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Metal clusters under strong laser field conditions

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Abstract

Neutral clusters are exposed to intense femtosecond laser pulses. Fragment distributions were measured for different laser pulse widths. In contrast to carbon, the platinum and lead clusters show an enhanced charging of the atomic fragments for longer pulse widths, e.g. atomic charge states up to $z = 20$ are detected for platinum at pulse widths of 600 fs. This behaviour can be explained by simulating the coulomb explosion of a metal sphere under tunneling ionization conditions. The calculated time dependent optical response of such a cluster within the framework of the random phase approximation gives evidence for a multiplasmon excitation. (Int J Mass Spectrom 192 (1999) 387–391) © 1999 Elsevier Science B.V.

Keywords: Metal clusters; Optical properties of clusters; Intense laser fields

1. Introduction

The coupling of intense radiation into matter is an interesting topic in fundamental and applied sciences. Here the excitation of low-dimensional objects possibly gives rise to a time-resolved observation of the dynamics of the charging process and the subsequent energy flow. For rare gas clusters, different authors have shown that electromagnetic energy can be efficiently coupled into matter when clusters are used instead of atoms [1–4]. Ion emission with extremely high kinetic energies reaching up to 1 MeV [5] and electron emission with up to 3 keV [6] give an impression of the violence of such processes. The interaction of 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 [7], despite the relatively low target concentration in a molecular beam. Several theoretical approaches have been introduced to explain these observations. Rhodes and co-workers [8] used a simple model based on a collective electron motion. The electron oscillation driven by the laser field induces electron–ion collisions that enhance the ionization inside the cluster. Based on a hydrodynamic approach Ditmire et al. [9] 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 plasmon energy of a classical dielectric sphere.

Also, photoexcitation of metal clusters has been subject of a large number of investigations probing the optical and electronic responses of these small systems. One of the most striking results is the

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observation of plasmon excitations in alkali metal clusters calculated by Ekardt [10] and later measured by de Heer et al. [11]. Based on quantum-chemical configuration interaction (CI) calculations Bonačić-Koutecký et al. [12] explained these measurements by many-electron excitations. Later clusters of several metals were found to show collective excitation effects [13]. Excitations in an energy range close to the dipole resonance have been found to exhibit high absorption cross sections ($\approx$1 Å^2/s electron). The resonance energies are located in the visible to the near UV spectral region, e.g. 4 eV for silver clusters [14]. Only recently several attempts were made to calculate the optical response of sodium clusters to the irradiation by intense laser fields [15,16]. For intensities of 10^{12} W/cm^2 Reinhard and Suraud [15] found an enhanced ionization probability when the exciting laser wavelength is in the vicinity of the dipole resonance of the system. Fullerenes also show collective electron motions. However, the dipole resonance in these systems resides deep in the visible–UV region around 20 eV [17].

In this work we will concentrate on the coupling of intense femtosecond laser light into metal clusters and especially onto the role of possible plasmon excitations involved.

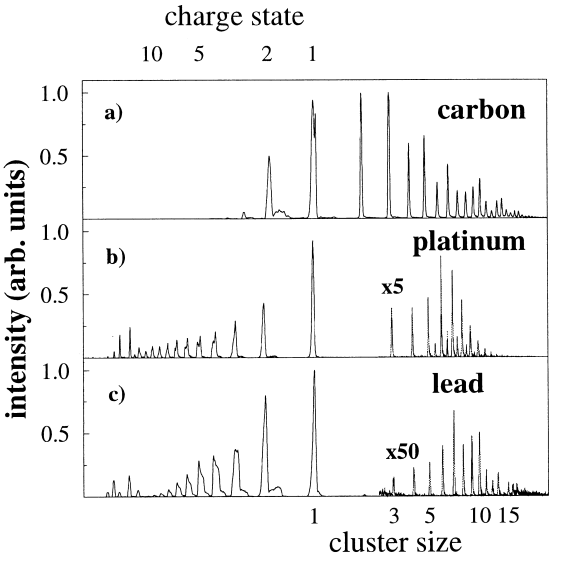

Fig. 1. Mass spectra of carbon, platinum, and lead clusters and atomic ions after excitation of neutral clusters by femtosecond laser pulses of 3×10^{15} W/cm^{-2} at 800 nm (note that the mass spectrometer also maps ionized clusters which arise from the interaction in the low intensity region of the laser focus); in contrast to carbon where only a small fraction of the ion intensity originates from the higher charged ions, the metal cluster spectra show that the main intensity emerges from the abundance of atomic Pt^{z+} and Pb^{z+}, see the left-hand side of the spectra.

