Ultrafast electron dynamics and inner-shell ionization in laser driven clusters

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The ionization dynamics of small rare-gas clusters in intense, ultrafast laser fields are studied via classical trajectory Monte Carlo simulations. Our results indicate that for similar laser pulses the charge states reached by atoms in a cluster can be significantly higher than those for atoms in the gas phase. The ionization enhancement is strongly dependent on the cluster density and exhibits a rapid increase in charge state once the laser intensity has reached the threshold for single ionization. This ''ionization ignition model'' is driven by the combination of the laser field and the strong field from the ionized cluster atoms. Approximate atomic inner-shell ionization probabilities are calculated for several cluster densities and peak laser intensities and provide evidence for the generation of inner-shell holes on an ultrafast time scale. This is a necessary condition for the generation of x-ray pulses with temporal widths comparable to that of the driving laser pulses.
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I. INTRODUCTION

Small atomic and molecular clusters offer a unique environment for studying high-intensity laser-matter interactions [1–8]. While the average particle density in a gas of clusters can be almost arbitrarily small, the local particle density of each cluster is approximately that of a solid. This distinction between average and local density leads to important differences between clusters and solids, as well as between clusters and individual atoms, when they interact with strong laser fields. First, every atom in a given cluster can experience the same laser field, much like the atoms in a gas phase experiment, whereas the laser field experienced by an atom in a solid is a strong function of its position. This leads to a natural comparison between cluster and gas phase results for equivalent laser pulses, since the atoms in both cases are exposed to the same laser field but have very different local densities. Second, once significant ionization begins, the density of the cluster, though initially very high, drops rapidly, i.e., there is a ''Coulomb explosion.'' This means that there is a definite time scale for processes that are strongly density dependent, for example electron-impact ionization or recombination, both processes that are central to the production of x rays. Clusters have therefore attracted a great deal of interest as a potential source of femtosecond duration x-ray pulses for ultrafast diffraction and absorption experiments [9].

Several groups have carried out experiments on clusters ranging in size from a few up to 10 000 atoms using subpicosecond laser pulses with wavelengths between 248 nm and 1 μm and intensities up to 10^{18} W/cm^2. These experiments reveal important differences between the interaction of high-intensity light pulses with atoms in clusters as opposed to atoms in the gas phase. Among these are (i) the average charge states (the average number of electrons removed from an atom) of the ions from clusters, are distinctly higher than for equivalent laser pulses applied to atoms in the gas phase [3–8]. (ii) The observation of L- and M-shell keV x radiation from Xe, Kr, and Ar clusters [4] and from C_{60} molecules [5]. This radiation is not observed when atoms in the gas phase are illuminated with equivalent pulses. (iii) The form of the x-ray spectra observed are distinctly nonthermal and show evidence for multiple inner-shell vacancies. Boyer *et al.* [1] and McPherson *et al.* [3] have suggested that such inner-shell holes are produced via impact ionization of atoms by energetic, laser-driven electrons inside the cluster. They measured very efficient x-ray emission and speculated that the emission time for ''hard'' (kilovolt) x rays may be shorter than 1 ps [1,2,10]. Ditmire *et al.* [8] irradiated Ar clusters with ultrashort laser pulses and measured energy conversion efficiencies of up to a few percent into x-ray photons at energies up to 400 eV. Such yields are comparable to those of solid targets. Given the differences between the cluster and gas phase results, as well as the similarities between the cluster and solid target results, the high density within the cluster clearly plays an important role in the ionization dynamics.

In order to explain the unexpectedly high charge states as well as the x rays that are produced when clusters are irradiated by intense laser pulses, an understanding of the electron ionization dynamics is essential. In this paper we focus in particular on the difference between the ionization dynamics of atoms in clusters and atoms in the gas phase. To this end we have carried out computer simulations of model systems, which include 25- and 55-atom neon and 25-atom argon clusters interacting with an 800 nm, 15 fs full width at half maximum (FWHM) laser pulse. These laser parameters are within the specifications of available laboratory systems [11]. The laser intensities studied range from 5×10^{15} to 5×10^{17} W/cm^2. The highest of these intensities should be sufficient to produce Ne^{8+} in the gas phase. Ideally we would like to calculate the time-dependent dynamics of all of the electrons and ions in a small cluster during this short

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laser pulse. Even this simplified problem defies an accurate quantum-mechanical solution. Because of this, we have chosen to model the dynamics using classical mechanics. The initial conditions are Monte Carlo sampled from a microcanonical ensemble with the total energy of each particle held fixed at a specified value. This constrains the ionization energies to have their experimentally known values. The relativistic classical equations of motion for all of the electrons and nuclei are then integrated over the duration of the laser pulse. This approach admits only classically allowed ''over the barrier'' ionization and ignores tunnel ionization as well as resonant ionization, but should provide qualitative insight into the ionization dynamics and their dependence on, e.g., cluster density or cluster size. To decrease the computational labor and increase the stability of the simulations, the interaction of electrons within the same atom is suppressed. Although neon atoms are too light to be of interest as hard x-ray sources (the inner-shell binding energy is only a $\sim$1 keV), we choose this system for most of our simulations because of the manageably small number of electrons per atom. The model we employ is generic and it may be supposed that the general phenomena observed in neon clusters will also be relevant to heavier atom clusters. The argon simulations serve as a partial confirmation of this supposition.

