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Ionization dynamics of Na_{93}^+: dependence on laser pulse length

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Abstract. We present a numerical study of the electron dynamics of Na_{93}^+ in laser pulses of fixed total energy and pulse lengths varying between 20 and 400 fs. The frequency of the laser is 3.1 eV, i.e. slightly above the plasmon frequency of Na_{93}^+. It turns out that there is a clear-cut transition between a short-pulse and a long-pulse regime for pulse lengths around 200 fs. For short pulses, resonance with the collective plasmon mode leads to strong ionization of more than 10 electrons on the average. On the other hand, ionization of long pulses is much less drastic and proceeds mainly via a steady heating of the cluster valence electron cloud. These observations and the proposed ionization mechanism are in general accordance with recent experimental findings.

PACS. 36.40.Gk Plasma and collective effects in clusters – 36.40.Wa Charged clusters – 71.24.+q Electronic structure of clusters and nanoparticles

The dynamical behavior of the valence electrons of metal clusters has been widely studied in recent time. The most prominent feature to be observed is a collective electronic excitation known as Mie plasmon. The existence of this collective mode in metal clusters is responsible for many of their optical properties [1]. The phenomena of interest run over a wide range, from the linear regime of weak excitations up to the highly nonlinear regime of multiphoton effects such as multiple ionization.

A number of theoretical studies have addressed this dominance of the Mie plasmon in various physical contexts. Some of them were confined to the linear response regime [2, 3], whereas more recent work has focused on metal clusters in strong laser pulses [4].

A very recent experimental study [5] deals with the role of the plasmon in the ionization dynamics of Na_{93}^+. In the experiment, mass selected Na_{93}^+ clusters were irradiated with 100-femtosecond laser pulses with photon energy $\hbar\omega = 3.1\,\mathrm{eV}$. A large amount of doubly and triply charged fragments was detected. This effect was absent when nanosecond pulses of the same wavelength and pulse energy were applied. Arguing with a simple rate model, these highly efficient ionization processes were interpreted in [5] as resulting from an autoionization mechanism of a multiply excited plasmon resonance.

In this paper, we want to revisit these experimental results from a theoretical point of view, using numerical simulations based on time-dependent density functional theory. Our goal is to study the ionization dynamics of Na_{93}^+ excited by laser pulses of varying length but constant pulse energy and photon frequency. In particular, we aim at clarifying the role played by the Mie plasmon. It will turn out that the experimental findings from [5] may be understood as involving a resonance phenomenon between the laser field and the plasmon. Note furthermore that within our approach the concept of a multiply excited plasmon is not explicitly invoked. This, however, is not necessarily in disagreement with the mechanism put forward in [5], as will be discussed below.

Let us begin by relating the position of the Mie plasmon of clusters in different charge states to the photon energy 3.1 eV used in the experiment. Figure 1 shows the spectral dipole strength function for three spherical clusters containing 92 valence electrons. The calculations have been done using the linear response formalism developed in [6]. It is seen very clearly that the Mie plasmon peak moves to higher frequencies for increasing charge state. While for Na_{93}^+ the main peak lies at about 2.75 eV (note the fragmentation of the plasmon related to Landau damping), it moves to 3.0 eV for Na_{97}^{5+} and to 3.15 eV for Na_{102}^{10+}. One can estimate that the photon energy of 3.1 eV should just be in resonance with the plasmon of the cluster of charge state 8+.

Note that, to be more precise, the above calculations should have been performed on clusters with constant number of ions 93 while decreasing the number of electrons, rather than, for simplicity, keeping the number of electrons fixed at 92 and increasing the number of ions. However, the differences in the spectra may safely be assumed to be small, so that the above estimates are directly relevant for the experiment. We conclude that the cluster has to shed at least 7 electrons in order to pass through a resonance with the laser field at some time during the

