Time-resolved studies on the collapse of magnesium atom foam in helium nanodroplets

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Abstract. Magnesium atoms embedded in superfluid helium nanodroplets have been identified to arrange themselves in a metastable network, referred to as foam. In order to investigate the ionization dynamics of this unique structure with respect to a possible light-induced collapse, the femtosecond dual-pulse spectroscopy technique is applied. Around zero optical delay a strong feature is obtained which represents a direct probe of the foam response. We found that upon collapse, ionization is reduced. A particular intensity ratio of the pulses allows us to address either direct ionization or photoactivation of the neutral complexes, thus affecting reaction pathways. A simplified scheme visualizes possible excitation scenarios in accordance with the experimental observations.

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1. Introduction

In cluster physics, the size-dependent evolution of fundamental properties is of special interest [1], e.g. changes in bond character, in particular, the non-metal to metal transition phenomenon [2]. Much effort has been devoted to identifying the critical size $N_c$ characterizing the transitional regime, see, e.g., [3] for a summary. For magnesium, which is the subject of this study, it was found that the transition takes place at around $N_c = 20$ atoms [4, 5]. Meanwhile, it became possible to determine $N_c$ also in elements with $s^2p^2$ orbital configurations such as tin [6] or lead [7]. Up to now, studies on clusters have concentrated on various aspects that depend on the number of their constituents. Hence, referring to the original suggestion by Mott [8] that a phase transition is induced via the change in the atomic density has not been tackled with clusters up to now. In general, when small clusters in the gas phase aggregate, they do so near their electronic and structural ground state with excitations of the order of $k_B T$. An interesting issue would be to study finite systems in which the interatomic distances can to some extent be controlled. Examples are atoms in optical lattices [9] and cold Rydberg gases where the van der Waals interaction leads to Coulomb blockade of optical transitions [10]. However, these systems are designed to probe the response at $\mu$m interatomic distances.

The liquid or even superfluid properties of bulk helium at ultralow temperatures allow the formation of ensembles in which the constituents are separated by nanometers, see [11] for a recent review. An interesting idea was presented in the early 1970s by Gordon et al [12] who proposed that single atoms or molecules surrounded by dense helium agglomerate to weakly bound complexes. Consequently, a network with regular spacing forms. However, in bulk it has been proven that, instead of helium-encapsulated atoms, larger particles such as clusters form the superordinate structure [13]. In the literature those complexes are referred to as impurity helium solids (IHS) [12] or icebergs [14]. Alternatively, doping of helium nanodroplets offers a promising approach to control the growth process, which is the main disadvantage in the preparation of IHS [15]. Spectroscopic evidence has been found that metastable complexes of well-defined size can be formed, e.g. chains of polar molecules [16] and fractals [17] (structural selection) as well as clusters in high-spin states (electronic selection) [18–20]. However, these species do not represent the structure originally proposed by Gordon. Ideal candidates are atoms interacting via van der Waals forces and having binding energies close to the He–He interaction, e.g. noble gas atoms or divalent metal atoms, with respect to the non-metal to metal transition. Indeed, in density functional theory (DFT) simulations of the neon dimer the anticipated structure has been found [21].

