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Clusters in strong laser fields: Comparison between carbon, platinum, and lead clusters

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Abstract. Carbon and metal clusters are excited by strong femtosecond laser pulses with up to 10^{16} W/cm^2, yielding ionized clusters and highly charged atomic ions. For small carbon clusters and fullerenes the abundance of charged species correlates with the laser power, while for metal clusters the ionization efficiency is additionally strongly affected by the chosen laser pulse width which may result in an enhanced up–charging of the metal particle. In the case of platinum atomic charge states up to $z = 20$ are detected at a pulse duration of about 600 fs. This observation is in accordance with a model based on a multi–plasmon excitation process.

PACS. 36.40.Vz Optical properties of clusters – 36.40.Gk Plasma and collective effects in clusters

1 Introduction

Photoexcitation of metal clusters has been subject to a large number of investigations probing the optical and electronic response of these small systems. One of the most striking results is the observation of plasmon excitations in alkali metal clusters first calculated by Ekardt [1] and measured by de Heer *et al.* [2]. Based on quantum–chemical CI calculations Bonačić–Koutecký *et al.* [3] explained these measurements by an interference of many–electron excitations. Later several other systems were found to show collective excitation effects [4, 5]. The corresponding dipole resonance has been found to exhibit a high absorption cross section (≈ 1 Å^2/s–electron), where the resonance energies are located in the visible to the near UV spectral region, e.g. 4 eV for silver clusters [6]. Fullerenes also show collective electron motions. However, the dipole resonance in these systems resides deep in the VUV region around an excitation energy of 20 eV [7].

The increased absorption cross section as a result of the plasmon resonance might also play a role in the excitation of electrons by *intense* electromagnetic radiation. For rare gas clusters different authors have shown that electromagnetic energy can effectively be coupled into matter when clusters are used instead of atoms [8–10]. Ion emission with extremely high kinetic energies reaching up to 1 MeV [11, 12] and electron emission with up to 3 keV [13] give an impression of the violence of such processes. The interaction of the light pulses with clusters can be so intense that the light absorption reaches nearly 100% as has recently been shown by the group of Hutchinson [14], despite the relatively low target concentration in a molecular cluster beam in comparison to the surface. Several theoretical approaches have been introduced to explain these observations. Rhodes and co–workers [15] 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.* [16] calculated the probability for the multi–ionization of noble gas clusters. They considered highly excited large clusters as being spherical micro-plasmas which undergo enhanced light absorption whenever the electron density approaches a critical value where the plasmon energy of a classical dielectric sphere matches the photon energy. Only recently Reinhard and co–workers [17] investigated the response of intense light fields on small sodium metal clusters and found enhanced field amplification in the vicinity of the plasmon resonance.

2 Experimental setup

In our experiment a Pulsed Arc Cluster Ion Source (PACIS) [18, 19] produces metal clusters by co–expanding a metal vapour plasma and helium forming a supersonic beam. Before entering the interaction region the charged particles are ejected from the beam. For the experiments with the fullerenes a pulsed CO_2 laser brings C_{60} and C_{70} molecules from a powder target into the vapour phase. The cup with the fullerene powder is located 1 cm below the acceleration volume of the time–of–flight mass spectrometer (TOF). Femtosecond light pulses are focused into the center of the acceleration region in the TOF and excite the neutral clusters. The mass distribution of the ions emer-

ging from the interaction is measured in the TOF. In order to achieve a high mass resolution the spectra are taken using a delayed pulse extraction scheme, where the ionized products are accelerated several μs after the interaction with the laser pulse. Therefore especially ions with high recoil velocities are discriminated and the mass spectra do not exactly image the true ion distribution. Nevertheless, relative abundance changes upon light pulse width variations can easily be detected. The spectra are sampled over 2000 shots and stored in a multichannel analyser.

The laser system consists of a Ti:Saphir 82 MHz oscillator with a 30 Hz regenerative amplifier and two additional amplification stages. The shortest pulse width is approx. 140 fs@800 nm. A lens with a focal length of 50 cm yields an intensity of up to 10^{16} W/cm^2. We check the pulse intensity by monitoring the appearance of He^{2+} [20]. In order to investigate the dependence of the multi–ionization of the clusters on the light pulse width, the compressor inside the laser amplifier is detuned. By doing 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 extent beyond 10 nm. Figure 1 shows an overview of the experimental setup.

