# Plasmon-Enhanced Multi-Ionization of Small Metal Clusters in Strong Femtosecond Laser Fields

L. Köller, M. Schumacher, J. Köhn, S. Teuber, J. Tiggesbäumker, and K. H. Meiwes-Broer
*Fachbereich Physik, Universität Rostock, 18055 Rostock, Germany*
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The multiply charging process of platinum cluster ions under intense field conditions show a strong dependence on the width of the femtosecond laser pulse. Increasing the pulse width from 140 to 600 fs while keeping the energy per pulse constant leads to an increase in the highest observed charge state $z^*$ of the ejected atoms from $z^* = 13$ to $z^* = 20$. This increased charging efficiency is explained by the evolution of the plasmon energy of the metal cluster upon the change in electron density during the Coulomb explosion process. Thus the time dependence of the charging of a cluster in an intense light field has been observed in real time. [S0031-9007(99)09060-2]

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During the last decade the production of dense plasmas by strong laser pulses has received increased attention. Relevant for a number of applications, e.g., the fast ignitor scheme [1] for inertial confinement fusion or the particle acceleration by plasma waves [2], one is interested in producing plasmas at a high temperature with little energy dissipation into the surrounding material. For microstructured targets it was observed [3] that the x-ray yield increases by 2 orders of magnitude when compared to flat surfaces. Possibly small unsupported particles, i.e., clusters in a beam, could be even more efficient since there is no environment which could absorb the excitation energy. In contrast to an atomic gas, however, the clusters provide practically the density of the solid state target. Thus many-body effects could additionally lead to an increased excitation rate.

Indeed, with rare gas and molecular clusters different authors have already shown that electromagnetic energy can effectively be coupled into matter when clusters are used instead of atoms. Along this line, Rhodes and co-workers [4] investigated the interaction of strong laser pulses with noble gas clusters which have been generated in a supersonic nozzle expansion. They found x-ray emission which was attributed to the presence of hollow atoms within the cluster. Rare gas clusters can also serve as nonlinear media for the conversion of laser light; high harmonics up to the 33rd order were measured by the group of Perry [5]. Castleman and co-workers [6] reported on ions with a charge state $z$ up to $z = 20$ when irradiating Xe clusters. Ion emission with extremely high kinetic energies reaching up to 1 MeV [7,8] and electron emission with up to 3 keV [9] give an impression of the violence of such processes. The interaction of the light pulses with clusters can be so intense that the absorption reaches nearly 100% as has recently been shown by the group of Hutchinson [10].

Several theoretical approaches have been introduced to explain these observations. Rhodes and co-workers [11] used a simple model based on a collective electron motion. The electron oscillation driven by the laser field induces electron-ion collisions which enhance the ionization inside the cluster. Based on a hydrodynamic approach Ditmire *et al.* [12] calculated the probability for the multi-ionization of noble gas clusters. They considered highly excited large clusters as being spherical microplasmas which undergo enhanced light absorption whenever the electron density approaches a critical value where the photon energy matches the dipole resonance.

So far all experimental investigations with such intensive laser fields have been performed on rare gas and molecular clusters. For metals it is well known that collective electron excitations can already be observed in clusters having less than ten atoms even with ns lasers [13–15]. Recent time-dependent density functional calculations (TDDFT) on sodium clusters by Reinhard *et al.* [16] have shown that with femtosecond laser pulses in the vicinity of the plasmon resonance enormous field amplifications could be achieved. In contrast to rare gas clusters even the cold metal particle can be viewed as being a nanometer-sized plasma into which electromagnetic radiation would couple. In simple metallic systems with delocalized electrons the plasmon energies $E_{\mathrm{plas}}$ depend on the charge density inside the cluster as well as on its surface. For example, in the case of a positively charged silver cluster with nine atoms, $E_{\mathrm{plas}}$ is about 4.0 eV. If one uses a light source with a photon energy well below $E_{\mathrm{plas}}$, e.g., a femtosecond Ti-sapphire laser with 1.5 eV, it should be possible to learn about the time evolution of the ionization process when—upon expansion of the system—$E_{\mathrm{plas}}$ decreases and approaches the photon energy of the light source. As soon as the energies match a significant enhancement of the excitation cross section is conceivable which should lead to an increased charging of the cluster. This is the topic of our work where we focus on the laser pulse width dependence of the multi-ionization of platinum clusters.