In an intense subpicosecond laser pulse, the threshold intensity for which single ionization becomes probable is crossed very quickly. During this time the atoms are inertially confined and very strong electric fields within the cluster due to the closely packed ions can result. Assuming that each atom of a small cluster is singly ionized, the electric-field strength at its surface is of the order of 5×10^{12} V/m, which can be sufficient to further field ionize the atoms in the cluster. Indeed, it is known that the ionization potential of atoms is reduced by the close proximity of other charged particles [12]. Quantum-mechanical calculations of linear diatomic [13–15] and triatomic molecules [13] as well as experimental studies of diatomic molecules [16] have found an enhancement of the high-intensity laser-induced photoionization probability with increasing charge state for internuclear distances where there is a high probability for the electrons to be localized on one of the atomic centers. Both theory and experiment have shown that the charge states of ionized molecular fragments is greater than those that are accessible when ionizing isolated atoms of the same kind with similar laser pulses. As noted above, a similar effect has been seen in small cluster experiments as well. One of the main results of the simulations we report in this paper is that our classical ionization model also exhibits enhanced ionization driven by the combination of the intense short laser pulse and the large fields from the inertially confined ions. Since our model artificially suppresses some ionization pathways (i.e., tunnel ionization) we can expect this effect to be enhanced in more elaborate calculations.

The clusters we model have initially a density that is approximately that of a solid, and therefore electrons that are ionized before the cluster can expand experience multiple collisions with the surrounding atoms and ions before reaching the cluster boundary. Since, on the average, particles gain energy from dephasing collisions in the presence of an external field (collisional heating), the electron temperature should be higher than for isolated atoms in the gas phase. Consequently, we also calculate the electron temperature along with the electron density inside the cluster during the short laser pulse. These two parameters should be very important for the production of inner-shell vacancies in the ions and the subsequent emission of x-ray line radiation. Another interesting feature of this process in clusters is that as the cluster expands in response to the strong Coulomb repulsion between the ions, the density drops and density-dependent processes such as impact ionization and x-ray emission are quenched. Thus clusters might provide an ultrafast x-ray source, one that is ignited by a short optical pulse and quenched by a Coulomb explosion.

The first results from our classical cluster ionization model were obtained for clusters with higher densities and different atomic structures than the ones considered here [17]. These earlier simulations showed strong ionization enhancement and striking differences for the electron dynamics in clusters as opposed to the gas phase, similar to the results that we present here. At the beginning of the ionization, the nuclei in the cluster are inertially confined while the ionized electrons are substantially heated by inverse bremsstrahlung and are quickly removed from the cluster by the laser field. Thus an ultrafast pulse of hot electrons is generated that could produce inner-shell vacancies and might explain the x-ray emission found in experiments such as the ones mentioned above [1–8]. The high charge density of the ions along with the fast fluctuations of the electric field due to the electrons further enhances the ionization of the ions. This subsequent ionization proceeds very quickly and can have the appearance of an ''ionization ignition'' once the threshold intensity for single ionization is reached. This results, as we have already indicated, in an average charge state that is much higher than for atoms in the gas phase irradiated with similar laser fields. Our results are qualitative and require confirmation by quantum-mechanical calculations. However, considering the magnitude of the electric field generated by the ion cores and the ionized electrons in the cluster, they are physically reasonable and offer insight into experimentally observed processes.

In Sec. II we outline the main points of our classical ionization model and its numerical implementation. The initialization of the cluster and the calculation of valence and inner-shell electron ionization probabilities are described. Results on ionization dynamics as a function of cluster size and density are then given. We close with some discussion of the relation of our results to recent experiments.

II. CLASSICAL IONIZATION MODEL

In the regime of laser intensities and wavelengths that are of interest in cluster experiments (intensities above 5×10^{14} W/cm^2 and wavelengths of 0.25–1.0 μm), the photon energy is much smaller than all of the ionization potentials and the laser intensity is high enough to field ionize at least one of the valence electrons in the target atoms. In the gas phase a sequential ionization model, in which electrons are removed in order of increasing ionization potential as the laser intensity increases, provides a good description of the ionization dynamics. The outermost (least tightly bound) electron at any given time can be thought of as moving in the combined potential formed by the residual ion charge and the laser field. This combined potential exhibits a time-dependent barrier along the laser polarization. The ionization probability is a highly nonlinear function of this barrier, rising rapidly as the barrier height drops with increasing laser intensity. Ionization first proceeds by tunneling through this barrier for low intensities and then classically as the barrier falls below the bound-state energy, for intensities above a threshold intensity. This is qualitatively described by the barrier suppression model (BSM) [18]. In the BSM, the intensity of the external field corresponding to zero barrier height is regarded as the appearance intensity for a given charge state. The threshold intensity, $I_{\rm th}$ necessary to reach the nth charge state, is a function of the nth ionization energy (E_n) and the ion charge Q, scaling as

$$I_{\rm th} \propto \frac{E_n^4}{Q^2}. \tag{1}$$

The BSM yields a simple correlation between the intensity of the external field and the observed charge state that can be treated analytically. In gas phase experiments on rare-gas atoms, where sequential, nonresonant ionization dominates [19,20] and there are no atom-atom interactions, the barrier suppression model has been found to be a good predictor of the observed charge state reached for a given laser intensity. The failure of the isolated-atom-BSM that ignores the close proximity of high charge densities to explain the charge states observed in cluster experiments has been well documented.

