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Femtosecond ionization of magnesium clusters grown in ultracold helium droplets

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Abstract. Magnesium clusters grown in helium droplets and ionized with femtosecond laser pulses have been studied by high resolution mass spectrometry. For moderate laser intensities the abundance spectra show characteristic features indicating electronic shell effects. Compared to clusters of s^1–electron metals additional shell closures appear resulting from an electron rearrangement. Irradiation with higher laser intensities leads to a decomposition of the magnesium clusters into atomic ions. Due to charge exchange with the surrounding helium matrix mainly singly and doubly charged magnesium ions remain. In addition, the occurrence of $MgHe_N^+$–complexes is observed. Their abundance depends on the shape of the laser field, *i.e.* the laser width and the optical delay when applying the pump–probe technique.

PACS. 36.40.Cg Electronic and magnetic properties of clusters – 71.30.+h Metal-insulator transitions and other electronic transitions

1 Introduction

Due to their electronic configuration clusters of divalent atoms are interesting objects for studying, *e.g.*, the non–metal to metal transition in nano–sized materials. Only little theoretical work focuses so far on magnesium clusters (see, *e.g.*, [1,2]). An experimental study has been constricted for a long time by the strong oxidation of magnesium particles. Up to now only the group of Martin [3] reported on a mass spectrum of larger clusters ($N > 147$), whose structure was attributed to geometrical shell effects.

The capture of atoms by liquid helium droplets has recently opened a possible route to overcome the problems related to the generation of bare clusters of highly reactive elements like magnesium. This pick-up technique is used by several groups for experiments on atoms and molecules [5]. For clusters it has the advantage of a controlled and selective growth and allows spectroscopy near absolute zero. But for some elements the cluster aggregation is unfavorable due to the fact that the atoms tend to be kept in dimples on the surface of the droplet [6]. Using a He–dopant pair potential a simple approach to estimate whether a particle remains on the surface or penetrates into the droplet is given by Ancilotto [7]. The solvation of magnesium appears to be critical in this respect. Recently Reho *et al.* [8] investigated magnesium experimentally and found that the atom enters the droplet.

Because of the charge transport through the helium surrounding the ionization of embedded atoms and clusters requires an excess energy which is about 1 eV in liquid helium [9]. Therefore the anyway difficult single–photon ionization of atoms and clusters now needs even higher photon energies. As these are not available by standard laser systems, multiphoton processes have to be used. In this contribution we report on experiments using femtosecond ionization. Applying moderate pulse intensities results in singly and doubly charged clusters. In the size range up to about 80 atoms the abundance is clearly dominated by electronic shell effects. When using higher intensities the interaction with the laser field can lead to multiple ionization of each atom within the metal kernel. Like in earlier investigations of the Coulomb explosion of bare metal clusters [10] a plasmon enhanced ionization efficiency is found for longer pulse widths. Here we will concentrate on the abundance of $MgHe_N^+$–complexes, *i.e.* the helium snowball formation around a positively charged impurity [11].

2 Experimental setup

Ultracold helium droplets are produced by supersonic expansion of pre-cooled helium gas [4]. The source conditions are tuned in such a way that the droplets contain on average a hundred thousand atoms. The skimmed beam passes a heated oven containing up to 10^{-4} mbar of magnesium vapor. By pick–up of individual atoms, bare magnesium clusters grow inside the droplet. Evaporative cooling reduces the temperature of the doped system to a value of about 0.4 K [5]. Identification of the clusters after ionization is achieved by high resolution mass spectrometry using a reflectron time–of–flight setup. The doped helium droplet beam enters the ionization region of the mass spectrometer through a 3 mm hole in the back of the repeller electrode. For ionization a Ti:sapphire chirped pulse

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amplification laser system is used which delivers sub–100 fs pulses at 800 nm with a pulse energy of up to 25 mJ. A pulsed 4 kV extraction voltage accelerates the ionized clusters. In order to enhance the mass resolution a static ion mirror is used. Before detection the particles are accelerated to an energy of 15 keV.

3 Results and discussion

Moderate pulse intensities

A spectrum of magnesium clusters, Mg_N, ionized by laser pulses of moderate intensity (10^{11} W/cm^2) is shown in Fig. 1. For clarity the isotopic distribution is smoothed. In addition, the ion intensity is multiplied by the number of pick-up events. Under the chosen experimental conditions a helium droplet contains an average number of fifteen magnesium atoms. The cluster size distribution shows outstanding peaks, significant intensity drops and pronounced minima. The latter can be found at $N = 22$, 37 and 57. In order to rule out possible resonance effects, mass spectra were also recorded using nanosecond laser excitation and electron impact ionization. The structures found in the abundance distribution turn out to be independent of the ionization method and must originate from the same physical reason.