A PACIS (pulsed arc cluster ion source)-type [17] source produces metal clusters by coexpanding a metal

  

plasma and helium forming a supersonic beam. Before entering the interaction region the charged particles are ejected from the beam. The exact cluster size distribution of the neutral species cannot be recorded. Nevertheless it can be estimated to range below $N = 100$ atoms with a maximum around $N = 20$ as the negatively as well as the positively charged clusters show this distribution. Note that the PACIS produces besides the neutral clusters also charged ones without the need of any additional ionization.

The femtosecond light is focused collinear to the cluster beam into the center of a time-of-flight mass spectrometer (TOF) where it excites the neutral clusters in a low pressure environment at $10^{-8}$ mbar. This thin cluster target ensures that the excitation of single noninteracting clusters is investigated. The mass distribution of the ions emerging from the interaction is measured in the TOF. As the setup discriminates against ions with high recoil energies the nascent mass spectra do not exactly image the true ion distributions. Nevertheless, relative abundance changes upon laser pulse width variations can be detected.

The laser system consists of a Ti:sapphire 82 MHz oscillator with a 30 Hz regenerative amplifier and two additional amplification stages. The shortest pulse width is approximately 140 fs at 800 nm. A lens with a focal length of 50 cm focuses the light which yields an intensity of up to $10^{16}$ W/cm$^2$. We check the pulse intensity by monitoring the appearance of $He^{2+}$ [18]. In order to investigate the dependence of the multi-ionization of the clusters on the light pulse width, the compressor geometry inside the laser amplifier is varied. By this the duration of the pulses can be adjusted from 140 fs to several ps. The quality of the modified light beam is checked using the 3rd order polarization gate autocorrelation technique (FROG). As a matter of fact, however, the enlargement of the pulse width is accompanied by a spectral chirp. For the process under consideration this should not significantly influence the results as the spectral width of the light does not extend beyond 10 nm. Changing the sign of the chirp turned out to have no influence on the measured results.

Ionizing neutral Pt clusters with 600 fs laser pulses giving $2 \times 10^{15}$ W/cm$^2$ yields a spectrum of small singly and doubly charged clusters and in addition a significant intensity of atomic ions $Pt^{z+}$; see Fig. 1. For this record the TOF parameters are chosen as to monitor the ionization products from the focal region as well as from an area with lower light intensity. When imaging ions only from the light focus by, e.g., using a narrow slit within the TOF drift tube, no clusters will be recorded. Compared to an experiment with platinum *atoms* where only small charge states up to $z = 4$ are observed, the $Pt^{z+}$ ions under these pulse conditions show a charge state distribution which ranges up to $z = 20$. Thus in the case of the particle excitation the appearance of highly ionized Pt atoms hints at an efficient coupling of the electromagnetic radiation into the

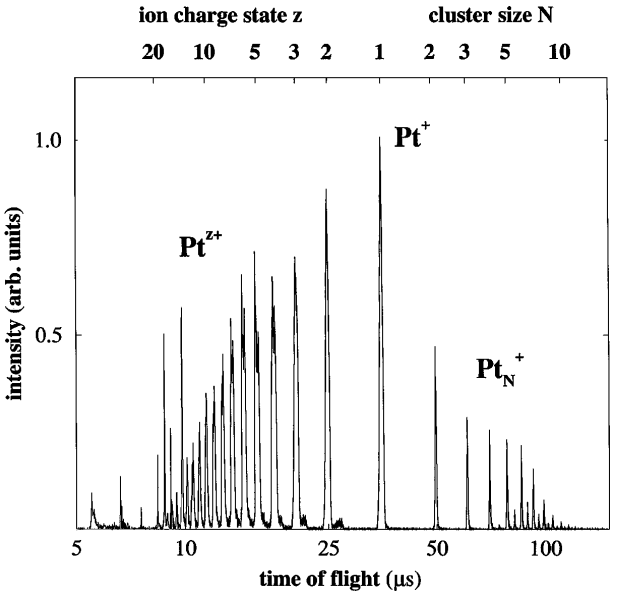


FIG. 1. Time-of-flight mass spectrum of positively charged Pt clusters and ions after irradiation of neutral $Pt_N$ with 600 fs laser light pulses and a pulse intensity of $2 \times 10^{15}$ W/cm$^2$. The ionized clusters, see the right side of the spectrum, arise from a spatial region with lower intensity. No clusters survive the excitation within the light focus. The main intensity (below a flight time of 50 $\mu$s) originates from singly and multiply charged atomic ions, which are emitted from the excited clusters. Note the logarithmic scale of the time axis.