2. Experimental setup

A pulsed arc cluster ion source (PACIS) [18–20] produces neutral clusters by co-expanding a vapour plasma and helium forming a supersonic beam. The laser pulses are generated by a Ti:sapphire chirped-pulse amplification (CPA) system which delivers intensities of up to 10^{16} W/cm^2 at 800 nm. In order to investigate the dependence of the multi-ionization of the clusters on the light pulse width, the compressor inside the CPA system is detuned. By doing so the duration of the pulses can be adjusted from 140 fs to several picoseconds. After interaction with the laser field the charged cluster fragments are accelerated by a Wiley-McLaren type electric field setup [21] and detected with respect to their time of flight (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 microseconds after the interaction with the laser pulse. Therefore, especially ions with high recoil energies 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.

3. Results and discussion

The resulting mass spectra of carbon, lead, and platinum clusters after ionization with laser pulses with a peak intensity of approximately 3×10^{15} W/cm^2 are shown in Fig. 1. For carbon, besides C_N^+, also atomic ions with up to four charges are present [see Fig. 1(a)].

However, the remaining atomic 1*s* 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. For carbon both possibilities lead to a drop of the overall abundance of the cluster and the atomic ions.

In the case of platinum, the neutral 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. As a result of the irradiation process small clusters are detected [see Fig. 1(b)]. In addition, doubly charged Pt_N^{2+} is recorded with lower abundance. No triply charged clusters are present. It turns out, that this part of the spectra originates from the ionization of clusters within the lower intensity region of the laser focus. Clusters that are exposed to high intensities are completely destroyed and only atomic ions are detected. This has been tested by mapping only the high intensity region of the laser focus. Tuning the PACIS 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 atoms indicating a different excitation mechanism. Fig. 1(c) shows a TOF spectrum of ionized Pb clusters 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 platinum also triply charged clusters are present. The appearance of Pb_N^{3+} may be due to the presence of larger clusters within the neutral beam in comparison to Pt clusters, which favours the stability of higher charged cluster ions.

Recently it has been reported [22] that the laser pulse width appears to be important for the charging of metal clusters. No such dependence is found for carbon clusters. For clusters of heavy metal atoms a pulse width of 600 fs leads to a maximum in the charging process. For this pulse width, ionizing neutral Pt clusters at the highest pulse intensity yields a spectrum with atomic charge states of up to $z = 20$

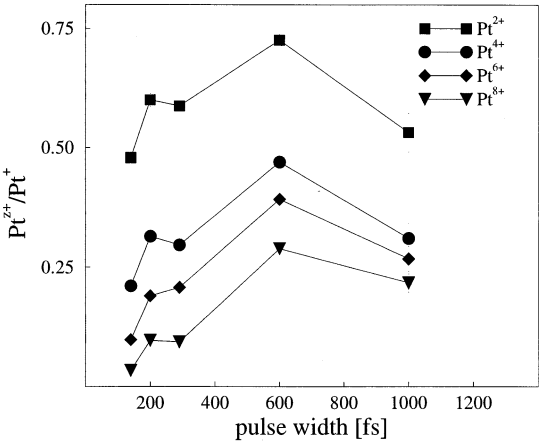

Fig. 2. Ratio $I(Pt^{z+})/I(Pt^+)$ ($z = 2,4,6,8$) as function of the laser pulse width for a pulse energy of 15 mJ (note that the laser intensity drops by nearly a factor of 7 when increasing the width from 140 fs to 1 ps); a maximum ratio is achieved at a pulse width of about 600 fs.

