

Small Rare-Gas Clusters in Soft X-Ray Pulses

Christian Siedschlag* and Jan-Michael Rost

Max-Planck-Institute for the Physics of Complex Systems, Nöthnitzer Strasse 38, D-01187 Dresden, Germany

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We develop a microscopic model for the interaction of small rare-gas clusters with soft x-ray radiation from a free electron laser. It is shown that, while the overall charging of the clusters is rather low, unexpectedly high atomic charge states can arise due to charge imbalances inside the cluster. These findings are explained by an increased absorption via inverse bremsstrahlung due to high intermediate charge states and by a nonhomogenous charge distribution inside the cluster.

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The interaction of strong lasers with atomic and molecular systems at optical frequencies has become a vivid field of research, triggering new developments on both the experimental and the theoretical side [1]. For clusters, an important aspect has been the strongly increased energy absorption compared to the single atom case. The mechanisms for this phenomenon differ depending on the size of the cluster. They reach from *enhanced ionization* for small clusters [2], also known from molecules, over a resonant coupling of the laser frequency ω to a collectively oscillating electron cloud in intermediate clusters [3], to plasma oscillations whose resonant coupling to the laser frequency is believed to make energy absorption effective in very large clusters [4]. The order of magnitude of the absorbed energy and the observation of highly charged ions and energetic particles could be clearly reproduced by the corresponding calculations. On the basis of the insight gained so far, it seemed clear that in a frequency regime where neither a resonant coupling to the laser frequency is accessible nor the inverse laser frequency is large enough to allow for a quasistatic description, enhanced energy absorption in clusters should not occur.

Hence, it came as quite a surprise when the first free electron laser (FEL) experiment at the DESY in Hamburg [5], using soft x-ray radiation with $\omega = 12.7$ eV and xenon clusters of up to 30 000 atoms, revealed a complete breakup of the clusters and final ionic charge states of $4+$ for clusters with $N_{\text{Atom}} \approx 80$ and up to $8+$ when $N_{\text{Atom}} \approx 30\,000$, even more since the maximum intensity was only $I = 7 \times 10^{13}$ W/cm². At this intensity, single xenon atoms could be ionized only once by absorbing a single photon, which is just enough to overcome the first ionization threshold of xenon (12.1 eV). Obviously, multiphoton processes do not play a role.

On the other hand, the (surface) plasmon frequency of a spherical nanoplasma with radius R , consisting of N atoms with charge Z and $N_{\text{el}} \leq NZ$ electrons, is [6]

$$\omega_{\text{pl}} = \sqrt{NZ/R^3} \quad (1)$$

which would require charge states of $Z > 16$ for the FEL

frequency to come into resonance with the plasma frequency for a Xe cluster (we use atomic units). This seems extremely unlikely. Moreover, due to the expected expansion of the cluster, Z would have to be shifted towards even higher values during the interaction with the pulse. To summarize, none of the concepts from the IR regime can be taken over to the case of vacuum ultraviolet (VUV) pulses.

In this Letter we present a theoretical explanation of the observed phenomenon, based on a mixed quantum-classical model. Although the situation is quite different from the IR case, the high charge states can once again be explained from the fact that a cluster is a dense, but finite system, i.e., neither an atom nor a quasi-infinite solid or plasma. We consider relatively small ($N < 100$) xenon clusters in a short, soft x-ray pulse. The model we have developed is microscopic, allowing one to follow all particles and their mutual interactions in time.

As will become clear below, the concept of *inner* and *outer ionization*, originally introduced for the case of IR pulses [7] is equally useful in the VUV case. Inner ionization means the ionization of an electron from its mother atom (ion), whereas outer ionization denotes the process of an electron leaving the cluster as a whole. Akin to our previously developed model for rare-gas clusters in IR fields [2], we treat the inner ionization process using quantum mechanical photoabsorption rates while all subsequent time evolution, including outer ionization, is described by classical mechanics.