clusters. Moreover, the atomic ion intensities significantly depend on the chosen pulse width $\tau$. Figure 2 shows the appearance distribution with $\tau$ ranging from 140 fs to 1 ps while the pulse *energy* is kept constant at 5 mJ. Note that the light *intensity* drops correspondingly with increasing $\tau$. For the shortest pulse $\tau = 140$ fs,

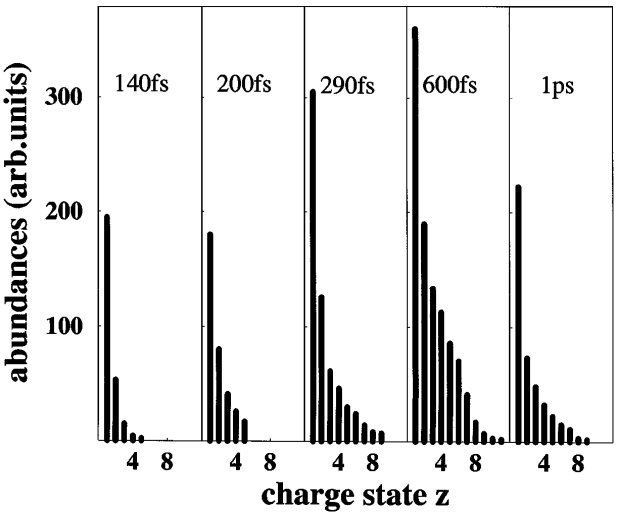


FIG. 2. Abundances of platinum ions $Pt^{z+}$ ($z = 1, \ldots, 11$) emerging from excited clusters as function of the light pulse width $\tau$ ranging from 140 to 1000 fs at a pulse energy of 5 mJ. From left to right the pulse intensity drops by a factor of 7.

with, e.g., $2 \times 10^{15}$ W/cm$^2$, only low-$z$ ions, $z \leq 5$, are present. Taking longer pulses with the same pulse energy of 5 mJ, an increase of the intensity of the multiply charged ions is observed with a maximum at about $\tau = 600$ fs. Figure 3 shows the highest detected charge state $z^*$ in dependence of the pulse width and laser pulse energy. Clearly for all pulse energies the maximum charge states depend on $\tau$, but the shapes of the $z^*$ distributions as function of the pulse width are similar. For example, for 1 ps/25 mJ pulses $z^*$ reaches a value of $z^* = 16$, whereas for 140 fs/25 mJ the highest charge state is only $z^* = 13$. Because of the fixed pulse energy chosen here the corresponding intensity of the long pulse (1 ps) is a factor of about 7 smaller than that of the short pulse (140 fs). Thus $z^*$ increases in spite of the intensity drop.

In order to explain the underlying physics we consider the cluster as being a jellium sphere which expands after having lost a given number of electrons at the beginning of the ionizing pulse. During the expansion the electron density decreases which, on the other hand, will influence the further coupling of the radiation into the cluster. Thus, the ionization efficiency should depend on the length of the exciting light pulse as we have seen in the experiment. For a quantitative analysis first the time development of the electron density has to be calculated, which in a second step will serve as input for the calculation of the response of the particle on the radiation. In the model calculation used here each second valence electron is assumed to be emitted by tunneling ionization during the rising edge of the laser pulse. Because of this initial charging the cluster undergoes a rapid expansion which is mainly due to the Coulomb forces. As an example we calculate this "Coulomb explosion" for a ninefold charged platinum cluster with 18 atoms, i.e., $Pt_{18}^{9+}$, in a classical electrodynamic simulation solving all trajectories. The ions are taken as point charges with the mass of the platinum atom, neglecting all further effects. From the average position of the ions as function of time during the explosion we get a time-dependent charge density distribution. As expected it turns out that the charge density decreases with the time but it remains nearly homogeneously spread over the cluster radius. Next, the optical response of the cluster is treated within the random-phase approximation (RPA) formalism where the momentary electron density serves as input. We apply the program of Bertsch [19] which is restricted to spherically shaped (closed-shell) clusters. With the density which corresponds to each time step the LDA ground state and the resulting collective dipole resonance energies are calculated; see Fig. 4. Obviously the decreasing electron density induces a dramatic change in the plasmon energy of the cluster towards lower values as can be seen in the figure. Therefore an enhancement in the ionization probability should be observed when the laser frequency matches the cluster dipole resonance which is the case at about 350 fs. The RPA calculations, however, show only a weak shift of the dipole resonance towards higher energies with increasing cluster charge state. When an up-charging of the cluster during its expansion is anticipated, the blueshift of the plasmon energy would move the matching condition to a slightly later time. Note that the theoretical result is obtained under the assumption of an initial ionization which is kept fixed during the expansion. Therefore the theoretical value of 350 fs is in fairly good agreement with the measured 600 fs pulse width when we anticipate that the, say, first 30% of the pulse is needed to induce the initial charging. In a more sophisticated model the charge flow of the electrons off the cluster and possible excitations of