A simple model of cluster ionization dynamics that takes into account the close proximity of the ionizing atoms in a cluster is to employ the BSM calculating at each time step the total field (laser plus charged particles) seen by each electron on each atomic center. This model has the disadvantage that the energy of the system at the moment of ionization is not necessarily conserved, but can jump by large amounts. This makes the classical simulations inherently unstable. In order to improve upon this simplest model, we implemented a classical trajectory Monte Carlo model (CTMC) which, in essence, allows for continuous ''deformation'' of classical orbits of bound electrons as they ionize. This method yields a stable algorithm that can be integrated to any desired accuracy.

Several authors have used CTMC simulations to study single atom, single-electron dynamics in strong laser fields [12–23]. There have also been studies of two-electron atoms [24,25]. For a one-electron hydrogenic atom, the CTMC method may be simply stated. The initial momentum and position of the electron are sampled from a microcanonical ensemble with the correct total energy (i.e., the ionization potential is specified) which amounts to choosing a Kepler orbit with the right total energy. The ionization potentials used are experimentally measured values [26,27]. It is also possible to use a known ground-state wave function to generate the distribution of initial positions and momenta. Given that multiphoton ionization rates are very sensitive to the ionization potential, this gives a distribution of ionization potentials and might create nonphysical effects. Having defined the initial conditions, we subsequently integrate the relativistic form of Newton's equations of motion for the nucleus and the electron, considering their interactions with each other and with the laser field via the Lorentz force. Integrating this one-electron model, one finds ionization thresholds very similar to the ones given by the BSM. As the field strengths increase during the laser pulse, the electron's orbit distorts until an intensity threshold is reached, whereupon the electron rapidly ionizes, i.e., it moves far from the atom with a time-averaged total energy above the ionization limit. Running many trajectories with different Monte Carlo seeds for the starting conditions yields a statistical description of the classical ionization process. This method has successfully been applied to investigate high-frequency stabilization, field ionization and high-harmonic generation [21–25].

Since we are interested in a model that describes multielectron atoms and, moreover, allows us to treat such atoms in a van der Waals cluster, we have extended the CTMC method. This task was eased by the fact that sequential ionization is the dominant ionization mechanism for long wavelengths and, in fact, our model strictly enforces sequential ionization. As with the single-electron CTMC model, N electrons are put in N-Kepler orbits such that the total energy of each electron matches one of the known ionization energies of the atom. The total energy of each bound electron is calculated assuming that it interacts with a nucleus that has an effective charge corresponding to the ionization potential assigned to that electron. This also insures the correct asymptotic behavior as the electron ionizes. As an example, for neon the first electron has $E_{\rm tot}=-1362$ eV and sees a potential due to its ''parent'' ion that falls as $-10/r$, the second has $E_{\rm tot}=-1196$ eV, and so forth on up to the 10th electron with $E_{\rm tot}=-21.6$ eV that sees a potential due to the parent ion that decreases as $-1/r$. This amounts to assuming that the $i-1$ electrons that are more tightly bound than the ith electron perfectly shield $i-1$ nuclear charges. Each electron also interacts with the external fields.

In the framework of such a classical treatment, the interelectron interaction among electrons on the same atom, even in simple atoms such as helium, can allow one of the electrons to gain sufficient energy to ionize. This is a nonphysical result that we wish to avoid. Since our primary goal is to correctly mimic ionization and not to develop a sophisticated classical atom model, we have imposed a few rules to govern the interactions within each atom so that the system behaves in a physically reasonable way.

(i) Bound electrons do not interact directly with other bound electrons. Instead, they interact with the nucleus as if the more tightly bound electrons perfectly shield an equivalent amount of positive charge.

(ii) Sequential ionization is strictly enforced by only allowing the outermost, least tightly bound electron at any given time to ionize.

(iii) A bound electron that is eligible to ionize is declared to be ionized as soon as its distance from its parent ion exceeds a critical radius r_c. As long as r_c is not chosen to be too small, the ionization is not expected to be sensitive to the particular value of r_c. In practice, we choose $r_c=300$ pm, which is of the order of the average nearest-neighbor distance of the nuclei in the cluster.

In this single atom, N-electron model, each particle, the nuclei and all electrons, interact with the laser field at all times. This allows the outermost as well as more tightly bound electron orbits to smoothly deform as the laser intensity increases. We have found, that for a single atom, this model mimics the ionization thresholds, e.g., as predicted by the barrier suppression model, quite well and we expect that it describes the strong-field, single atom multielectron ionization qualitatively.

Simulating a van der Waals cluster consisting of such atoms requires some additional simplifications with respect to the particle interactions in order to keep the computational effort manageable. The additional rules for clusters are as follows.