Whereas in the case of a single Xe atom double ionization with two photons is energetically forbidden, multiple inner ionization can take place in a cluster due to the influence of the neighboring ions. The situation is illustrated in Fig. 1: the interionic barriers are pulled down by the surrounding charges, so that the difference ΔE in energy between the level to be ionized and the top of the nearest barrier becomes less than the energy of one photon. Consequently, in our treatment an electron can be inner ionized as long as $\omega > \Delta E$. If such a photon is absorbed, its energy is transferred into kinetic energy of the electron (i.e., $|\vec{p}| = \sqrt{2\omega}$) and the electron is henceforth

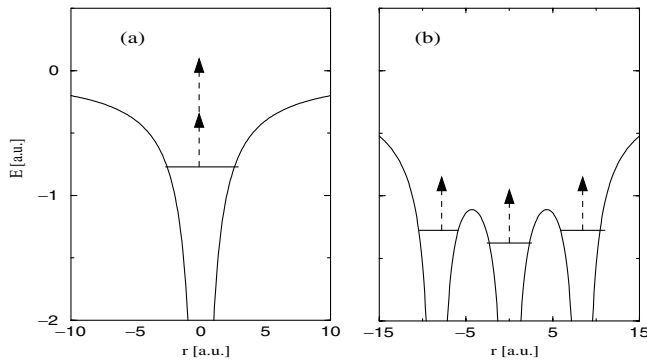


FIG. 1. Schematic picture of the (inner) ionization process (a) in a single ion (e.g., Xe^+) and (b) in a simple cluster of three ions. While it takes two photons to ionize the single ion, one photon is sufficient to achieve inner ionization in the case of the cluster.

treated as a classical particle, starting its trajectory at the nucleus with momentum p . We use specially adapted soft core potentials for the classical electron-ion interaction as in [2] to avoid numerical singularities and unphysical autoionization processes. The initial configuration of the cluster atoms is determined assuming pairwise Lennard-Jones interaction [8].

The probability of an atom or ion absorbing a photon is calculated using atomic photoabsorption cross sections [9]. This is justified since these cross sections can be derived using the reflection principle [10], where the electronic wave function has to be evaluated only once at a distance $r_\omega = \omega^{-1/2}$ from the nucleus. In our case this gives $r_\omega = 1.46$ a.u., which is small enough to assume that the atomic wave function at r_ω is hardly changed by the presence of the neighboring cluster atoms (at least in the case of van der Waals clusters).

The inner-ionized electrons, together with the ions created by the ionization process, form a nanoplasma which is described classically in our calculation. Here, we do not take into account $e-2e$ processes since the mean free path for electron-ion scattering is much larger than the cluster size [11]. Hence, transfer of thermal energy from the nanoplasma electrons to electrons still bound is not accounted for. However, the electrons will transfer thermal energy to the ions causing a slow expansion of the cluster even if, as a whole, it would stay neutral (*hydrodynamic expansion*, cf. [4]).

The latter is of course not the case: The initial energy the electrons get from the photons is only sufficient for the first few electrons to leave the cluster before its increasing charge starts to hold them back. The remaining electrons will evolve into a Maxwellian velocity distribution so that in the course of time more electrons will gain sufficient kinetic energy to outer ionize. Moreover, there is the possibility of inverse bremsstrahlung processes which are included on the classical level: the electrons can absorb energy from the laser field when undergoing collisions with the ions in the cluster. We

will see later that this process leads to a considerable heating of the nanoplasma electrons, causing further outer ionization.

First of all, however, we shall examine the time dependence of characteristic observables. Figure 2 shows the total energy of the system, the mean internuclear distance, the number of inner-ionized electrons, and the number of electrons with positive energy (i.e., the number of outer-ionized electrons). The pulse parameters are as indicated in the figure caption.

We see that the scenario is qualitatively the same as for IR pulses: after the first electrons have left the cluster, the ions start to repel each other so that the mean internuclear distance slowly increases, and the cluster completely disintegrates into ions and atoms. However, the whole process is much less violent in the VUV case: only about 550 eV per atom are absorbed, at least 1 order of magnitude less than in IR pulses (however, 1 order of magnitude more than in the case of an isolated atom). Because of barrier suppression almost eight electrons per Xe atom are inner ionized. The number of outer-ionized electrons is still slowly increasing well after the end of the pulse, since, due to continuing rethermalization, some electrons can acquire sufficient kinetic energy to leave the cluster.