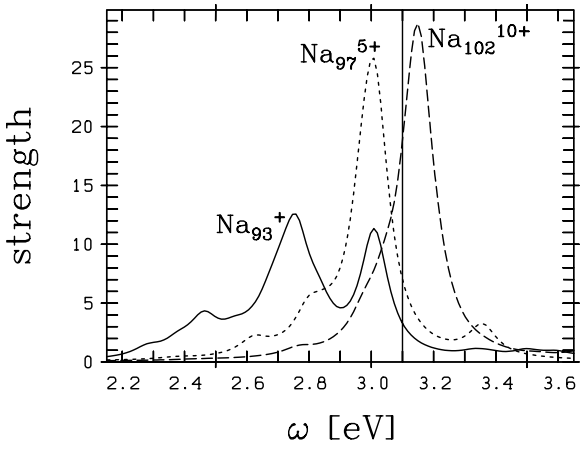

Fig. 1. Strength distribution $S(\omega) = \langle 0|\hat{D}\delta(\hat{H}-\omega)\hat{D}|0\rangle$ for three different charge states of a Na cluster with $N_{\rm el} = 92$ computed in linear response on a Kohn-Sham ground state using a soft spherical jellium background. The vertical line indicates the laser photon energy used in the experiment of [5].

pulse. As we shall see below, this is the preferred mechanism for short, intense laser pulses.

To make contact with the experiment from [5], we have simulated the ionization of Na_{93}^+ in laser pulses of varying length. Our calculations use a time-dependent density-functional approach within the local density approximation (TDLDA). Compared to more sophisticated models (such as self-interaction correction [7]), the TDLDA has been shown to yield a good description of electron escape. Technical details are given in [4, 8]. In short, we solve the time-dependent Kohn–Sham equations for Na_{93}^+ whereby the laser pulses enter as an external potential of the form $E_0\, z\, f(t)\, \sin(\omega t)$. Here, $f(t)$ parametrizes the pulse shape, taken to be trapezoidal with a linear switching-on and off during the first and last 10% of the total pulse length $T_{\rm pulse}$. The peak electric field strength E_0 of the pulse is related to the peak intensity I_0 via $E_0 \sim \sqrt{I_0}$. We choose a value of $E_0 = 0.0018\,{\rm Ry}/a_0$, corresponding to $I_0 = 2.85 \times 10^{10}\,{\rm W/cm^2}$, for a pulse duration $T_{\rm pulse} = 100\,{\rm fs}$. When varying the pulse length, the product $I_0 T_{\rm pulse}$ is kept constant so as to guarantee a fixed total fluence of the pulse. This corresponds to an experimental pulse energy of 0.3 mJ if we assume a focal spot of 2.5 mm width.

The ionic background of the cluster has been treated in the soft jellium model [8]. Within this approach, the motion of the ions is ignored, which is acceptable for time spans not much greater than about 100 fs and sufficiently accurate for the present exploratory purposes. Moreover, the soft jellium produces an ionization threshold which is somewhat too small, and therefore the flow of escaping electrons will be slightly overestimated. We expect, however, that the trends which we study will be correct.

We monitor the electron dynamics of the Na_{93}^+ cluster by calculating the time dependence of some characteristic observables. First of all, the number of escaped electrons, $N_{\rm esc}$, and the dipole moment $d(t) = \int d^3r\, z\rho(\mathbf{r}, t)$ are calculated according to the usual prescriptions [8] inside an analyzing volume of radius $R + 2r_s = 26.1\, a_0$, where R is the jellium radius and $r_s = 4\, a_0$ for sodium.