[22]. In order to show that indeed the atomic charge distribution significantly depends on the pulse width τ, Fig. 2 shows the intensity ratios $I(Pt^{z+})/I(Pt^+)$ for selected charge states, e.g. $z = 2,4,6,8$, as a function of pulse width. Note that the light intensity drops with increasing τ. Clearly 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 than that obtained for the shortest pulse giving the highest light intensity.

Trying to explain the physical basis we consider the cluster as being a metal sphere where we calculate the optical response within the random phase approximation (RPA) [23]. Assuming at first a fixed ionization state the electron density of the cluster will decrease since the coulomb repulsion of the charges will lead to an expansion of the sphere. 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 as we have seen in the experiment. For a quantitative analysis the time development of the electron density has to be calculated first, which, in a second step, will serve as input for the computation of the response of

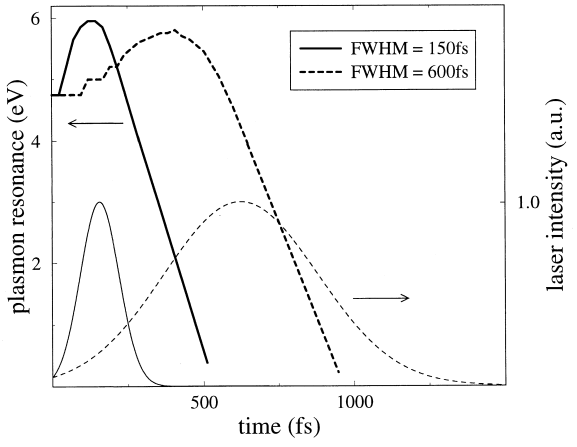

Fig. 3. Time evolution of the dipole resonance of Pt_{58} as a result of the interaction with laser intensities of 10^{13} W/cm^2 for a 150 fs (solid line) and a 600 fs (dashed line) pulse; the corresponding pulse envelopes are shown in the lower half (note the different times that are needed until the plasmon resonances reach the laser photon energy of 1.5 eV).

the jellium cluster on the radiation. Here we restrict ourselves to relatively low intensities of approximately 10^{13} W/cm^2. In the model calculation Pt_{58} is assumed to be ionized up to $z = 29$ by a 150 and a 600 fs (full width at half maximum) Gaussian laser pulse exclusively via tunneling ionization. The charge state, which can be reached by this process, is proportional to the peak intensity of the laser pulse. Hence supposing a constant charge state means keeping the laser intensity constant in contrast to the experiment where the pulse energy is left unchanged for different pulse widths. We also assume that the charging is complete when the maximum of the laser pulse is reached, i.e. the ionization process takes place only at the rising edge. Upon charging the cluster undergoes an expansion due to the coulomb forces. However, in the beginning of this process the charge state of the cluster dominates the resonance position since the electron density stays relatively constant. Thus the plasmon first shifts to higher energies. This result is illustrated in Fig. 3 for two different laser pulse widths. After a certain time, depending on the chosen pulse width, the electron density starts to decrease significantly and determines the plasmon resonance which consequently drops to lower energies. Clearly with the short pulse there is not enough time for a sufficient expansion which would shift the plasmon into resonance with the photon energy of the laser. In the 600 fs case, however, the plasmon energy decreases from 6 to below 1.5 eV within the time scale of the laser pulse even though the expansion is slower. Thus the pulse has to have a sufficient width in order to bring the system into resonance with the exciting laser field.

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. [9]. However, several mechanisms are different in our model. First, the expansion is not forced by collisions but instead by a 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 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 surface.

In conclusion, carbon, platinum, and lead clusters have been investigated under strong laser field conditions. For C_N it was found that the charging process is only limited by the chosen pulse intensity, whereas Pt_N and Pb_N show a significant dependence on the width of the laser pulse. Highly ionized platinum atoms carrying up to 20 charges have been identified. Modeling the situation shows that the ionization process is 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 a simulation of the Coulomb explosion process induced by tunneling ionization 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.

Acknowledgements

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