Note, that the final average charge per atom is only about 1.5. Nevertheless, charges up to $5+$ can be observed. Before we come to this point, we must clarify the mechanism of energy absorption. The cluster can absorb energy in two ways: first, if an electron is inner ionized the energy of the cluster increases by ω . Second, inner-ionized electrons inside the cluster can absorb energy by inverse bremsstrahlung (IBS) when colliding

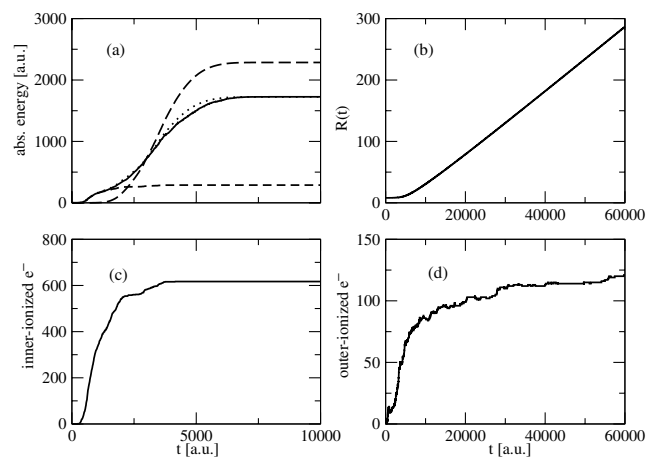


FIG. 2. Absorbed energy (a), mean interionic distance (b), inner-ionized electrons (c), and outer-ionized electrons (d) as a function of time for a Xe_{80} cluster. $I = 7 \times 10^{13}$ W/cm², $T_{\text{FWHM}} = 100$ fs, and $\omega = 12.7$ eV. The different lines in (a) indicate absorbed energy due to inner ionization, i.e., photoabsorption (E_{ii} , short-dashed line), due to IBS according to Eq. (2) (E_{IBS} , long-dashed line) and the total energy absorption from our calculations (E_{tot} , full line). The dotted line, E_{tot}' , is the absorbed energy constructed from E_{ii} and E_{IBS} ; see text.

with the ions. The average rate of energy absorption by IBS for a Maxwellian distribution of electrons with temperature T colliding with ions of charge Z and density n_i in a field of intensity I and frequency ω is [12]

$$\left\langle \frac{dE}{dt} \right\rangle = \frac{4\pi^{3/2} Z^2 n_i I}{15 \times 3^{5/6} \omega^2 \sqrt{2T}} \left(\frac{2}{Z\omega} \right)^{2/3} \frac{\Gamma(1/3)}{\Gamma(2/3)}. \quad (2)$$

In Fig. 2(a) we analyze the contributions to energy absorption from single photon absorption leading to inner ionization (E_{ii}) and from the subsequent IBS processes (E_{IBS}). IBS contributes about 80% to the absorbed energy as one can see comparing the full curve E_{tot} with the short-dashed one (E_{ii}). E_{IBS} can be calculated directly with Eq. (2) taking $T = 2/3 \langle E_{kin} \rangle$ to be the (time-dependent) temperature of the electrons inside the cluster. The result (long-dashed line) is too high which can be understood since Eq. (2) is strictly valid only when plasma screening effects can be neglected, which means that the Debye length $\sqrt{T/(4\pi Z n_i)}$ should be much larger than the distance between neighboring ions. This condition is not fulfilled in our case, so that the effective ionic charge seen by the electrons is smaller by a certain factor f , or, equivalently, the energy absorption is smaller by a factor $f^{4/3}$. With $f^{4/3} = 0.6$, one obtains $E'_{tot} = f^{4/3} E_{IBS} + E_{ii}$ shown as the dotted line in Fig. 2(a) in good agreement with the numerical result E_{tot} . To summarize this part, we find that the unexpectedly large absorption of energy is a consequence of the fact that, at least intermediately, charge states of up to 8+ are created inside the cluster, thus explaining the order of magnitude which has been missing in previous simulations [5], where only ions with $Z = 1$ were taken into account.