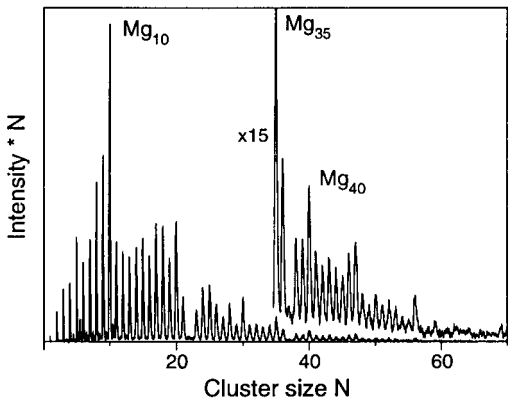

Fig. 1. Abundance spectrum of magnesium clusters grown in superfluid helium droplets and ionized by laser pulses of moderate intensity ($I = 10^{11}$ W/cm^2, $\lambda = 400$ nm, $\tau = 200$ fs). Prominent peaks and striking minima are present indicating electronic shell effects.

In contrast to the findings for larger magnesium clusters [3] no clear indication for geometrical isocahedral shell closures can be found. Instead, the abundance pattern shown in Fig. 1 resembles some magic numbers known from the s^1–metal clusters which can be explained by the jellium model [12]. Since magnesium is a divalent element one expects the most stable clusters for $N = N_e/2$, where N_e is the number of electrons at a shell closure. Note, that the spectrum in Fig. 1 shows singly charged clusters which, in contrast to the neutral ones, do not match the shell closures exactly.

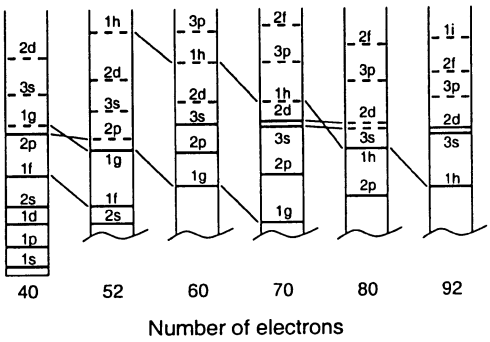

Fig. 2. Schematic illustration of the energy level order for magnesium clusters with corresponding number of electrons (solid lines: fully occupied energy levels, dashed lines: unoccupied levels). With the proposed level crossings the additional magic numbers in magnesium clusters can be explained.

In order to understand the details in the abundance pattern, particularly the *additional* shell closures, we assume a level interchange process, which is illustrated in Fig. 2. For a more detailed explanation we refer to Ref. [13]. As an example let us explain the magic number at $N = 40$, *i.e.* the 80 electron system. The enhanced intensity at $N_e = 70$ can reasonably be explained within LDA calculations [14]. The next shell closure in the spectra obviously appears at $N_e = 80$ ($N = 40$), see Fig. 1, which is not predicted by the standard jellium model. Within our model the explanation is the following: While successively adding electrons, between $N_e = 70$ and $N_e = 80$ the system rearranges and the $1h$ level dives underneath $2d$ and $3s$ accumulating all of their electrons. As a consequence a new shell closing appears at $N_e = 80$. A similar situation might be responsible for the additional magic numbers at $N_e = 52$, 118 and 124. We have identified three regions as possible candidates ($N_e = 40$–52, 70–80, 112–118) for an level interchange process. Note, that the crossings coincide with the most striking dips in the abundance spectra.

The effect that high–ℓ momentum states dive underneath low–ℓ ones is well known from a simple harmonic oscillator model which includes a momentum correction parameter U [12]. The eigenvalues in units of the oscillator frequency and the shell number m are $(m+3/2) - U(\ell^2 - m(m+3)/6)$. U is usually small and a value of $U = 0.06$ is sufficient to explain magic numbers at $N_e = 80$, 118 and 148. For comparison $U = 0.045$ gives the shell closing sequence for the alkalis. Shell crossing effects were also found in density functional calculations for ^{3}He droplets [15,16]. The principal reason for the observed abundance spectra of magnesium clusters and the level exchange seem to be a Friedel potential dip at the edge of the cluster [17]. This effect favors surface states and thus an especially pronounced down shift of high–ℓ levels as a function of the total number of electrons. In ^{3}He droplets this occurs exceptionally strong for already filled shells [15]. In magnesium clusters the contribution of the Friedel–dip must become significant while levels being occupied, leading to the observed level interchange.

