striking contrast to the observed behavior of rare-gas clusters in intense optical laser pulses. We have identified two effects responsible for this phenomenon: A high space charge of the cluster in combination with a small quiver amplitude and delocalization of electrons in the cluster. We elucidate their impact for different field strengths and cluster sizes.

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The advent of femtosecond laser pulses has triggered numerous activities in the field of laser-matter interaction. In particular novel, nonlinear processes in atoms induced by the available *high intense* fields from these ultrashort pulses have been a challenge for experiment and theory [1,2]. To understand more generally the energy transfer from intense laser light to matter, complex targets such as atomic clusters have been studied [3–6]. These experiments received considerable attention due to the observed dramatic effects like emission of very fast ions [3] and electrons [4] or the production of coherent x-ray radiation [5]. So far such studies are almost exclusively restricted to visible or infrared wavelengths [7]. The new x-ray free electron laser (XFEL) sources, under construction at DESY in Hamburg [8] and at the LCLS in Stanford [9], will change this situation. They can deliver intense laser pulses at *high frequencies* [from vacuum ultraviolet (VUV) to hard x-ray] and thus open a new regime of strong-field atomic physics.

Here we present theoretical investigations of x-ray (frequency $\hbar\omega = 350\,\mathrm{eV}$, i.e., wavelength $\lambda \approx 3.5\,\mathrm{nm}$) laser interaction with argon clusters at intensities of $I \approx 3.5 \times 10^{14} \ldots 3.5 \times 10^{18}\ \mathrm{W/cm^2}$. In this laser regime the interaction is notably different from long-wavelength pulses which is evident from the ponderomotive energy $E_{\mathrm{pond}} \sim I/\omega^2$. It represents the average kinetic energy of a free electron in a laser field, while $\Delta x \sim \sqrt{I}/\omega^2$ is the quiver amplitude of the electron, i.e., the spatial excursion in the laser field. For the given laser parameters one finds $E_{\mathrm{pond}} \approx 0.4\ \mathrm{meV} \ldots 4\ \mathrm{eV}$, vastly different from $E_{\mathrm{pond}} \approx 20\ \mathrm{eV} \ldots 200\ \mathrm{keV}$ for a 780 nm laser at the same intensities. The small ponderomotive energy has two important consequences: (i) Despite the high intensities the laser-atom interaction is of nonrelativistic and perturbative nature. The latter is also clear from the so-called Keldysh parameter γ which gives the ratio between the tunneling time and the laser period [10] and can be rewritten in terms of the binding energy E_{bind} and the ponderomotive energy E_{pond} as $\gamma = (E_{\mathrm{bind}}/2E_{\mathrm{pond}})^{1/2}$. For the L and M shells of argon with $E_{\mathrm{bind}} = 326, 249, 29.3, 15.8\,\mathrm{eV}$ we always find $\gamma > 1$ and for the inner shells even $\gamma \gg 1$. Obviously the laser period is far too small for field- or tunnel-ionization. Rather, ionization is due to single-photon absorption. (ii) Ponderomotive effects [11] are completely negligible with quiver amplitudes of $\Delta x \approx 0.0003 \ldots 0.03$ Å.

Under the aforementioned laser conditions one expects exhaustive ionization leading subsequently to a gigantic Coulomb explosion of the irradiated argon clusters, since ionization proceeds fundamentally different from that under optical laser impact. Ionization starts from the inside because photoionization cross sections at x-ray wavelengths are considerably higher for the inner shells than for the valence shells [12]. Typically the inverse rates are with $1 \ldots 10$ fs [13] much smaller than the pulse length of about 100 fs. Hence, multiple single-photon ionization is possible, in particular, because the inner-shell holes created by photoionization are refilled by Auger-like processes. The Auger decay is more or less independent of the atomic charge state and occurs fast; typical times are $0.2 \ldots 5$ fs [15]. Because of this almost instantaneous refilling of the inner shells they can be ionized many times during the pulse and thus the atoms can be efficiently "pumped dry." This occurs "inside-out" and is the exact opposite to the ionization mechanism in the visible wavelengths regime where the electrons are removed from the outside like shells of an onion [16]. Finally, local ionic charges in the cluster, generated in the course of the ionization process, may be screened by the weakly bound valence electrons of cluster atoms. Therefore, these electrons are allowed to tunnel through the barriers between the mother atom and neighboring ions. Such electrons will predominantly move *inside* the cluster since there is no field (such as the quasistatic electric field of low-frequency lasers) which would drive them away from the charged cluster into the continuum.