We now turn our attention to the distribution of ionic charges one observes when the cluster has completely disintegrated. The charge spectrum for Xe_{80} after being irradiated by the pulse from Fig. 2 is shown in Fig. 3. First of all, charge states of up to 5+ can be observed in the focus of the pulse [Fig. 3(a)]. To compare our results to the measurements in [5], one (i) has to integrate over the spatial intensity distribution of the FEL laser and (ii) take into account the geometrical detector acceptance for dif-

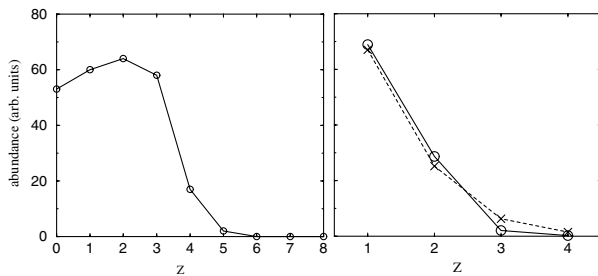


FIG. 3. Abundance of ionic charge states of Xe_{80} after irradiation from a soft x-ray pulse: (a) yield in the focus of the pulse; (b) yield integrated over a Gaussian (spatial) pulse profile (circles: our calculations; crosses: measurements from [5]). Pulse parameters are the same as in Fig. 2.

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ferent charge states, which can be calculated only from the detailed experimental setup and has not yet been included in the experimental results [13]. However, with the integration over the Gaussian beam profile performed, we can at least qualitatively compare our theoretical results with the experiment, as shown in Fig. 3(b). Note that the yield of ions with charges of five or higher is negligible for Xe_{80} when the volume integration is performed, which coincides well with the experimental findings.

The probably most surprising feature are the high charge states, observed in the experiment and obtained in our calculation. In a recent theoretical work [14] it has been proposed that the high charge states in *large* clusters ($N_{Atom} > 1000$) are due to thermal equilibration among the particles. While thermal effects might influence the distribution of the lower charge states, at least for smaller clusters studied here, the highest charge states arise due to the finite volume of a cluster which leads to large charge gradients. For simplicity, we will discuss the case of spherical symmetry in the following. It is known from the laws of electrostatics that a particle with charge q located at a distance r_q from the center of a spherically symmetric charge distribution with density $\rho(r)$ interacts with this charge distribution as if it were a point charge at the center of strength $Q(r_q) = \int_0^{r_q} \rho(r) dr$. A homogeneous density $\rho(r) = \rho_0$ leads to $Q = \frac{4}{3} \pi \rho_0 r_q^3$. Bearing in mind the r^{-2} dependence of the Coulomb force, an electron inside a positive, spherically symmetric charge density behaves like a harmonic oscillator (which is just where the surface plasmon comes from). For this reason, once a few electrons with high kinetic energy have left the cluster, the remaining electrons will be pulled towards

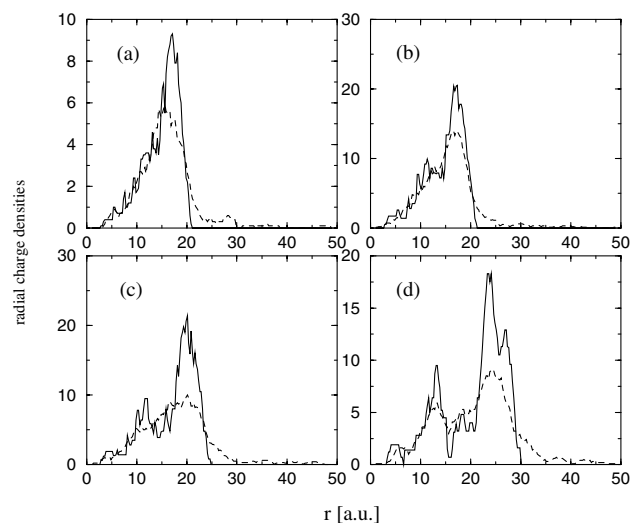


FIG. 4. Electronic (dashed line) and ionic (solid line) charge densities $r^2 \rho(r)$ at different times during the interaction: (a) $t = 500$ a.u.; (b) $t = 1500$ a.u.; (c) $t = 3000$ a.u.; and (d) $t = 4000$ a.u.