In addition to the well–resolved Mg_N for $N \leq 80$, for large masses the spectrum shows distinct but unresolved intensity, see Fig. 3. The abundance signal first decreases by more than 3 orders of magnitude up to about 100 magnesium atoms and then rises again to exhibit a broad feature ranging up to 60000 amu. It could result either from clusters containing several hundreds of magnesium atoms or small magnesium clusters which are still embedded in the helium droplet. It cannot completely ruled out that even pure helium droplets contribute. The helium source parameters are tuned to a regime close to the critical expansion. Therefore the helium droplets probably have a bimodal size and velocity distribution, *i.e.* droplets with enormous differences in size and speed are produced [5]. Large magnesium clusters can be formed as a result of the enhanced pick–up cross section and the lower velocity of huge helium droplets having more than 10^6 atoms. Already a slight variation in the helium source temperature leads to very different mass spectra, see Fig. 3.

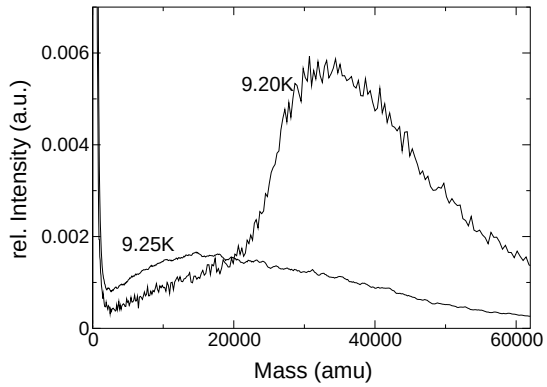

Fig. 3. Abundance distribution of magnesium clusters in helium droplets concentrating on the high mass range up to 60,000 amu. Note, that the displayed spectra are normalized to the signal in the mass range up to Mg_{10}. So far we cannot resolve whether this intensity origins from pure Mg_N or $Mg_N He_M$ complexes.

In addition to singly charged clusters, ionization with femtosecond laser pulses and electron impact shows abundance of doubly charged species, see Fig. 4. The isotopic distribution, which is well resolved by the time–of–flight mass spectrometer, also allows for the non–ambiguous identification of even numbered Mg_N^{++}. Without doubt the abundance is dominated by fragmentation. Therefore the detected magic numbers are governed by the stability of the cluster ions. The total number of electrons in these systems is even and consequently can match the magic numbers exactly, *e.g.*, $Mg_{11}{}^{++}$ ($N_e = 20$) and $Mg_{21}{}^{++}$ ($N_e = 40$). Within the time window of the experiment the smallest doubly charged cluster detected is Mg_5^{++}. This cluster size fits well to the $1s^2 1p^6$ shell closure in the jellium model. The appearance of a critical size indicates that the formation of an Mg^{++} core as a fragment is unfavorable, in contrast to mercury clusters [18].

Strong field conditions

In a recent contribution [10] we have shown that metal clusters under strong laser field conditions disassemble completely by Coulomb explosion into atomic ions having up to 180 keV of kinetic energy, see also Teuber *et al.*, this issue. Many–body effects, *i.e.* plasmon excitations, are responsible for an enhancement of the charging process at certain laser pulse conditions resulting in atomic charge states of up to $z = 28$ for Pb_N [19]. Pump–probe measurements as well as molecular dynamics simulations in connection with RPA calculations have shown that the charging *via* multi–plasmon excitations is particularly efficient at about 800 fs after the initial ionization [19]. For metal clusters in droplets the situation could be different. Due to the surrounding matrix a high charge state of the cluster might have only a fairly low lifetime since charge exchange with helium is certainly a strong decay channel.

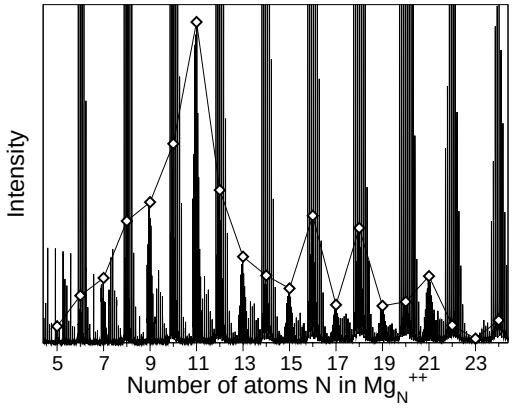

Fig. 4. Isotopically resolved mass spectra showing singly charged (large peaks) and doubly charged Mg_N. The intensity of the Mg_N^{++} is visualized by the diamonds. The high resolution of the time–of–flight mass spectrometer allows for an non-ambiguous identification also of even–numbered Mg_N^{++}. Enhanced abundance and intensity steps are found exactly for those cluster sizes which fit to electronic shell closures, *e.g.*, Mg_{11}^{++} ($N_e = 20$) and Mg_{21}^{++} ($N_e = 40$).