(i) Bound electrons do not interact with other particles outside of their atom. This influences the results of the simulations unnoticeably because bound electrons require much greater field strengths to ionize than outer electrons.

(ii) Ions interact with other ions, and with outermost and ionized electrons as if they were a single particle with a total charge that is the sum of the nuclear and remaining electron charges.

Since the more tightly bound electrons do not interact with ionized ones, there is no inner-shell ionization due to, e.g., electron impact. Thus, the ionization probabilities we calculate are conservative estimates of those likely to be found in real clusters. The interaction of bound, i.e., not yet ionized, electrons of different atoms via the ion-ion interaction improves the stability and the speed of the calculations and prevents atoms from ionizing solely because they are close to another nucleus with orbiting electrons that contain rapidly oscillating dipoles. It is important to note that even though all these constraints tend to reduce the ionization probabilities of the cluster atoms, we still observe that the results differ dramatically from the ionization of atoms in the gas phase.

The shape of the laser-pulse envelope is chosen to be proportional to cosine squared within the normalized time interval $[-\pi,\pi]$. Outside this interval the pulse amplitude is set to zero. At the beginning of each calculation, the cluster is placed in a laser-field-free region.

A. Cluster geometry

We construct clusters by initially defining a boundary volume that contains 25 or 55 atoms at approximately solid density. Within this volume the atoms are randomly placed with the constraints that no nearest-neighbor distance deviates more than 1% from a predefined value R_{nn}. Subsequently this arrangement is equilibrated at $T=0$ by potential-energy minimization using Lennard-Jones potentials for the atom-atom interactions. This relaxation reduces the total energy of the cluster by approximately 30% and is terminated when a local energy minimum is found to within a relative accuracy of 10^{-7}. The drop in total energy is mostly due to the fact that R_{nn} was chosen to be about 10% smaller than the equilibriated average nearest-neighbor distance. This allows for a faster relaxation due to the steeper gradient of the Lennard-Jones potential for distances smaller than the minimum energy distance. Since the potential surface has a large number of geometrically different minima [28–31], we do not assume that our relaxation procedure finds the global minimum. Nevertheless, the procedure constructs clusters exhibiting a shell structure that is typical for rare-gas clusters. In particular, the 55-atom cluster relaxes into an icosahedral geometry that is in accord with theoretical as well as experimental studies for heavier rare-gas atoms [32,33]. In contrast to our earlier work [16], this method generates cluster structures that exhibit smaller fluctuations of the nearest-neighbor distances of the atoms.

B. Integration of trajectories

The work involved in the calculation is about equal parts bookkeeping and numerical integration of the relativistic equations of motion. These equations are integrated using the Richardson extrapolation method [34] with an underlying second-order ''velocity Verlet'' integration scheme [35] for taking primitive steps. The adaptive step size integrator insures that at each time step the position in phase space of each particle is individually determined within the specified accuracy, which in turn insures that the phase-space trajectory of the entire system is obtained with at least this accuracy. Further details of the program that is part of the software package PARATEC++ are described elsewhere [17,36].

Throughout the computations a relative accuracy for finding the correct position of each particle in phase space of 10^{-8} is maintained. Test calculations with the relative accuracy tolerance set to 10^{-7} and 10^{-9} confirmed that we have converged results. Several other tests were performed, the most relevant being that the electron orbits are stable over several picoseconds if the laser intensity is too low to initiate ionization.

C. Inner-shell ionization

The collisional heating of ionized electrons in a laser irradiated cluster can be very efficient. These hot electrons can subsequently produce inner-shell vacancies that can in turn result in prompt emission of hard x-ray line radiation. Modeling of the exact fluorescence yield of a plasma requires the solution of coupled rate equations that describe, among other things, ionization and recombination processes and is beyond the scope of this work. Furthermore, such rate equations must be modeled along with the dynamics of the plasma interacting with the laser field, which is difficult within the framework followed here. Nevertheless, it is possible to estimate the relative ionization probabilities of various inner shells and thus the relative merit of clusters as a potential short pulse x-ray source. We assume that such impact ionization contributes little to the total dynamics. Therefore, we first simulate the electron dynamics as described above and subsequently use data collected about each particle's trajectory to calculate the probability for electron-impact ionization of inner atomic shells per cluster and calculation run.

An electron impact is assumed to occur as soon as an electron approaches an ion closer than a classical atomic radius R_a, which we take to be 154 pm for neon atoms and 188 pm for argon atoms. The particular choice of the value of R_a is found to be of insignificant influence on the relative ionization probabilities of different atomic shells. Further collisions are considered as soon as the electron has again left the classical atom volume. Assuming that electron impacts are evenly distributed over the classical atom area, the electron kinetic energy is a sufficient characteristic of the impact. Therefore, the ionization cross section Q_i is calculated according to the Lotz formula [37]

$$Q_i = \pi e^4 b_s Z_s \frac{\ln U}{U E_{c,i}^2}, \quad (2)$$

with $U = E/E_{c,i}$ being the "excess energy," defined as the ratio of the kinetic energy of the electron to the ionization energy of the level to be ionized. The parameters b_s and Z_s are chosen for a particular shell according to [36],

$$s = K: \quad Z_s = 2, \; b_s = 0.35$$

$$s = L: \quad Z_s = 8, \; b_s = 0.25.$$

The probability of ionization per electron impact is estimated by

$$P_s = \frac{Q_i}{\pi R_a^2}. \quad (3)$$

Since the absolute value of P_s is dependent on the particular choice of R_a, this quantity only serves as a relative measure for comparing ionization probabilities of different atom shells and simulation runs. However, since the probability for electron impacts is proportional to R_a^2, the total ionization probability of inner shells per calculation run is found to be quite insensitive to R_a.