In order to gain insight into the laser induced dynamics we use a mixed quantum/classical approach similar to those successfully applied in studying rare-gas clusters in strong pulses of visible light [16–18]. Electrons initially bound to atoms in the cluster are not explicitly

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treated, they only enter through their binding energy. The ionization from the mother atom in the cluster, also called inner ionization, is modeled statistically by sudden transitions according to quantum mechanical rates. An inner ionization event gives birth to a quasifree electron which is subsequently propagated classically along with the ions and other quasifree electrons with all Coulomb forces included. Note that a quasifree electron is not necessarily ionized with respect to the cluster as a whole, quasifree means only inner-ionized with respect to the mother atom or ion.

The ionization/excitation dynamics in strong x-ray pulses is considerably more complicated than field [16] or tunnel [17,18] ionization in optical pulses because inner-shell electrons and intra-atomic processes are involved. For the photoionization rates we use a parametrization of the cross section which covers all charge states of atomic argon [14]. For high ionic charges the electronic binding energy can become so large that single photoionization is impossible. Nondipole effects do not have any crucial impact apart from distortions of the angular distribution of the photoelectrons [19]. For modeling the intra-atomic decay cascades we use direct Hartree-Fock calculations [15]. They provide branching ratios and decay rates for Auger, Coster-Kroning, and radiative transitions. The latter ones are typically at least 1 order of magnitude slower [15]. For the intracluster charge equilibration we calculate tunnel (or over-the-barrier) rates in analogy to [17,18]. All the rates are used to decide at every time step of the simulation whether a particular transition occurs or not. Once the electrons are created at the position of their mother ion and with their respective kinetic energy (to guarantee energy conservation in the photoabsorption process or in the Auger decay [20]) they are propagated in the field of the other particles.

From the physics described so far it is clear that the initial coupling to the laser is individual atom-photon interaction only. Hence, it is particularly interesting to see how the cluster environment affects the laser interaction which can be most clearly seen from calculations comparing atoms and clusters. The laser pulse is given by $f(t) = fs(t)\sin(\omega t)$ with the electric field strength f, the laser frequency ω, and the pulse shape function: $s(t) = \sin^2[(\frac{\pi}{2})\frac{t}{\Delta T}]$ for $0 \leq t \leq \Delta T$, $s(t) = 1$ for $\Delta T \leq t \leq 4\Delta T$, $s(t) = \sin^2[(\frac{\pi}{2})(\frac{T-t}{\Delta T})]$ for $4\Delta T \leq t \leq T$, and $s(t) = 0$ otherwise. The overall pulse length is $T = 5\Delta T$. Figure 1 shows the final charge per atom for two different clusters, Ar_{13} and Ar_{55}, compared to a single atom for a laser pulse with $\hbar\omega = 350$ eV, $T = 100$ fs, and $f = 0.1 \ldots 10$ a.u. (atomic unit). At lower field strengths ($f = 0.1$ a.u.), only a single photoionization event with one subsequent Auger decay per atom occurs independently of the cluster size. After a quite steep rise the final charge starts to saturate in the atomic case for stronger fields ($f > 0.3$ a.u.) due to the fact that single photoionization becomes impossible beyond a certain charge state of the ion