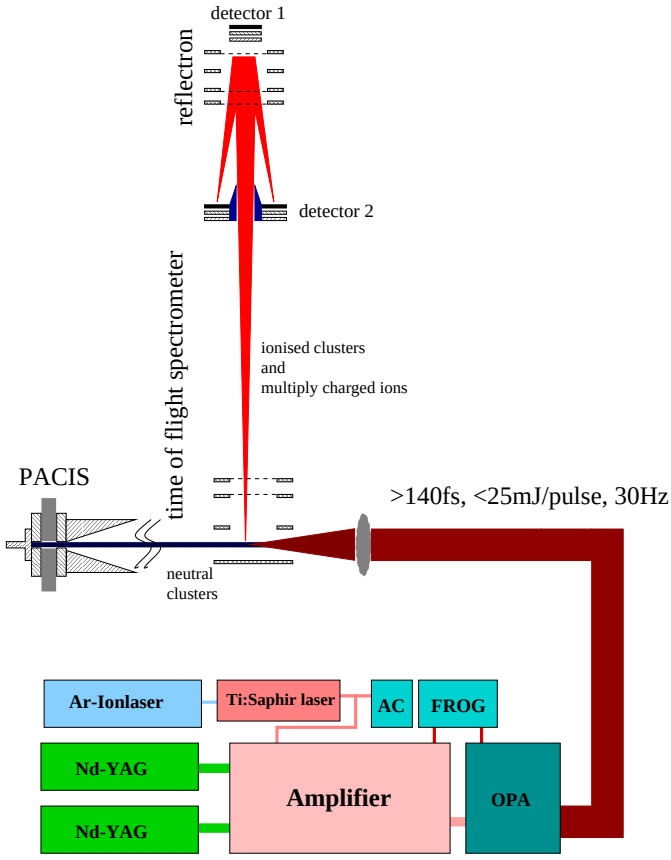

Fig. 1. Experimental setup for detecting highly charged metal ions after the interaction of strong laser light pulses with a neutral cluster beam (PACIS: cluster source, OPA: optical parametric amplifier, AC: autocorrelator, FROG: Frequency Resolved Optical Gating).

3 Results and discussion

3.1 Carbon clusters and fullerenes

The resulting mass spectra of carbon, lead and platinum clusters after ionization with 140 fs laser pulses with a peak intensity of approx. 3×10^{15} W/cm^2 are shown in Fig. 2. The mass spectrometer is set up to also image ions generated within regions of the laser pulse where the peak intensity is one to two orders of magnitudes lower compared to the central focus region. However, it turns out, that pulse intensities of approx. 10^{13} W/cm^2 are needed to ionize the clusters.

For carbon, besides $C_N{}^+$ also atomic ions with up to 4 charges are present (see Fig. 2a). However, the remaining atomic 1s–electrons are too strongly bound to be ionized by the laser field. A reduction of the light intensity is achieved by either reducing the pulse energy or by taking a longer pulse width. In the case of carbon both possibilities lead to a drop of the overall intensity of the cluster and atomic ions. To check whether fullerenes show this behaviour too we have performed measurements by ionizing molecular C_{60} and C_{70} [21]. Both show the same dependence on the chosen pulse intensity, i.e. the highest intensities yield ions with the highest z. Ionizing C_{60} with femtosecond laser pulses was also subject of other investigations [22]. It was argued, that plasmon excitations are responsible for the high charging in C_{60}. However, due to the high energy of the dipole resonance, a strong laser field is necessary to access the collective mode via a multi–photon absorption process.

