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. For clusters, an important aspect has been the strongly increased energy absorption compared to the single atom case. The mechanisms for this phenomenon differ dependent on the size of the cluster. They reach from enhanced ionization for small clusters, also known from molecules, over a resonant coupling of the laser frequency $\omega$ to a collectively oscillating electron cloud in intermediate clusters to plasma oscillations whose resonant coupling to the laser frequency are believed to make energy absorption effective in very large clusters. 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 quite as a surprise when the first XFEL experiment at the DESY in Hamburg, using soft X-ray radiation with $\omega = 12.7$ eV and Xenon clusters of up to 30000 atoms, revealed a complete breakup of the clusters and final ion charge states of 4+ for clusters with $N_{\text{Atom}} \approx 80$ and up to 8+ when $N_{\text{Atom}} \approx 30000$, even more, since the maximum intensity was only $I = 7 \times 10^{13}$ W/cm². At this intensity, single Xenon atoms could only be ionized 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 $N_{el} \leq NZ$ electrons, is

$$\omega_{pl} = \sqrt{NZ/R^3}$$

which would require charge states of $Z > 16$ for the XFEI frequency to come into resonance with the plasma frequency in the case of a Xe cluster. 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 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 to follow all particles and their mutual interactions in time.

As it will become clear below, the concept of inner and outer ionization, originally introduced for the case of IR pulses 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, we treat the inner ionization process using quantum mechanical photo absorption 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 neighbouring ions. The situation is illustrated in Fig. 1. The ionic barriers are pulled down by the surrounding charges, so that the difference $\Delta E$ 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., $|p| = \sqrt{2\omega}$) and the electron is henceforth treated as a classical particle, starting its trajectory at the nu-
cules 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 $r_\omega$ 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]).

This 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. Fig. 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 one order of magnitude less than in IR pulses (however, one order of magnitude more than in the case of an isolated atom). Due to barrier suppression almost 8 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 ob-
served. Before we come to this point, we must clarify the mechanism of energy absorption. The cluster can absorb energy in two ways: firstly, if an electron is inner-ionized the energy of the cluster increases by \(\omega\). Secondly, inner-ionized electrons inside the cluster can absorb energy by inverse bremsstrahlung (IBS) when colliding 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 \(\omega\) is \(|12|\)

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

In Fig. 2, 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 neighbouring 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 \(f^2\). With \(f^2 = 0.6\), one obtains \(E_{tot} = f^2 \cdot E_{IBS} + E_{ii}\) shown as dotted line in Fig. 2a in good agreement with the numerical result \(E_{tot}\).

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. 3a)). To compare our results to the measurements in [13], one i) has to integrate over the spatial intensity distribution of the FEL laser and ii) would have to take into account the geometrical detector acceptance for different charge states, which can only be calculated 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. 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 [13] 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 was 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 \(Q = \frac{4}{3} \pi \rho_0 r_q^3\). Baring 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 the center of the cluster, leaving the ions of the outermost shell essentially stripped [10].

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 starts already to explode during the time covered by Fig. 4 (charge center of the outer shell at about 20 a.u. in (c) and at more than 25 a.u. in (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 signifi-
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 $\sqrt{T/\omega^2} < 0.2$ 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 [14].

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 [15]. 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 [15]. 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 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. Once the nanoplasma is formed, the energy absorption and final average ionic charge turn out to be within the limits set by standard inverse bremsstrahlung theory; nevertheless, the geometric properties of clusters lead to unusually high charge states originating from the surface region of the cluster.

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This requires that the excited cluster indeed behaves like a spherically symmetric nanoplasma, which we have confirmed by comparing the radial electronic density with the outcome of a plasma code where $\rho_e(r) \sim \exp -\phi(r)/kT$ and $\phi(r)$ is the meanfield potential calculated from the microscopic electron and ion density. These results will be published elsewhere.