Recently, we found experimental evidence that Mg atoms arrange in a Gordon-like assembly resembling a foam-like structure [22]. Those studies have been conducted by means of resonant two-photon ionization mass spectrometry with nanosecond laser pulses, taking the atomic $3^1P_0 \leftarrow 3^1S_0$ transition of single embedded Mg atoms as a spectral reference [23, 24]. For droplets containing more than one atom on average, a nearby narrow peak shows up that is red-shifted by a few nm, i.e. from $\lambda_{\text{atom}} = 279$ nm to $\lambda_{\text{aggregate}} = 282$ nm. The optical spectra of all clusters (up to $\text{Mg}_7^{+}$), which appear as result of the excitation in the mass spectra, peak at the same $\lambda_{\text{aggregate}}$. This spectroscopic finding suggests that before excitation single Mg atoms are dissolved within the droplet. From the peak shift with respect to the monomer signal, an interatomic Mg–Mg distance of 10 Å has been deduced. It is therefore likely that the atoms arrange in a regular foam-like network. We can thus assume that the increase in helium density around Mg impurities as a result of van der Waals forces and modified by the
superfluid properties of the nanodroplet [25] leads to the formation of a shallow potential barrier of the order of a few K. This effect prevents Mg atoms from collapsing to the cluster ground state. Our results are supported by chemiluminescence studies on Mg atoms embedded in He droplets conducted in [26] the Krasnokutski and Huisken group. From the theoretical side, DFT calculations by the group of Barranco confirm that a helium-induced potential barrier prevents the formation of ground state Mg dimers [27, 28].

In the present paper, we test the existence of a possible Mg foam by means of femtosecond pump–probe spectroscopy. Because the barrier is expected to be low, photon absorption will be sufficient to destroy the metastable state and initiate a rapid collapse on a ps timescale. We follow this idea using fs-laser pulses to trigger the transition and study the temporal development of the involved dynamics. Dual pulses with a particular intensity ratio have been applied to explore the relaxation pathways. We found that the specific yields crucially depend on the pulse order. The analysis of the complex photoinduced dynamics provides further evidence of the anticipated foam structure.

2. Experimental setup

A schematic view of the experimental setup is shown in figure 1. The femtosecond laser system provides pulses with a variable width (30 fs–1 ps) at a repetition rate of 1 kHz with a maximum energy of 2.5 mJ at \( \lambda_L = 810 \) nm. The pulses are fully analyzed using a home-built SHG-FROG device [29]. In the experiment, we choose a pulse width of about 200 fs (full-width at half-maximum (FWHM)). For the dual-pulse measurements, the optical delay is generated by a Mach–Zehnder setup. An attenuator in one of the interferometer arms allows to select the pulse energy ratio.
Figure 2. Typical TOF spectrum of magnesium complexes \( (N_{avg} = 7) \) formed in 10 nm-sized helium droplets (40 000 atoms) recorded after femtosecond MPI. As a result of the interaction, Mg\(_{5}\) clusters and Mg\(^{+}\)He\(_M\) snowballs (red) are formed. The single pulse laser intensity is \( 6 \times 10^{11} \) W cm\(^{-2}\). The multiple-peak structure of Mg\(_{N}\) arises from the atomic isotope distribution.

The helium droplet pick-up technique \([30, 31]\) is applied to produce complexes of embedded Mg atoms, the details of which are provided elsewhere \([15, 32, 33]\). In short, a cold helium gas at 20 bar is expanded through a 5 \( \mu \)m orifice. By tuning the nozzle temperature between 9 and 14 K, the droplet sizes vary from 70 to 7 nm \([34]\). The molecular beam passes through a 4 cm-long heated cell containing magnesium pellets. By tuning the oven temperature, the number of atoms being picked up by the droplets can be adjusted. After differential pumping the doped droplets enter the interaction region where the laser beam perpendicularly intersects the molecular beam. The intensity conditions have carefully been checked and calibrated to the ion appearance intensity of xenon \([35]\) gas with an uncertainty factor of about 2. The resulting ionic products of the interactions are analyzed by reflectron TOF mass spectrometry.

In the present study, the source is tuned to conditions similar to those in \([22]\): helium droplets with a mean size of about 40 000 atoms are doped with \( N_{avg} = 7 \) Mg atoms on average. We cross-checked the actual target composition by simulating the pick-up process taking the helium droplet distribution for the experimental nozzle temperature and the Mg vapor pressure in the oven cell into account \((T_{source} = 10 \text{ K}, p_{Mg} = 5 \times 10^{-5} \text{ mbar})\). A slightly off-focus configuration of the laser beam with respect to the molecular beam axis leads to a power density of \( I = 6 \times 10^{11} \) W cm\(^{-2}\). At this reduced laser intensity Mg atoms undergo multiphoton ionization (MPI), whereas the charging of helium is negligible due to its higher ionization energy. Laser conditions are chosen that neither \( \lambda_{L} \) nor its harmonics are close to \( \lambda_{aggregate} = 282 \) nm \([22]\). However, ionization can be enhanced by near-resonant three-photon absorption into \( \lambda_{aggregate} \) with reduced cross-section or possible higher excited states.