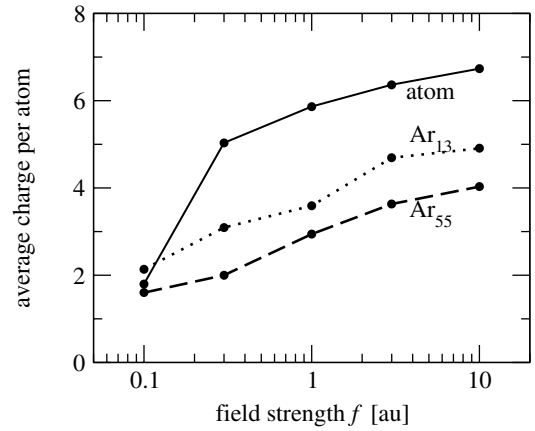

FIG. 1. Average charge per atom for two cluster sizes Ar_{13} and Ar_{55} produced by an XFEL pulse ($\hbar\omega = 350$ eV, $T = 100$ fs) as a function of the field strength f compared to atomic argon as target. The points are averages from ten simulations.

at the given photon frequency. The rise of the final charge per atom in the cluster is notably weaker. Therefore—in striking contrast to optical laser-cluster interaction—clusters are less effectively ionized at high fields than atoms. The reduction is even more pronounced for the larger cluster (cf. Fig. 1). One reason for the reduced ionization in the cluster compared to the atom is the much larger space charge produced in a cluster. At $f = 10$ a.u. the total cluster charges Q after the pulse are $Q_1 \approx 7$, $Q_{13} \approx 65$, and $Q_{55} \approx 220$ for atoms and clusters of 13 and 55 atoms, respectively. Such high space charges suppress ionization, because the absorption of one single-photon transfers only a fixed amount of energy to the electron. In our model, these postcollisional interaction effects are taken into account by the propagation of the photoionized electrons. For larger cluster and higher fields, i.e., higher space charges, one finds that an increasing number of electrons are bound at the end of the pulse to one of the fragment ions.

Figure 2 shows the energy absorbed from the laser pulse for the same clusters. This observable provides direct insight into the photoionization since all the other processes (intra-atomic decay, intracluster screening) are not influenced by the laser due to its high frequency. Surprisingly, for all field strengths considered, the absorption of photons itself is reduced in the environment provided by the cluster. This was unexpected because of the fact that predominantly deep-lying inner-shell electrons are affected and possible effects on the photoionization rates of these strongly localized electrons from neighboring ions are unlikely and in fact not contained in the model.

The time evolution of the cluster dynamics reveals that a delocalization of the valence electrons is indirectly responsible. It has mainly two effects: First, the photoionization cross sections become very small since the

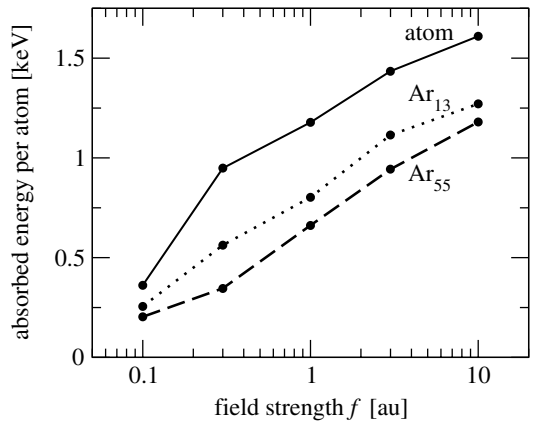

FIG. 2. Absorbed energy per atom as a function of the field strength f for the three targets and the laser pulse shown in Fig. 1.