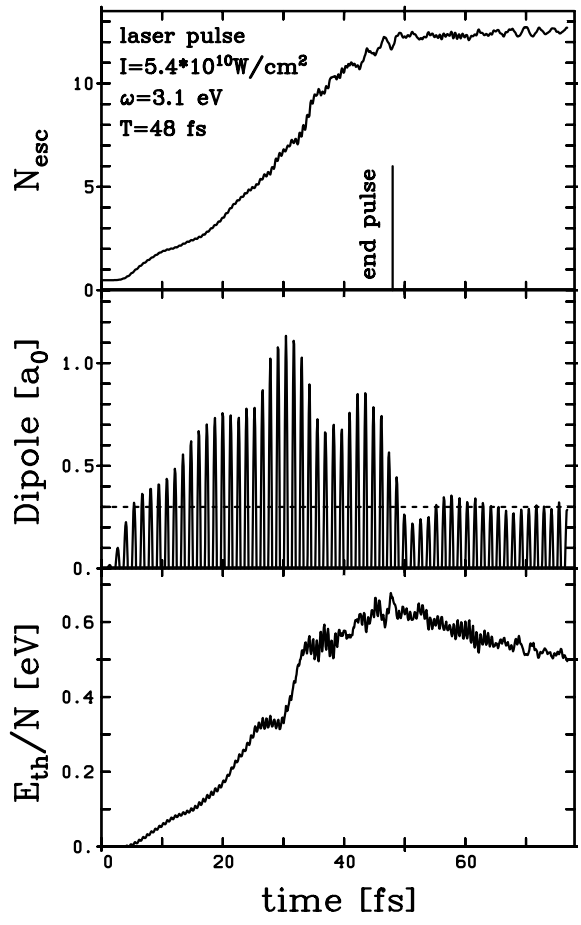

Fig. 2. Time evolution of key observables: the number of escaped electrons $N_{\rm esc}$, the dipole amplitude, and the intrinsic thermal excitation energy $E_{\rm th}$, for a Na_{93}^+ cluster with spherical jellium background excited by a laser pulse with parameters as indicated. The shape of the pulse was trapezoidal, ramped to its maximum with 10% switching time at both sides.

We plot the time evolution of $N_{\rm esc}$ and $d(t)$ in Fig. 2 for a short pulse of length $T_{\rm pulse} = 48$ fs. It can be seen that $N_{\rm esc}$ rises steadily to its final value of about 11 emitted electrons at the end of the pulse. One can also clearly see that the amplitude of $d(t)$ goes through a maximum for $N_{\rm esc} \approx 7$, which indicates that at this moment the charge state of the cluster is such that the plasmon mode of the residual electron cloud is in resonance with the laser field. At the end of the pulse, the dipole oscillation stabilizes at an amplitude where the average energy of the electron cloud corresponds to the excitation of one plasmon, as indicated by the dashed line. This suggests that in the presence of the driving laser field the system may indeed sustain multiple plasmon excitations (as indicated by the large amplitude of $d(t)$), which, however, quickly die off after the pulse is over. This shows that a metal cluster cannot be kept in a multi-plasmon regime for long because excess excitation is immediately (i.e. within 2 fs) drawn off by direct electron emission.

In addition to these observables, we compute characteristic energies which contain valuable information about the dynamics of the processes under study. We first define

$$E_{\rm ext} = \int_0^{T_{\rm pulse}} {\rm d}t\, E_0 f(t) \sin(\omega t)\, \frac{\rm d}{{\rm d}t} \langle \hat{D} \rangle \,, \qquad (1)$$

which measures the total energy transferred to the cluster by the external laser field. We then define the intrinsic thermal energy as

$$E_{\rm th} = \int_{\rm vol.} d^3r \left(\tau - \frac{m\mathbf{j}^2}{2\rho} - \tau_{\rm ETF} \right) \,. \qquad (2)$$

Here, $\rho(\mathbf{r},t)$ and $\mathbf{j}(\mathbf{r},t)$ are the particle and current densities and $\tau(\mathbf{r},t)$ is the (noninteracting) kinetic energy density of the Kohn–Sham system. $\tau_{\rm ETF} = 0.6(3\pi^2)^{2/3}\rho^{5/3} + (\nabla\rho)^2/(18\rho)$ is the ground-state kinetic energy density of a system with density ρ in extended Thomas-Fermi approximation. The quantity $\int_{\rm vol.} {\rm d}^3r\, m\mathbf{j}^2/(2\rho)$ indicates the collective energy of the system. Its maximum value during the time evolution will be denoted by $E_{\rm coll}$.

The bottom panel of Fig. 2 shows the behavior of $E_{\rm th}$. One can see that the emission of electrons is paralleled by a steady heating up of the residual electron cloud. The reason is that emission removes preferably outer shells. This, in turn, drives the dipole oscillations of the various shells out of phase, thus damping collective motion. After the end of the pulse, we observe still a slight decrease of $E_{\rm th}$. This effect is linked to those electrons which have escaped the analyzing volume (accounted for in $N_{\rm esc}$) and are now travelling to the boundaries of the numerical box where they are finally absorbed. Some $E_{\rm th}$ from the interior is transferred to the escaping electrons via the long-range Coulomb forces.