### 3. Results

Figure 2 depicts a section of a TOF spectrum resulting from ionization with fs laser pulses. Cluster ions with \( N \leq 20 \) atoms can be detected. Concentrating on the low mass range, Mg\(_5\)
Figure 3. Total ion yields after dual-pulse excitation of droplets containing $N_{\text{avg}} = 7$ Mg atoms. Evidently, the signal sensitively depends on whether the strong pulse is applied first or second. If the ionizing pulse arrives after the weak initial pulse ($\Delta t_{\text{pos}}$) the yield is reduced by a factor of 2 compared with the reversed order ($\Delta t_{\text{neg}}$). The strong peak around zero delay hints at an ultrafast response of the excited aggregates and contains only a small autocorrelation contribution. Yields obtained for single strong ($Y_{\text{tot}}^s$) and single weak ($Y_{\text{tot}}^w$) excitations are indicated by bold symbols. The dashed line represents the sum of these signals ($Y_{\text{tot}}^s + Y_{\text{tot}}^w$). Laser intensities: $I_s = 6 \times 10^{11}$ W cm$^{-2}$ and $I_w = 2 \times 10^{11}$ W cm$^{-2}$.

and Mg$_{10}^+$ show up with increased yields, indicating that these are more stable compared to adjacent ones. Similar features have also been observed utilizing ns-excitation as well as electron impact [4]. The spectrum shows strong contributions from ion snowballs (Mg$_s^+\text{He}_M$, marked in red in the figure), a well-known product observed in strong-field ionization, such as in Coloumb explosion of doped droplets [36]. In order to identify the foam response, one has to control the initial excitation, followed by an interrogation step. We manage this by fs-dual-pulse measurements choosing a pulse energy ratio of $E_s/E_w = 3$, with peak intensities in the interaction volume of $I_s = 6 \times 10^{11}$ W cm$^{-2}$ for the strong and $I_w = 2 \times 10^{11}$ W cm$^{-2}$ for the weak pulses, respectively. In these conditions a ten times higher ionization rate is observed for $I_s$ (the total rate at 1 kHz repetition rate $Y_{\text{tot}}^s = 210$ s$^{-1}$) compared with $I_w$ ($Y_{\text{tot}}^w = 18$ s$^{-1}$). Hence, the strong initial pulses create charged complexes, while the weak ones predominantly yield neutral electronically excited (termed photopactivated in the following) systems. Note that the total charge produced in the laser interaction with a single droplet is well below unity. In the experimental runs the time delays of the dual pulses as well as their order are varied.

Figure 3 shows the dual-pulse total ion yield $Y_{\text{tot}}$ as a function of pulse separation $\Delta t$. A distinct dependence on the order of the pulses is obtained. Moreover, except for the range around zero delay the dual-pulse signal stays well below that of the sum of individually applied pulses (see the dashed line in figure 3). This observation is less pronounced with strong leading pulses, i.e. negative delays $\Delta t_{\text{neg}}$, but becomes distinct when ionization with the strong pulse.
Figure 4. The same as figure 3, but resolving for selected reaction products. The specific yields shown on a logarithmic scale are normalized to the signals after exclusively applying single strong pulses. For $\Delta t_{\text{neg}}$, ions are produced already in the interaction with the first pulse. The impact of the weaker trailing pulse is marginal. However, slight differences are obtained when comparing molecular ions (e.g. $\text{Mg}_3^+$) and clusters. Weak initial pulses instead ($\Delta t_{\text{pos}}$) generate conditions where the impact of the strong pulse is reduced significantly. This holds true for all ion channels and is most obvious for $\text{Mg}^+$ and snowballs. In addition, a strong dynamical feature is observed, which gets less pronounced for larger clusters. After the minima at about $\Delta t = +20$ ps the signals recover on a timescale of 100 ps. The values for single weak pulse exposures are indicated (filled symbols).