III. RESULTS

We first present results for simulations of 25-atom neon clusters. For each set of parameters such as cluster density and laser intensity, typically five calculations were performed with only the seeds for the Monte Carlo sampling of the initial particle conditions varied. This amounts to varying the angular positions of each electron in its atomic orbit and to different placements of atoms in the cluster prior to the relaxation.

As discussed in the preceding section, irradiating a low-density atomic gas with an ultrashort, high-intensity laser pulse leads to an average charge state that only depends on the physical properties of the individual atom and the laser field. By simulating such a gas phase case, we find an average charge state of about 1.4 for a laser intensity of 5×10^{15} W/cm^2, which is in accord with experimental measurements. This charge state changes significantly when a cluster is used. In Fig. 1(a) it can be seen that for the 25-atom neon cluster the average charge state rises within 12 fs to approximately 2.5. Increasing the maximum laser intensity to 3.3×10^{16} W/cm^2 and finally to 5×10^{17} W/cm^2 increases the ionization until further progress becomes energetically unfavorable [Fig. 1(b) and 1(c)]. Each half cycle of the laser field further enhances the ionization until this limit. At the highest light intensities, the maximum ionization level is reached within a few femtoseconds. Examination of individual electron trajectories shows that ionized electrons do not escape the cluster immediately, but collide with the surrounding ions rather frequently. The total number of electron-ion collisions inside the cluster along with the final charge state is plotted in Fig. 2 for various laser intensities. While the final ionization level increases with increasing intensity, the total number of electron-ion collisions drops, which indicates that

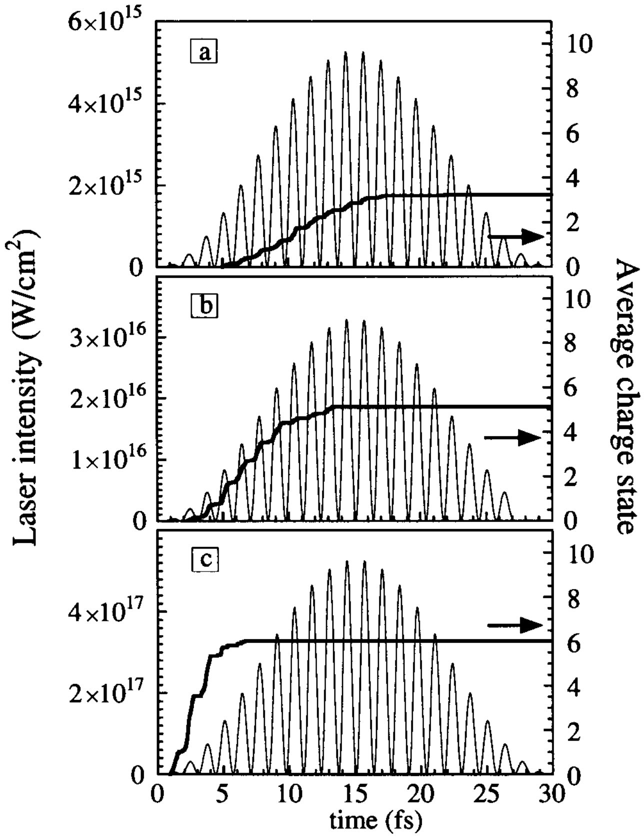

FIG. 1. Average charge state per atom as a function of time for 25-atom neon clusters at various peak laser intensities. The light line is the laser intensity and the heavy line is the charge state. The initial equilibriated cluster density corresponds to an average nearest-neighbor distance between the nuclei prior to the interaction of laser pulse and cluster of 353 pm. Peak intensities are (a) 5×10^{15} W/cm^2, (b) 3.3×10^{16} W/cm^2, and (c) 5×10^{17} W/cm^2. The relative 1 σ range for the charge state in all cases is smaller than $\pm5\times10^{-2}$. The arrows indicate the charge states reached for gas phase atoms with the same laser pulses.

the laser field removes the electrons from the cluster increasingly rapidly.