3.2 Platinum and lead clusters

In the case of platinum the neutral cluster beam contains small clusters with $N < 100$ where the maximum intensity is around 50 atoms, as checked by monitoring the charged clusters coming directly from the source. After ionization small clusters are detected (see Fig. 2b). In addition doubly charged $Pt_N{}^{2+}$ is produced during the interaction with the laser field. The critical size N_c observed so far is $Pt_9{}^{2+}$, which is comparatively low and hints at high binding energies [23] of these transition metal clusters. No triply charged clusters are present. In contrast to carbon a huge amount of multiply charged atomic ions are detected, in general with much higher intensity than the overall cluster intensity. Tuning the source to conditions where only monomers are generated the intensity of the highly charged ions drops dramatically. This means that the excitation cross section of clusters is far beyond that of the corresponding atom indicating a different excitation mechanism. Figure 2c shows a TOF spectrum of ionized Pb–clusters

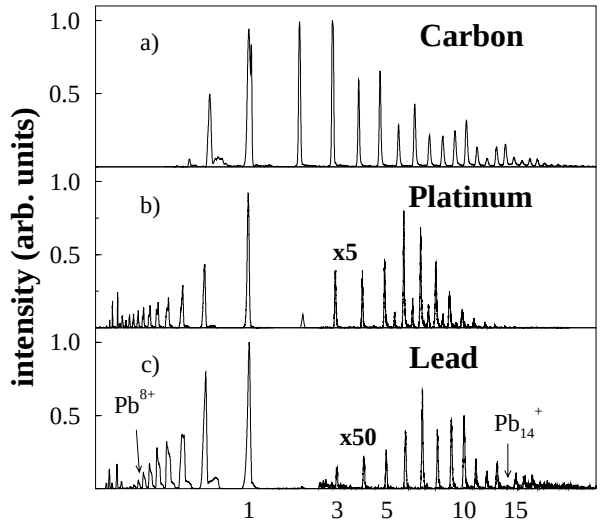

Fig. 2. Mass spectra of carbon, platinum and lead clusters ionized by a femtosecond laser pulse with 3×10^{15} W/cm^{-2} in the focal area. Note that the cluster size on the x axis assigns singly charged particles. The peaks below 1 represent atomic ions with $z > 1$. When monitoring the ionization products only from the high intensity region, no signals from the clusters remain.

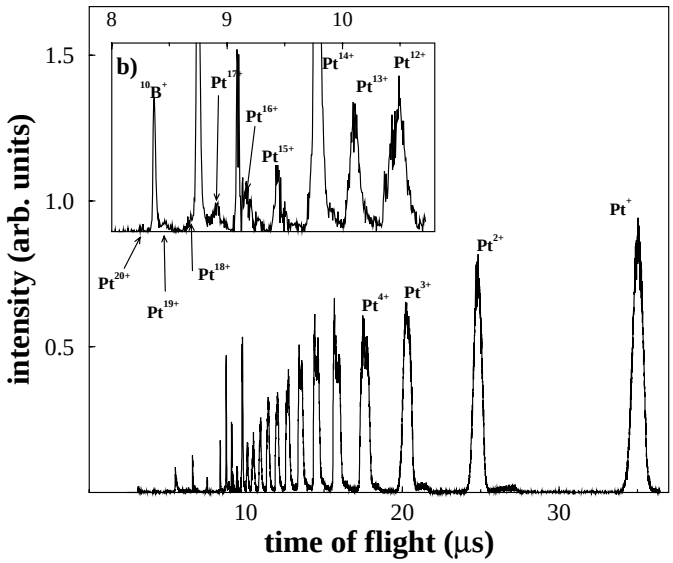

Fig. 3. Time-of-flight mass spectrum of highly charged platinum ions produced by irradiating Pt-clusters with 600 fs laser light pulses at an energy of 25 mJ giving 3×10^{15} W/cm^2. Under these conditions the highest charge state detected so far is Pt^{20+}, see inset.

taken under similar laser conditions as for carbon and platinum. Due to the larger differences in the binding energies compared to Pt_N the spectrum appears more structured. Note the nearly complete absence of $Pb_{14}{}^+$. In contrast to the Pt_N measurement also triply charged clusters are present. The critical number N_c for $Pb_N{}^{2+}$ is 35 and 46 for $Pb_N{}^{3+}$. The appearance of triply charged Pb–clusters could be explained by the higher masses within the neutral beam in comparison to Pt–clusters. Note that, however, due to the chosen experimental setup, the cluster ion intensity is overestimated and results from parts of the laser beam where a lower peak intensity is present. The dominating part of the spectra consists of highly charged atomic ions which is produced within the central focus region.