is delayed, i.e. positive delays $\Delta t_{\text{pos}}$. For $\Delta t_{\text{neg}}$ the yield is almost constant irrespective of the pulse separation, being close to the rate $Y_{\text{tot}}^+$ of the strong pulse alone. Pre-excitation with weak pulses instead results in a drop in the signal to about half of the former value $Y_{\text{tot}}^+$. Around zero delay the signal is strongly enhanced, partially originating from the temporal overlap of the pulses. However, the width of the feature is broader than expected from the autocorrelation, see the discussion below and figure 5 for a high-resolution study. In addition, a minimum evolves at around $\Delta t = +20$ ps. At larger optical delays the signal recovers, but at a lower level when compared to $\Delta t_{\text{neg}}$.

In order to sample possible reaction pathways, we now concentrate on selected ionic species for the same dual-pulse sequence, see figure 4. The spectra are normalized to the yield of the single strong pulses. In general, all interaction products qualitatively exhibit a signature
of the total ion yield. Around zero delay a strong enhancement is observed for all ions, followed by a rapid drop within the first ps. At larger $\Delta t_{\text{neg}}$ the second (weak) pulse contributes less and the yields stay close to that of the first strong pulse. However, the signals of larger clusters are slightly below those of smaller ones (e.g. $\text{Mg}_3^+$), irrespective of the delay. At positive delays $\Delta t_{\text{pos}}$ all ions show a significantly reduced count rate, with specific responses to the delayed ionization. Over the entire timescale, the yields are lowest for atoms and snowballs. For clusters, the signal increases with $N$ and is highest for $\text{Mg}_{10}^+$. However, the count rates stay a factor of two below the normalized single pulse reference. Furthermore, after the fast ps decay, $\text{Mg}_{10}^+$ shows a more or less time-independent signature, while snowballs and small clusters depict strong dynamics in this region. The minima around $\Delta t = +20$ ps are followed by a recovery of the signals on a timescale of about 100 ps. We emphasize that especially around the dip, no other ion channel gains intensity, which hints at a minimum of the ionization efficiency rather than controlling fragmentation pathways.

4. Discussion

An Mg foam in helium droplets would represent a unique state of matter and should show temporal fingerprints not expected for compact clusters. Because the atoms form a regular 10 Å-spaced network being far off the closed packed cluster ground state, a substantial energy reservoir is present. Perturbing the structure by, for example, photoabsorption will trigger a rapid collapse. The energy release of the order of 0.5 eV per atom will transiently convert the condensate into a highly excited system. The results of classical molecular dynamics simulations, where the foam artificially undergoes a sudden change to metallic binding, gives an implosion time of about 1 ps [38] in rough accordance with the fast decay times obtained around zero delay, see figures 3 and 4. In order to highlight this time regime, dual-pulse studies have been conducted with 60 fs (FWHM) pulses of equal intensity. As representative of the typical system response, the signal of $\text{Mg}_{10}^+$ is shown in figure 5. The experimental data can be approximated by a two-term fit: an exponential decay of about $\tau = 350$ fs describing the collapse and an autocorrelation function that accounts for nonlinearities when the subpulses overlap. We wish to emphasize that similar $\tau$ values are obtained for all ionic products.