electrons are far away from the nucleus. Second, also the Auger decay rates are reduced because the overlap with the core holes becomes smaller. Before quantifying these effects we will look at the electron dynamics in detail. Figure 3 shows the time evolution of an Ar_{55} cluster for the same pulse parameters as before at a field strength of $f = 1$ a.u. At every time step each electron is assigned to the cluster ion with which it has the largest instant binding energy. In this way we define a "hopping" time which is the time an electron stays at the same ion before it moves to another one. The upper panel of Fig. 3 shows that the average hopping time is less than 1 fs during the first half of the pulse ($t < 50$ fs). This is very short compared to typical inverse ionization rates and indicates that the electrons move almost freely inside the cluster volume. Hence, the low barriers between the cluster ions in the early phase of the pulse make inner ionization very effective. As can be seen in the middle panel of Fig. 3, a considerable fraction of the quasifree electrons has energies above the average of the barriers between adjacent ions. This will change only towards the end of the pulse ($t = 100$ fs) when due to the expansion of the cluster (cf. the cluster radius in Fig. 3) the barriers rise again.

It is difficult to assign photoionization or autoionization rates to this "sea" of electrons. However, one can give estimates of these rates using the fact that they depend in a characteristic manner on the energy of the respective bound electron. The quasifree electrons have a binding energy E_{free} (since they are still bound with respect to the full cluster). This energy will be compared to E_{bound} the binding energy of the weakest bound electron in the atom, which is among the bound electrons the most stable one against ionization. The ratios $E_{\mathrm{free}}/E_{\mathrm{bound}}$, averaged over all the electrons, are shown in the lower panel of Fig. 3. Compared to the low rates of the bound electrons the photoionization rate falls off like $(E_{\mathrm{free}}/E_{\mathrm{bound}})^{7/2}$ [12] and the Auger decay rate roughly like $(E_{\mathrm{free}}/E_{\mathrm{bound}})^{3/2}$ [21]. Because of this scaling the

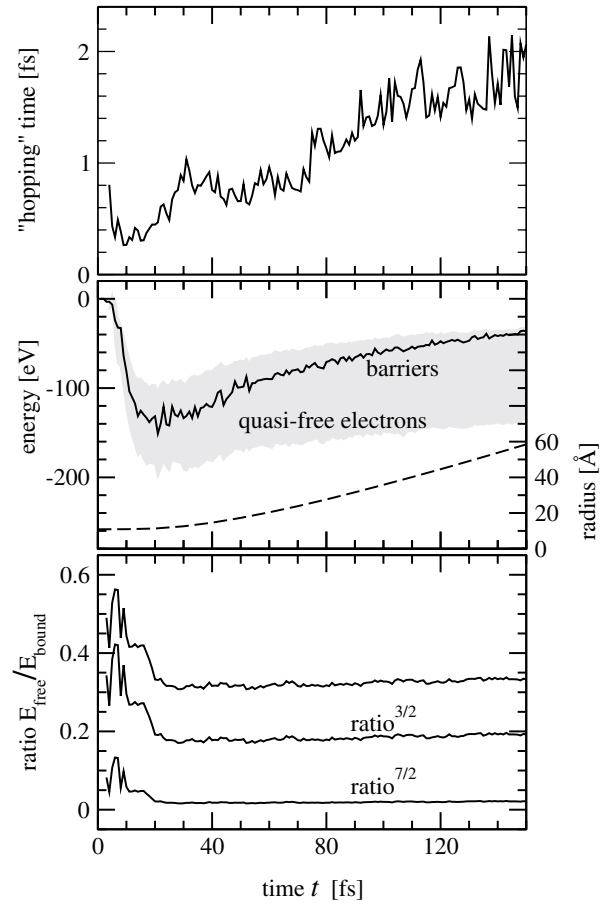

FIG. 3. Time evolution of an Ar_{55} cluster in an XFEL pulse with $\hbar\omega = 350$ eV, $f = 1$ a.u., and $T = 100$ fs. Upper panel: Average time a quasifree electron stays at a particular cluster atom. Middle panel: Energy range of quasifree electrons (mean value $\pm$ standard deviation) compared to the average of the barriers between adjacent ions in the cluster. Dashed line: Radius of the cluster, see right axis. Lower panel: Average of ratios $E_{\mathrm{free}}/E_{\mathrm{bound}}$ and powers of it; see text.

rates are reduced during the pulse by a factors of about 5 and 20, respectively. Obviously, also those electrons with energies below the barriers are still well above the highest bound electrons and hence fairly delocalized. One has to emphasize that this estimate is an upper bound since the rates decrease even more for higher angular momentum states [12,21] which are likely to be populated by the intracluster dynamics. Therefore, we regard it as save to neglect absorption of photons or autoionization of the quasifree electrons [22].