The relative probability for L- and K-shell ionization during the cluster illumination, as shown in Fig. 3 is a consequence of the dual dependence of the inner-shell ionization probabilities on the electron kinetic-energy distribution as well as on the time-dependent electron density inside the cluster. The drop in the number of electron impacts can be compensated, up to some laser intensity, by the higher kinetic energies produced by the stronger light field. With further increasing field strengths, however, the collisional heating becomes insufficient and the production of K-shell vacancies becomes less likely. Even though fewer electrons are heated to high energies, the impact ionization probability of L electrons remains approximately constant. We conclude that K-shell holes are most likely produced at intermediate laser intensities that are just high enough for efficient collisional heating but not so high as to diminish the electron density in the cluster too rapidly. The magnitude of these effects is expected to be related to the properties of the cluster, such as its size and the kind of atoms; however, in light of our argon cluster calculations discussed below this effect

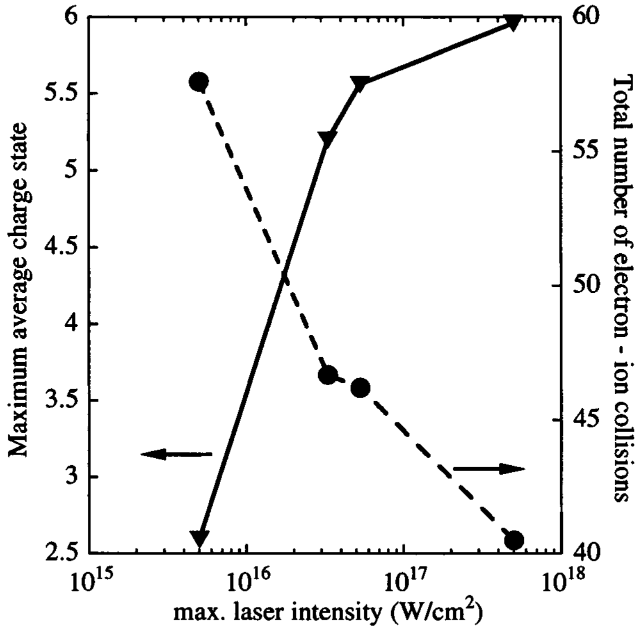

FIG. 2. Maximum charge states and total number of electron-ion impacts for constant laser-pulse length but different laser intensities, for 25-atom neon clusters. The initial cluster densities for all data shown correspond to an average nearest-neighbor distance between the nuclei of 353 pm prior to the interaction of the laser pulse and cluster.

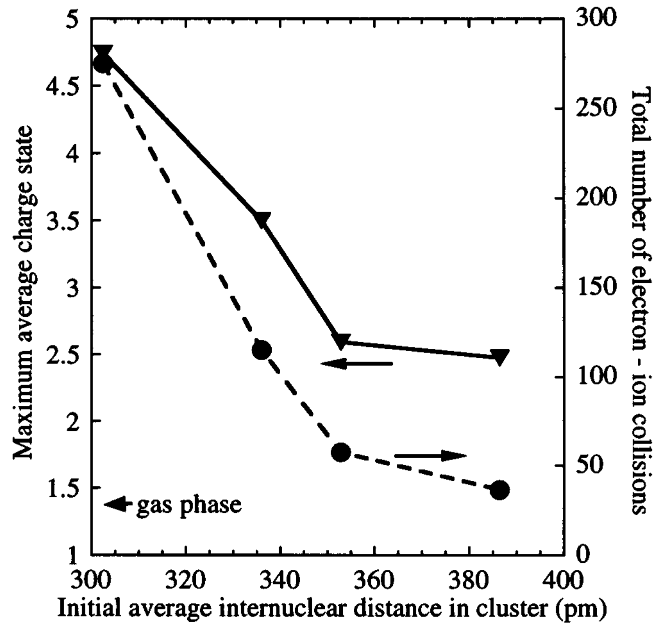

FIG. 4. Maximum charge state and total number of electron-ion impacts in 25-atom neon clusters at various average nearest-neighbor distances between the nuclei but constant laser-pulse parameters. The cluster density is varied by changing the minimum energy distance in the Lennard-Jones potential when equilibrating the cluster structure. The peak laser intensity is 5×10^{15} W/cm^2.

appears to be generic and may qualitatively carry over to other systems.

Next we investigate the influence of the cluster density on the ionization dynamics at a fixed peak laser intensity. We increase the density of the atoms in the cluster by varying the parameters in the Lennard-Jones potentials. As shown in Fig. 4, the maximum charge state of 1.4 for atoms in the gas phase increases to 4.5 for clusters with an average nearest-neighbor distance of 270 pm. We do not claim that neon clusters of such density could be experimentally produced but rather wish to illustrate the fact that the confinement of atoms in a cluster of approximately solid density significantly enhances ionization. In this scenario, the laser initiates the ionization process while at later times the high local electric-field strength produced within the plasma takes over and drives the ionization to high levels. The light field supports this process by providing the driving force necessary for collisional heating. At higher initial cluster density the average kinetic energy of the electrons rises faster. However, the maximum of the electron density is reached at later times. As a result, the higher the cluster density the more favorable the conditions for inner-shell impact ionization. This effect leads to an enhanced probability of inner-shell ionization, as shown in Fig. 5. We point out that the increase in ionization in our calculations is not due to impact ionization of inner shells because we strictly enforce sequential ionization and do not allow for direct interaction between inner-shell and ionized electrons. In this sense the results presented here are a conservative estimate of the processes to be expected in actual experiments. When the cluster size is increased the electrons will undergo more collisions while diffusing out of the cluster. This should result in stronger collisional heating and hence should further enhance the inner-shell ionization rate as long as (i) the cluster diameter is smaller than the penetration depth of the laser light into solid matter, i.e., all atoms experience the same laser field; (ii) there is no electron confinement in the cluster; and (iii) there is no significant interaction among free electrons which