In order to explain the fast decrease of the ion signal, we anticipate that the collapse will be reflected in a change of the ionization cross sections. With the reduction of the interatomic distances during the collapse, electronic properties are expected to evolve from atomic- to more bulk-like, which expresses the key concept of Mott [8]. The transition is accompanied by an increase in level density, which has an influence on the excited state lifetimes. In the metallic limit, lifetimes of excited states as short as fs have been determined [39]. Thus the change in bond character and electron relaxation time is expected to reduce the MPI efficiency when compared with the initial foam configuration.

At this point, we wish to mention the quantum optics aspect of the Mg atom ensemble. In the network the large Mg–Mg distance causes a weak overlap of the atomic wave functions, i.e. the foam represents a degenerate dipole ensemble which also introduces the question of collective excitations [40]. For such systems, optical properties may be modified when compared to single atoms due to the quantum coherence of the atomic states. Hence the fast decay of the signal could be a signature of decoherence, i.e. the time for establishing disorder which goes along with the system collapse. For a theoretical description of this problem,
Figure 5. High-resolution scan of Mg$_{10}^+$ close to zero optical delay with equal intensity dual pulses (60 fs (FWHM), $I = 8 \times 10^{11}$ W cm$^{-2}$ each) using the technique of colored double pulses [37]. Mg$_{10}^+$ is chosen as representative of larger clusters. In addition to a fast correlation signal (red) the fit yields a decay time of $\tau = 350$ fs (blue) which we attribute to the foam collapse. All ionic channels show the same $\tau$, which suggests that not clusters but the response of a weak interaction ensemble is sampled.

however, one would have to consider the coherent excitation of an ensemble of atoms under MPI conditions, a challenge which, to our knowledge, has not been tackled so far.

Before discussing details of the collapse, an alternative scenario has to be considered, i.e. the response of initially compact clusters with emphasis on typical timescales and energetics. Electronic decay times in small particles are of the order of some 100 fs, e.g. Ag$_N$ [41], Pd$_N$ [42], Al$_N$ [43] and Au$_N$ [44], which is close to our result. But all those studies exhibit strong size dependence, in contrast to our measurements which give the same value $\tau = 350$ fs for all products. Furthermore, photon absorption will lead to heating of the cluster. Fragmentation as a possible decay channel leads to neutral monomer and dimer ejection and shifts the size distribution toward smaller clusters (Mg$_N^{(+)} \rightarrow$ Mg$_{N-m}^{(+)} +$ Mg$_m$) [46]. Photoinduced fragmentation typically occurs on longer timescales compared to our pulse width, e.g. 500 fs for sodium clusters ($N < 20$) [45]. Therefore, in the experiment only delayed ionization would enhance the signal of small fragments, e.g. snowballs. In contrast, the corresponding pulse sequence ($\Delta t_{\text{pos}}$) in figure 4 leads to a significant reduction of Mg$^+$He$_M$. In general, fragmentation increases the number of particles and should give higher total ion yields for postponed ionization, again in contrast to our measurements (see figure 3). Since neither a distinct size dependence on $\tau$ nor a characteristic cluster fragmentation pattern on a ps timescale is observed, we infer that the results are incompatible with the response of initially compact clusters.

With respect to the induced collapse scenario of the foam, it appears to be possible to rationalize the strong dependence of $Y$ on the pulse order. For this, we discuss two different
Figure 6. Sketch of the Mg foam dynamics after dual-pulse excitation. Sequence (I) (middle to left): a strong initial pulse directly ionizes single atoms in the foam state. Ions act as seed forming charged compact clusters (ion-induced nucleation) and ion snowballs (increased snowball formation). Weak trailing pulses do not ionize further but contribute with heating of the ionic clusters. No delay dependence in the ion yields is expected. Sequence (II) (middle to right): a weak initial pulse photoactivates the foam and induces a fast relaxation into a neutral cluster (neutral foam collapse). The strong trailing pulse hits a compact system. Since the collapse is accompanied by a decrease in MPI efficiency fewer ions are produced. Ejection of exciplexes (Mg*HeM) will lead to a time dependence in the snowball signal.

decay pathways, i.e. (I) ion-induced nucleation for strong ($\Delta t_{neg}$) and (II) neutral foam dynamics for weak initial pulses ($\Delta t_{pos}$). Both sequences are illustrated in figure 6.