Let us now study how the ionization dynamics of Na_{93}^+ depends on the length of the laser pulse. Figure 3 summarizes the key results of our numerical simulations. We have plotted the number of escaped electrons $N_{\rm esc}$ and the characteristic energies $E_{\rm ext}$, $E_{\rm th}$ and $E_{\rm coll}$ per particle versus $T_{\rm pulse}$ ($N_{\rm esc}$ and $E_{\rm th}$ have been determined 30 fs after the end of the pulse). One clearly observes that there are two different dynamical regimes: The first regime covers pulse durations of less than 200 fs. Here we are in the short-pulse, high-intensity domain where the interaction of the laser with the cluster is a very fast and violent one. A large amount of energy (around 2 eV per particle) is transferred to the cluster, see the bottom panel in Fig. 3. This energy transfer can cause the system to emit more than 10 electrons. The remaining energy is stored in the collective oscillation and thermal heating of the residual electron cloud. The second regime comes for $T_{\rm pulse} > 200$ fs where we enter the long-pulse regime of weak excitation. Here, the energy transfer to the cluster is largely independent of the pulse length, and $N_{\rm esc}$ stabilizes at values of around 3. This clearly indicates a linear behavior, since the amount of energy contained in the pulse is kept constant.

This rather abrupt transition between the two dynamical regimes calls for explanation. We recall the discussion of Fig. 1, where it was shown how the position of the Mie plasmon shifts towards higher energies for increasing charge state of the system. This suggests that the short-pulse regime observed in Fig. 3 is characterized by a resonance of the laser field with the plasmon of the residual electron cloud. In other words, during the time evolution the cluster tries to reach a state where such a resonance can occur. To attain this goal, at least 7 valence electrons have to be emitted. Once the system has passed through the resonance, there may still emission be going on (due to the high energy content of the system, see bottom and top panel), so that the final charge state actually lies between 10 and 15. Note that the dip observed in $N_{\rm esc}$, $E_{\rm ext}/N$ and $E_{\rm th}/N$ at around $T_{\rm pulse} = 100$ fs may be related to a splitting of the Mie plasmon, see the full curve in Fig. 1.

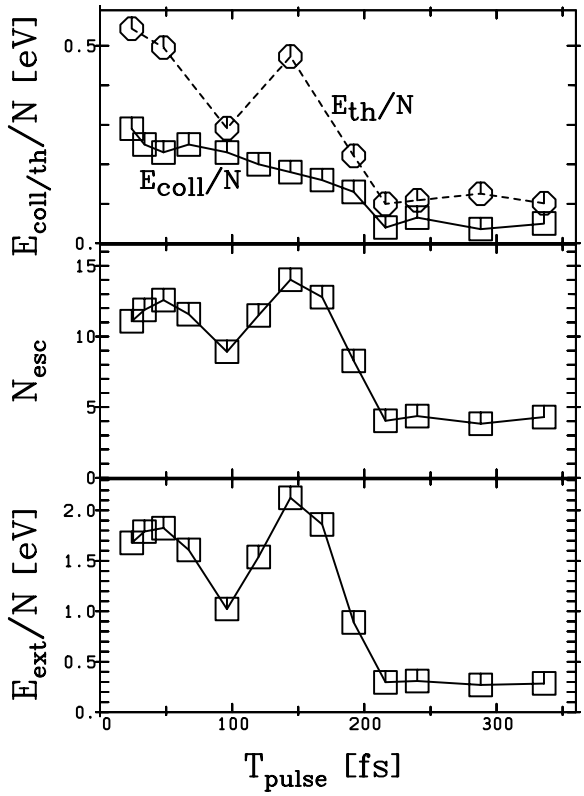

Fig. 3. Summary of the key results for laser excitation of Na_{93}^+ with spherical jellium background drawn versus the pulse length $T_{\rm pulse}$ of the laser. The intensity of the pulse varies as $I \sim T_{\rm pulse}^{-1}$, where $I = 2.85 \times 10^{12}$ W/cm^2 for $T_{\rm pulse} = 100$ fs.

Whether or not the state of resonance can be reached, is a highly nonlinear effect, depending in a crucial way on how fast the pulse is switched on and how large the peak intensity is. Pulses with $T_{\rm pulse} > 200$ fs are clearly incapable of triggering the fast emission processes which are necessary for the cluster to reach the charge state to pass through the resonance. The energy transfer to the cluster then proceeds much more smoothly, inducing small oscillations and a slow but steady excitation of the electron cloud, such that in the end a much smaller number of electrons gets released.