As we have seen in addition to simply lower absorption rates the reduction of photon absorption is also due to the fact that the inner shells to be ionized are no longer efficiently refilled by interatomic decay, i.e., the atoms in the cluster are temporarily hollow. In order to assess the relative importance of this effect compared to the suppression of ionization due to the cluster space charge we have repeated our cluster calculations without the

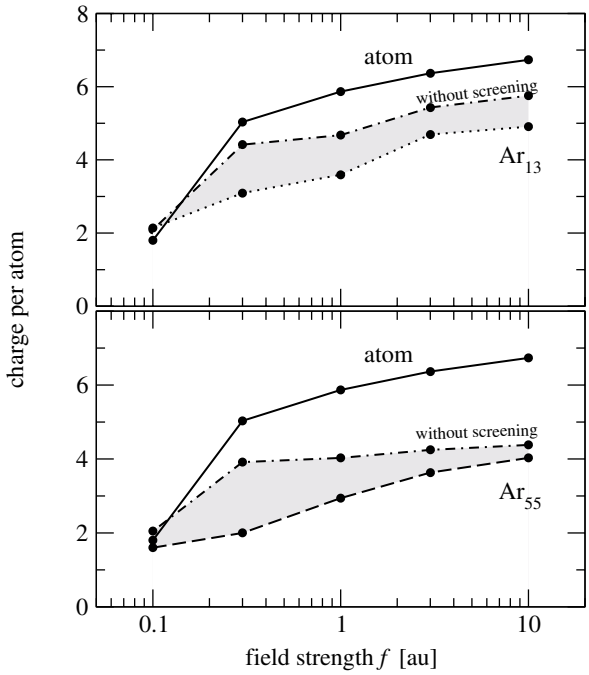

FIG. 4. Average charge per atom for two cluster sizes Ar_{13} and Ar_{55} produced by an XFEL pulse (same parameters as in Fig. 1) as a function of the field strength f. Dot-dashed line: Restricted cluster calculation where intracluster screening was precluded.

possibility for tunneling of electrons between cluster ions. Figure 4 shows the final charges from these restricted calculations for Ar_{13} and Ar_{55} along with the full calculation for these clusters and the atom. The difference between the two cluster calculations with and without tunneling (marked by gray shading in Fig. 4) accounts for the delocalization effect. The difference between the restricted cluster calculation (the dash-dotted line in Fig. 4) and that for the atom reveals the space charge effect. For field strengths $f \geq 0.3$ a.u., where differences between atom and clusters appear, the space charge effect is initially weaker. This changes for stronger fields: Whereas for the smaller cluster Ar_{13} both are of the same magnitude at $f = 10$ a.u., for the larger cluster Ar_{55} the space charge effect dominates at this field strength.

In conclusion, we have found suppression of ionization for small argon cluster compared to isolated atoms in the same pulse of intense x-ray radiation. This behavior is in striking contrast to that of rare-gas clusters in intense optical lasers. Two effects are responsible for the difference: First, the high positive space charge of the cluster hinders electron emission since the space charge is not compensated by a large quiver motion. Second, delocalization of electrons in the cluster reduces photoionization as well as autoionization drastically. Both effects are more important for the larger cluster investigated and the relative weight of both effects depends on field strength and cluster size. Our findings indicate that in general the coupling of energy from the laser light to matter is less effective at high frequencies. This has important consequences for XFEL imaging applications since it implies a higher damage threshold. That is, fragile samples might survive irradiation by intense pulses of high frequency better than anticipated.

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