3.3 Pulse width dependence

Only recently we have reported [24], that the pulse width appears to be an important feature for the up–charging of metal clusters. No such dependence is found for carbon clusters. For metal clusters we detected that a pulse width of 600 fs leads to a maximum enhancement of the up–charging process. With this pulse width, ionizing neutral Pt–clusters with a pulse intensity of 2×10^{15} W/cm^2 yields a spectrum with atomic charge states of up to $z = 20$, see Fig. 3. In order to demonstrate that indeed the atomic charge distribution significantly depends on the pulse width τ, Fig. 4 shows the ratio $I(Pt^{z+})/I(Pt^+)$ for selected charge states, e.g. $z = 2, 4, 6, 8$, as a function of pulse width for different laser pulse energies. Note that the light intensity drops correspondingly with increasing τ. Obviously the abundance of higher charged ions increases with longer pulse durations in spite of the drop in intensity. A maximum is reached at about 600 fs. However, even for pulse widths of 1 ps the multiply charged ion intensity is by far larger when compared to the shortest pulse giving the highest intensity.

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. The electron density decreases during the expansion. However, this will influence the further coupling of the radiation into the cluster. Thus, the ionization efficiency should depend on the width of the exciting light pulse like 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 tunnelling ionization during the rising edge of the laser pulse. This initial charging leads to a rapid expansion due to the Coulomb forces. The model calculations show that after an expansion time of approximately 350 fs the plasmon frequency matches the laser frequency, which is in qualitative agreement with our measurements. More details of the calculations are given in [24].

The dependence of the multi-ionization signal on the pulse width of the laser is also subject of the hydrodynamic approach by Ditmire *et al.* [16]. However, several mechanisms are different in our model. First, the expansion is not forced by collisions but instead by pure Coulomb explosion. 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

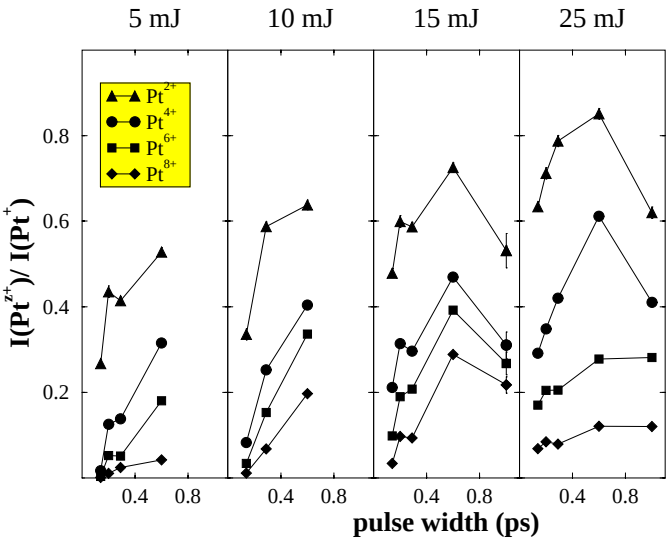

Fig. 4. Ratio $I(\mathrm{Pt}^{z+})/I(\mathrm{Pt}^{+})$ $(z = 2, 4, 6, 8)$ as function of the laser pulse width for different pulse energies. Note that the laser pulse intensity drops by nearly a factor of 10 when increasing the width from 140 fs to 1 ps. A maximum ratio is achieved at a pulse width of about 600 fs.

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, carbon, platinum and lead clusters have been investigated under strong laser field conditions. For C_N it was found that the up–charging process is only limited by the chosen pulse intensity, whereas the Pt_N and Pb_N show a significant increase of the efficiency with increasing pulse length. Highly ionized platinum atoms carrying up to 20 charges have been identified. Modelling the situation shows that the ionization process might be strongly enhanced by plasmon absorption whenever the collective resonance frequency of the metal cluster matches the photon energy of the laser beam. RPA calculations combined with the Coulomb explosion process show that several hundreds of femtoseconds are necessary until a maximum in the ionization cross section is obtained, which agrees well with the experimental observations.

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