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the center of the cluster, leaving the ions of the outermost shell essentially stripped [15].

This scenario is confirmed by the time evolution of the radial electron and ion densities during the pulse. From Fig. 4 it is clear that, once the sum of ionic charges exceeds the integrated electron density, the electrons tend to neutralize the inner part of the cluster (which in this case consists basically of two ionic shells). Hence, while the outer ionic shells already start to explode during the time covered by Fig. 4 [charge center of the outer shell at about 20 a.u. in 4(c) and at more than 25 a.u. in 4(d)], the inner ionic shell, shielded by the remaining electrons, does not expand; rather its charge center remains at about 12 a.u. The border between the neutral and the charged part of the cluster is not completely sharp, as the electrons possess a finite temperature which broadens their radial distribution, leading to a smooth distribution of ionic charges.

Hence, our calculations indeed confirm the aforementioned picture for the emergence of high charge states: it is the finite size of the cluster which leads to significant charge imbalances inside the cluster, and the highest ionic charges are therefore generated in the outer shell of the cluster. For simplicity, we have illustrated this effect with a spherical cluster. However, any geometric arrangement of the ions which has a clear "center" will lead to a strong charge gradient. What is required, however, is a negligible ponderomotive oscillation of the electrons due to the external field. In the VUV case the oscillation amplitude is $\sqrt{I}/\omega^2 < 0.2$ a.u. and hence much smaller than the interionic distances. For IR pulses the electrons are field driven throughout the whole cluster, so that any kind of charge imbalance is washed out. On the other hand, the laser frequency should be small enough to allow for significant IBS heating: as can be seen from Eq. (2), the rate of energy absorption decreases quadratically with the applied frequency. This is why our results should not apply to the case of keV photons [16].

Note that the appearance of higher charges at the border of the cluster has to be paid off by some neutral atoms in the center of the cluster (which also disintegrate due to hydrodynamic expansion). These neutral atoms, however, could not be detected in the DESY experiment [13]. In other words, only the relative abundance of *ions* has been measured, with the number of "dark" neutral atoms left unknown. This leads us to the question of the relevance of our results for the case of larger clusters, i.e., $N > 1000$. We expect the difference between electronic and ionic density at the surface of the cluster to be even bigger than for small clusters, since the space charge will be higher too. Thus, the maximum charge state attainable by charge imbalance will increase with the cluster size. On the other hand, the relative proportion of the surface region to the total volume of the cluster will decrease, leaving relatively more neutralized ions in the center of the cluster. As mentioned, these neutral atoms would have

been invisible in the experiment; the *relative* abundance, however, might well be reproducible by our model even for larger clusters. Moreover, a new set of experiments is planned at DESY where, e.g., argon clusters can be doped with a single xenon atom which can be placed in the center of the cluster or at the surface, respectively [13]. This kind of experiment could directly verify the predictions made by our model.

To summarize, we have presented a microscopic model which simulates the time evolution of rare-gas clusters in VUV laser fields. Single-photon processes, leading only to single ionization for isolated xenon atoms, can create a dense nanoplasma with intermediate charge states of up to $Z = 8$ in the case of a cluster, because inner ionization is facilitated by the charged environment of a cluster atom, effectively reducing the threshold for ionization. This results in a larger IBS absorption than previously expected; furthermore, the geometric properties of a cluster lead to a nonhomogenous charge distribution, with high charges at the surface of the cluster and a quasineutral region in the center. These two effects explain the findings of the DESY experiment.

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*Present address: FOM-Institute AMOLF, Kruislaan 407, 1098 SJ Amsterdam, The Netherlands.

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