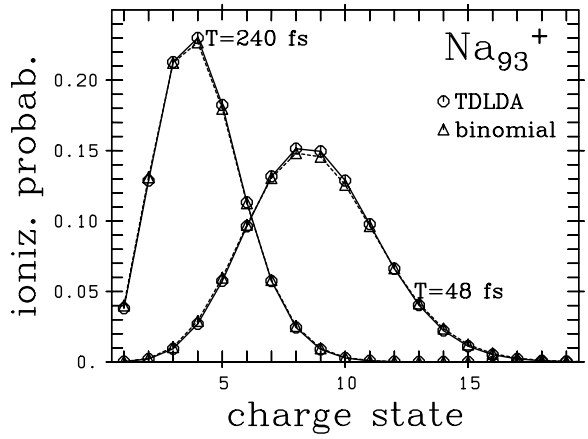

Fig. 4. The probabilities $P^{(n+)}$ to find the remaining cluster in a specific charge state $n+$ for two laser excitation of Na_{93}^+. The frequency of the laser pulse was $\omega = 3.1$ eV in both cases. The pulse length was varies as indicated, and the intensities were $I = 5.4 \times 10^{10}$ W/cm^2 for the shorter pulse and $I = 1.2 \times 10^{11}$ W/cm^2 for the longer one. The circles connected by full lines represent the result from TDLDA and the triangles connected by dotted lines are a binomial distribution with $n_{\max} = 93$ and tuned to reproduce the average electron escape.

The number of escaped electrons $N_{\rm esc}$ may be viewed as an average over a variety of different, discrete charge states of the cluster. Each of these charge states occurs with a probability $P^{(n+)}$. These probabilities can be obtained (approximatily) from our time-dependent Kohn–Sham calculations [4]. Figure 4 shows the distribution of the ion probabilities $P^{(n+)}$ for two different laser pulse lengths, 48 fs and 240 fs. For the short pulse, the most probable charge state is +8, whereas for the long pulse it is +4. We also see in Fig. 4 that the ion probabilities come very close to a binomial distribution. Similar observations have been made in the experiment [5]. It is noteworthy that our calculations deliver this binomial distribution within a fully coherent propagation mechanism where no statistical models or assumptions are implied.

In both the short- and the long-pulse regime, the energy stored in the excited valence electron cloud eventually gets converted into ionic motion. This phase of the cluster dynamics is beyond the scope of the present paper, although recent efforts have been aimed at a unified treatment of electronic and ionic dynamics [9]. Generally speaking, the cluster may choose to evaporate neutral atoms or split up into charged fragments [10].

In the experimental situation discussed in [5], one detects a large variety of products of the laser-cluster reaction. For 100-fs pulses, one finds numerous singly, doubly and triply charged fragments, whereas in the case of ns pulses one observes only singly charged clusters. This is in qualitative accordance with our simulations, which predict a much smaller ionization efficiency in the long-pulse regime. The fact that we still observe some ionization even for long pulses ($N_{\rm esc} \approx 3$) may be because our laser intensities are somewhat higher than the ones used in the experiment. Another reason for discrepancies may be linked to the simplified description in terms of the jellium model. However, these small deviations do not affect the general physical picture.

We have also explored with the same strategy the dependence on $T_{\rm pulse}$ for a laser with a frequency slightly below resonance. Again, we observe a regime of high electron emission for short pulses and of low emission for the long ones. In this case, however, the transition proceeds in a more gradual manner dropping step by step from the initial ionization state 11^+ to the asymptotic value.

In conclusion, we have proposed a mechanism to explain an enhanced ionization efficiency in Na_{93}^+ irradiated with short intense laser pulses. The cluster keeps emitting electrons until its charge state is such that the collective plasmon mode of the residual electron cloud goes through a resonance with the laser field. The transition to the long-pulse regime, where the energy transfer proceeds via a slow but steady heating of the cluster, was found to take place rather abruptly at pulse durations of 200 fs. This transition time depends, of course, sensitively on the relation between laser and plasmon frequency because we are exploring a resonant process here. Our approach also allows us to compute probability distributions of discrete charge states of the system. We obtain binomial distributions in all cases. The calculations presented here may be viewed as the first phase of electronic excitation, leading eventually to the fragmentation of the cluster.

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