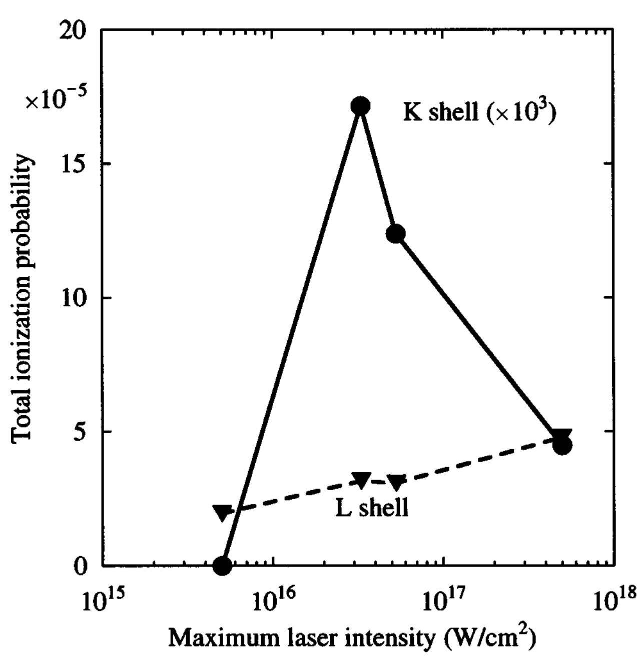

FIG. 3. Probabilities of K- and L-shell electron-impact ionization per calculation run for 25-atom neon clusters at various laser intensities and the same density as in Fig. 2.

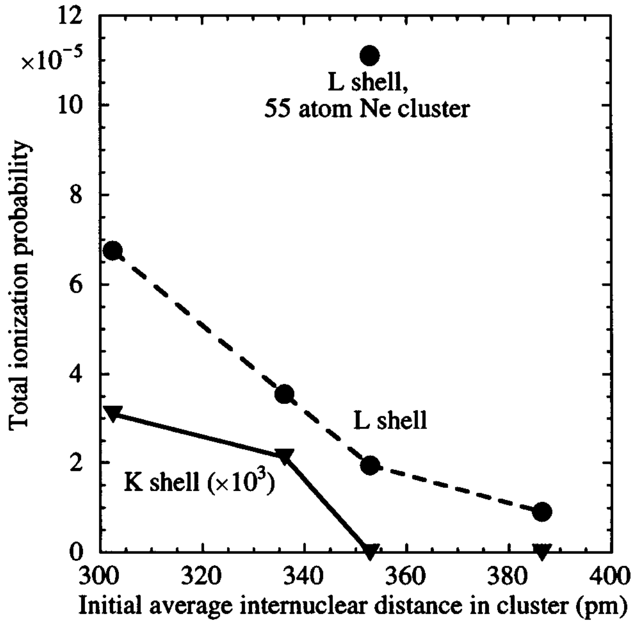

FIG. 5. Probabilities of K-shell and L-shell electron-impact ionization per calculation run for 25-atom neon clusters at various cluster densities for the same laser-pulse parameters used in Fig. 4 as well as one point for 55-atom neon clusters.

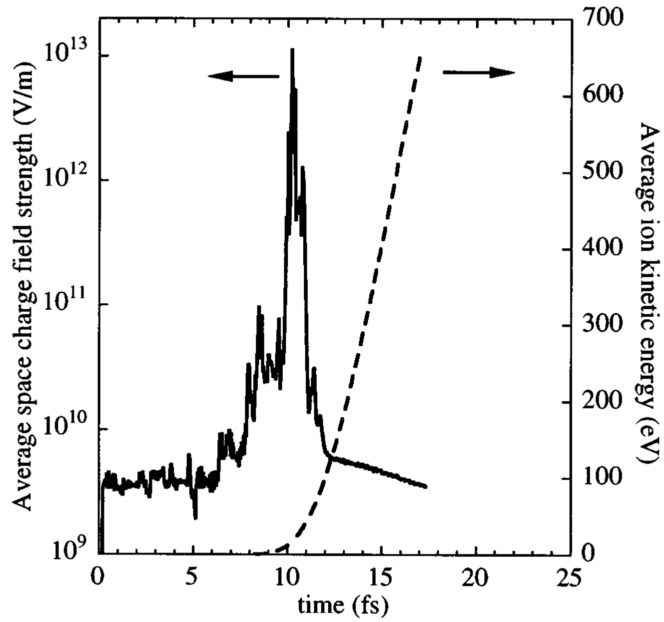

FIG. 6. Average Coulomb-field strength from other ions and ionized electrons at the position of each ion and average ion kinetic energy for a 25-atom argon cluster illuminated by a 800 nm, 15 fs (FWHM) laser pulse with a maximum intensity of 5×10^{15} W/cm^2. Note the logarithmic scale for the electric-field strength.

would lead to thermalization of the electron-energy distribution.