In sequence (I) strong initial pulses create ionic seeds acting as nucleation centers for the instantaneous formation of Mg$_2^+$. As a competing channel, Mg$_2^+$ snowballs are produced favored by the enhanced helium density surrounding each impurity atom in the foam state. The weak trailing pulses have almost no influence on the charging. Instead, they may heat the nascent complexes and induce some fragmentation. Indeed, only a tiny enhancement in the signal of molecular ions (Mg$_3^+$) is obtained when compared to larger clusters, see the left side of figure 4. Moreover, a delay-independent ion signal should evolve, in agreement with our experimental observation.

In sequence (II) the dynamics of the neutral photoactivated system is investigated. The weak preparatory pulse triggers a collapse of the neutral foam. The time evolution is probed by the delayed pulse which now ionizes the collapsing or the later compact cluster. As discussed above, MPI of compact clusters should be reduced when compared with the initial foam. Thus, a strong dependence on the pulse order and a reduced Y for positive delays are expected, in accordance with the results in figures 3 and 4. Note that the formation of snowball complexes upon ionization of compact clusters is less likely compared with the foam state.
Induced by the weak pulse the electronic configuration of the embedded atoms can be changed, leading to exciplex Mg\(^*\)He\(_M\) formation [47–49]. The increased local helium density around Mg\(^*\) isolates the complex from the rest of the foam. These systems are characterized by long-living excited states and thus electronic relaxations can be excluded over the entire timescale of the experiment. Compared to ions which tend to drift toward the center of the droplets [50, 51], it is well known that excited atoms and exciplexes are expelled from the host matrix, as a consequence of the extended valence orbital, see, e.g., [52, 53]. Ionization within the droplet (i.e. short \(\Delta t\)) will lead to recombination into a cluster ion. In contrast, once an exciplex has left the droplet, cluster ions built by recombination are rather unlikely and snowballs are formed instead. Hence the signal on Mg\(^*\)He\(_M\) should show a time dependence which is directly related to the exciplex ejection. For droplet sizes of 10 nm, ejection times of the order of 100 ps are expected taking the Landau velocity (58 ms\(^{-1}\)) into account. A corresponding signature is observed for (\(\Delta t_{\text{pos}}\)), see figure 4. The yields of atomic ions and snowballs show minima followed by a recovery of the signal. The increase of Mg\(^*\) and Mg\(^*\)He\(_M\) can thus be interpreted as exciplex escape time, which we estimate to about \(\tau_{\text{esc}} = 50\) ps. This consideration is supported by the fact that the minima are less developed for dimers and trimers and are almost absent for clusters.

5. Summary and conclusion

Femtosecond dual-pulse spectroscopy has been utilized to study the response of magnesium atoms embedded in helium droplets. The results are consistent with the hypothesis that single atoms arrange in a foam-like ensemble. By applying pulses of a certain intensity ratio, the light-induced dynamics by either instantaneous ionization or neutral photoactivation can be addressed. On a picosecond timescale the yields exhibit a rapid drop. A decay time of about \(\tau = 350\) fs has been determined, which is attributed to the collapse of the foam into a compact cluster. A qualitative model accounts for most of the spectral features in the experiments. The observed real-time dynamics could be of fundamental relevance, since the foam implosion might reflect the Mott transition. Further, the loss of the coherent character of the weakly interacting ensemble touches aspects of quantum optics. In this work, the focus was on excitation and charging dynamics at the lowest power to monitor exclusively dynamics in the multiphoton regime. At higher laser intensities, the onset of delayed plasmon-enhanced multi-electron ionization [54, 55] provides another approach to probe the foam. Moreover, these aggregates may serve as interesting targets for intense laser–cluster interaction studies.

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