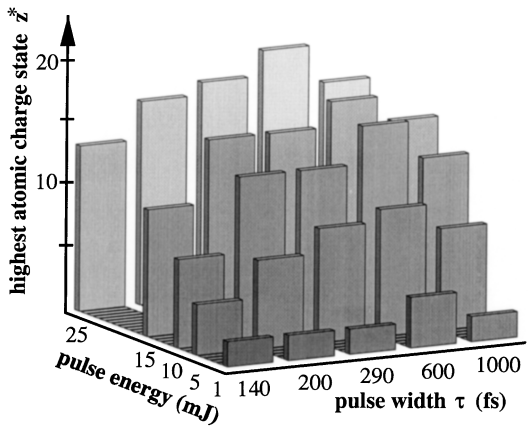


FIG. 3. Highest detected charge state $z^*$ of the emitted Pt ions as function of the pulse width $\tau$ and laser pulse energy. For all investigated energies an increased pulse width yields a higher $z^*$ and thus an enhancement of the ionization.

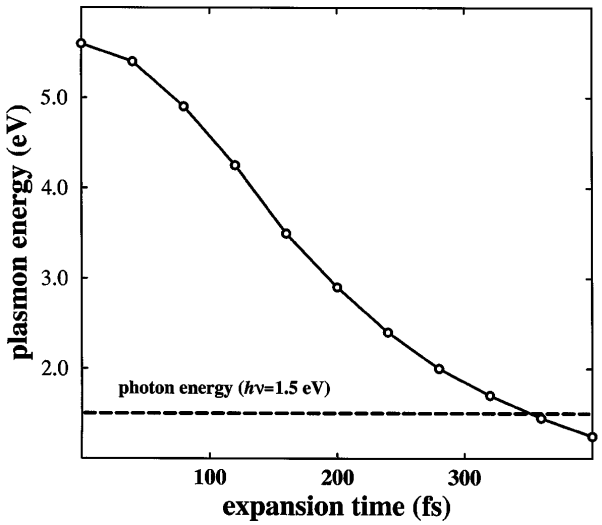


FIG. 4. Time dependence of the plasmon energies calculated with the RPA formalism for a ninefold charged metal cluster with 18 atoms and an initial Wigner-Seitz radius $r_s = 2.85$ a.u. About 350 fs after the beginning of the expansion the plasmon energy matches the photon energy of the exciting laser light.

core electrons to delocalized, e.g., metallic, states should be included.

The dependence of the multi-ionization signal on the pulse width of the laser is also the subject of the hydrodynamic approach by Ditmire *et al.* [12]. However, several mechanisms are different in our model. First, the expansion is not forced by collisions but instead by a pure Coulomb expansion. In contrast to the hydrodynamic model which explains the expansion of a large cluster with several thousands of atoms, here only some tens of atoms are present, most of which are on the surface. Second, the development of the plasmon energy is explicitly treated for metal clusters through the RPA calculations with the corresponding boundary conditions. For metal clusters it is well known that mainly the charge distribution at the surface induces the shift of the plasmon energy relative to that of the corresponding infinite surfaces.

In conclusion, the light pulse width dependence of the multiple ionization in small metal particles has been investigated. Highly ionized platinum atoms carrying up to 20 charges have been identified. We propose a simple model where the ionization process is strongly enhanced by plasmon absorption whenever the collective resonance frequency of the metal cluster matches the frequency of the exciting light. From a simulation of the charge density during the expansion and a calculation of the corresponding optical response it is shown that the maximum in the ionization cross section is obtained with a pulse width of several hundred femtoseconds which roughly agrees with the experimental observations. Thus the metal clusters are good candidates to investigate the fundamental process of the coupling of intense electromagnetic radiation into matter: In contrast to experiments involving surfaces here all decay channels can in principle be analyzed.

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