To illustrate the effect of increasing the cluster size, we performed simulations for 55-atom neon clusters with densities identical to the 25 atom clusters, as well as identical laser pulse parameters. These show increased heating and higher probability for inner-shell ionization. The corresponding data point is shown in Fig. 5.

The ionization features presented are also found for 25-atom argon clusters. In these simulations an initial internuclear distance of 382 pm was chosen [38]. The M shell of each argon atom in the cluster was completely ionized, producing a cluster consisting of Ar^{8+} ions within 11 fs from the beginning of the laser pulse. This ''ionization ignition'' generates a shower of electrons sufficient to ionize L-shell electrons. Due to the high K-shell ionization potential of 3205.9 eV, no vacancies in this shell are produced. Collisional heating of free electrons is insufficient to reach this energy because of the small cluster size. Increasing its size should eventually generate electrons energetic enough to produce K-shell vacancies. This is another indication that larger clusters in conjunction with heavy elements may be more likely to generate hard x rays, even though we have not evaluated the fluorescence yield itself. We emphasize that this ''ignition'' could be achieved with less particle density than in the case of neon clusters and, moreover, that this argon cluster density is typically produced under experimental conditions.

In general, for neon clusters as well as argon clusters, the density drops to one-tenth of its initial value within typically 10 fs due to the strong electric field of ions and electrons remaining in the cluster. In the case of an argon cluster with an initial average nearest-neighbor distance of 382 pm, this Coulomb explosion accelerates the ions to high kinetic energies within about 20 fs after the beginning of the laser pulse. This rapid acceleration is displayed in Fig. 6 along with the average electric-field strength at the position of each ion solely produced by surrounding ions and ionized electrons. Within 10 fs the field strength as shown in Fig. 6 rises to values of up to 10^{13} V/m, which is much higher than the peak laser-field strength of about 2×10^{11} V/m. This is, again, a signature of ''ionization ignition.'' As soon as a substantial number of electrons have left the cluster the density and, consequently, the electric-field strength drops.

IV. DISCUSSION

Purnell *et al.* [6] measured Ar^{7+} ions with kinetic energies of up to about 1 keV after illuminating $HIAr_m$ clusters ($m\leq10$) with 624-nm laser pulses with intensities of about 10^{15} W/cm^2. This energy release is of the same order of magnitude as our results. However, they could not achieve such high kinetic energies unless some heavy-ion (HI) molecules were present in the cluster. In light of the strong density dependence of the ionization demonstrated above, this might, among other effects, be due to an increase of average density caused by the strongly polar HI molecules. We can speculate that disturbances of the cluster symmetry caused by seeding with polar molecules might promote the effects reported here. This possibility finds further support when comparing the findings presented here with our earlier related work [17] that did not employ a relaxation of the cluster structure prior to the beginning of the simulations. This generated cluster densities that exhibited larger fluctuations in nearest-neighbor distances among atoms that made the formation of small areas of increased density within the cluster more likely. These appeared to serve as ''hotspots'' that substantially enhanced the ionization. This suggests that density fluctuations might, in fact, be desirable in order to further enhance the ''ionization ignition.'' This in addition to the possible effect of ''seeding'' of the ionization by molecules with smaller ionization potential introduced in clusters as done in the above-mentioned experiments of Purnell *et al.* [6].

The laser pulses we have used in our simulations are consistent with those produced by state of the art ultrafast laser systems [11] but are short compared to those used in all experimental studies on cluster based x-ray sources to date. It may be argued that in a longer pulse the relatively slow increase of the laser intensity will allow for some ionization to occur early in the pulse that reduces the cluster density via Coulomb repulsion before efficient collisional heating occurs. This in turn would diminish the probability of impact ionization and ''ionization ignition.'' We have seen, however, that ignition occurs shortly after the threshold for single ionization is crossed and it may be that the overall time scale of the pulse is irrelevant as long as the first ionization threshold is passed rapidly. This is certainly the case for a fixed pulse length if the peak intensity is high enough. This could result in rapid ionization even before the peak of the laser intensity and might explain why Purnell *et al.* observed strong ionization enhancement. Moreover, from the ion kinetic energies measured, these authors conclude that the disassembling of clusters occurs on time scales of tens of femtoseconds after ionization even though laser pulses of 350 fs are used. Further experimental studies of the dependence of cluster ionization on both the peak laser intensity and the laser-pulse length could provide additional insights into the physical basis of the dynamics of cluster ionization.

In conclusion, we have presented a classical ionization model for and simulations of the ultrafast dynamics of small rare-gas clusters ionized by ultrafast laser pulses. This model predicts that, as the ionization proceeds beyond the first ionization stage, strong electric fields build up within the cluster that further enhance the ionization. Efficient collisional heating is expected to facilitate impact ionization of L and K shells, which might subsequently lead to the emission of prompt-line x radiation. Since this heating increases with cluster size, larger clusters are more likely to generate K-shell hard x rays. The influence of the ionization-induced electric fields within the cluster on the dynamics becomes more significant with higher initial cluster density. These properties are found for neon as well as argon clusters, which suggests that they may be generic and may carry over to systems of heavier atoms.

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