In order to study the dynamics in these coupled systems we started first experiments on the Coulomb explosion of metal clusters in helium droplets. Fig. 5 shows a spectrum where magnesium atoms and small clusters are irradiated by 150 fs laser pulses having a pulse intensity of 2×10^{15} W/cm^2 at 800 nm. The abundance distribution mainly consists of singly and doubly charged magnesium ions with up to 150 helium atoms attached to Mg^+. A sharp drop in the intensity of small complexes with up to twenty helium atoms is followed by a broad plateau which is a clear sign that they arrange themselves in shells around the magnesium ion. Note, that for moderate laser intensities such a distinct snowball formation is not present (see Figs. 1 and 4). The structure of the spectrum suggests a partial crystallization of helium atoms close to the magnesium ion. This observation agrees well

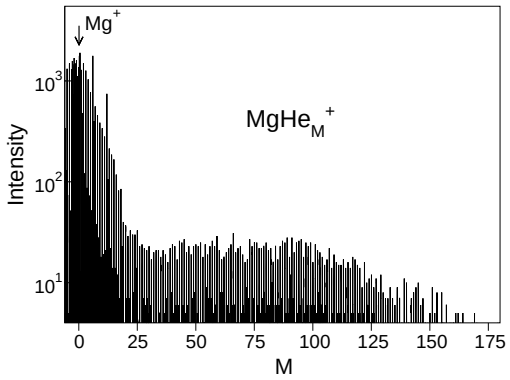

Fig. 5. Helium–Mg^+ snowball formation upon irradiation of embedded magnesium clusters. A significant drop in the abundance up to about twenty helium atoms is followed by a broad plateau which indicates the formation of partially solid helium shells. Note the logarithmic scale.

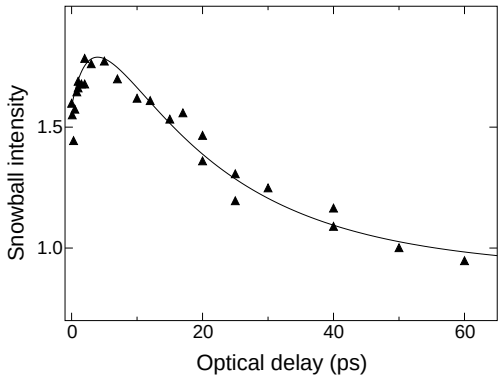

Fig. 6. Femtosecond pump–probe experiment concentrating on the overall abundance of $MgHe_M^+$. The snowball intensity shows a strong dependence on the time–delay between the two pulses. Dynamics in the pump–probe signal is clearly present up to more than 50 ps.

with recent calculations of Duminuco *et al.* [20], who analyzed the local order of helium atoms around a potassium ion.

When decreasing the laser intensity the magnesium cluster signal recovers. In this intensity regime it is interesting to investigate the laser pulse width dependence. Keeping the pulse energy constant and increasing the pulse duration, the signal of Mg_N^+ diminishes whereas the $MgHe_M^+$ and $MgHe_M^{++}$ abundance becomes stronger. This is accompanied by a considerable change of their relative abundance. For pulse widths of about 3 ps the number of helium atoms attached to Mg^+ falls off exponentially with size, *i.e.* the distinct signatures of helium shells like in Fig. 5 are not present anymore. In order to explore this effect in more detail we have performed a set of measurements using the pump–probe technique, see Fig. 6. In contrast to the just described experiment now the pulse *intensity* is kept constant (5×10^{12} W/cm^2). Up to about 4 ps the overall $MgHe_M$ (snowball) intensity increases by about 40%. A qualitatively similar dynamics has been found earlier in the Coulomb explosion of bare metal clusters [19], even though there the maximum signal was achieved at a delay of approx. 0.8 ps. Up to now the underlying physical process is not fully understood. If a plasmon enhanced ionization process is responsible for the intensity gain at about 4 ps the expansion of the cluster would significantly be hampered by the helium surrounding. Most remarkably a pump–probe effect is present up to more than 50 ps indicating a long time interaction dynamics between the metal cluster and the helium droplet.

4 Summary

Bare magnesium clusters have been investigated by high resolution mass spectrometry. With moderate femtosecond laser intensities magic numbers can be identified which are related to the appearance of electronic shell effects in these small clusters. Higher pulse intensities lead to snowball formation around the magnesium atom, which crucially depends on the laser pulse width. With the pump–probe technique it is possible to follow the long time interaction dynamics up to several tens of picoseconds.

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