

Light-induced collapse of metastable magnesium complexes formed in helium nanodroplets

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Doping helium nanodroplets with more than a single Mg atom leads to a shift of the atomic absorption from 279 nm to 282 nm. This behavior is stable against a change of the chosen droplet size. There is evidence that the interplay of the weak long-range potential between individual Mg atoms and the interaction with the surrounding quantum fluid leads to the formation of metastable very weakly bound complexes high above the global energy minimum. They resemble a bubble foam, where the individual Mg atoms are separated by a helium layer. The formation of compact Mg clusters is hindered by density variations within the superfluid solvent. The distance between the Mg atoms is substantially larger compared to the ground state. We estimate a value of roughly 10 Å and the barrier, preventing the formation of compact Mg clusters to only a few kelvin. Upon laser excitation the metastable complexes collapse on a time scale of 20 ps as measured with a femto-second pump-probe experiment.

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The spectroscopy of atoms, molecules, and clusters embedded in nanosized helium droplets is an interesting tool as it allows one to investigate both the optical and electronic properties of the dopants at very low temperatures as well as their interaction with the superfluid solvent [1]. In the case of a single atom, the Pauli repulsion between the electrons of the helium and the foreign atom causes a small bubblelike cavity around the dopant. Therefore, a location on the surface of a helium droplet is energetically favorable for some elements—e.g., the alkali metals. The interaction between the helium and the dopant influences electronic transitions, thus enabling the assessment of the position of a foreign atom. Atoms inside helium droplets show a blueshifted and broad absorption compared to the free atom, whereas the absorption of atoms on the surface is broadened asymmetrically to the blue and no or only a slight shift is observed.

The ultracold but liquid nature of the helium droplet permits the formation of metastable complexes. Examples are the high-spin states of alkali-metal and silver clusters [2,3] or the linear chains of HCN molecules [4]. In the latter case the geometry is frozen in a linear high-energy structure, due to the *directional* interaction of the permanent dipoles of the HCN molecules. The low temperature of only 0.37 K does not allow a rearrangement towards the global minimum. Otherwise, negligible weak long-range interactions become important and determine the geometrical structure of the complex. In the case of an *undirectional* (i.e., isotropic) interaction, one would expect the growth of three-dimensional structures. Small potential barriers resulting from helium density fluctuations induced by the presence of dopants could suppress the formation of compact clusters in the ground state. We note that in two dimensions an analogous behavior can be observed with the formation of a superstructure by adsorbates on a metallic surface [5,6]. Furthermore, Gordon *et al.* have proposed a similar structure for so-called impurity helium solids [7]. However, experiments have shown that these metastable solids are highly porous systems consisting of nanosized clusters, each containing a few thousand atoms surrounded by helium [8].

The focus of this contribution is the formation of metastable Mg complexes in liquid helium droplets. Magnesium

is an ideal candidate as two Mg atoms in the ground state show only van der Waals interactions. The Mg dimer is bound by about 50 meV in the ground state [9]; however, the Mg-Mg interaction is comparable to the Mg-He interaction at the characteristic length of one bubble diameter (about 9 Å) [10]. The interplay between these two could therefore create a barrier for dimer formation, which originates from density modulations of superfluid helium. Calculations have shown that the Mg atom slightly repels the He, thus forming a bubble. This cavity is surrounded by several solvation layers. In the first layer the helium density increases by 45% compared to the bulk liquid [10]. The radius of this layer of about 5.2 Å marks the minimum of the Mg-He potential. With two Mg atoms at a distance twice this radius, the helium density oscillations overlap, increasing the density between the Mg atoms even further and enhancing the Mg-He binding energy. Figure 1 visualizes the situation at a distance of 10 Å (see the discussion below). When the two atoms approach closer, a fraction of the inner He solvation layers of both atoms have to disappear, creating a small barrier. As the Mg-Mg potential energies are very weak at these distances

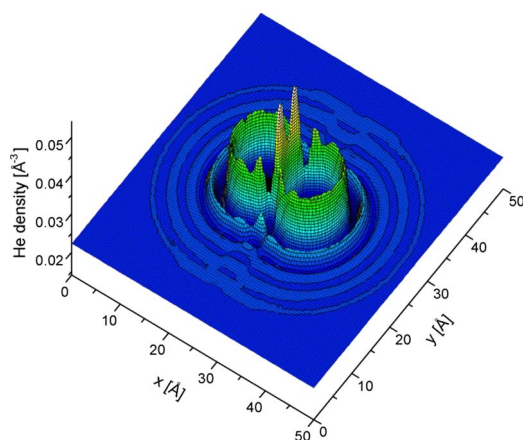


FIG. 1. (Color online) Cut through the calculated helium density around two magnesium atoms separated by a distance of 10 Å. A region of increased helium density is clearly visible between the Mg atoms, corresponding to a local energy minimum.

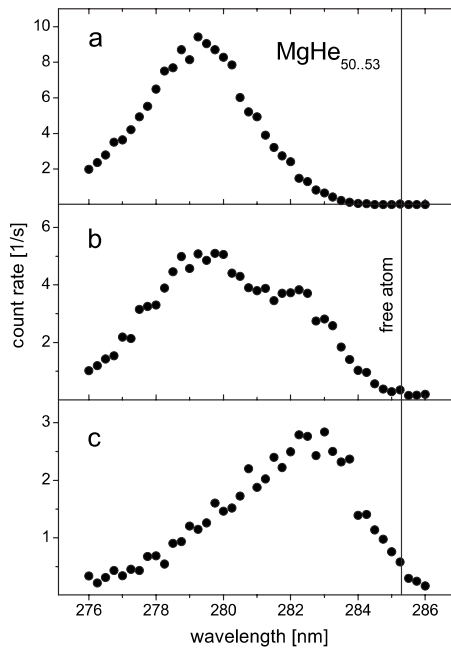


FIG. 2. R2PI spectra of magnesium doped helium droplets consisting of 6000 atoms detected on the Mg monomer mass channel [15] at different doping conditions. With fewer than one Mg atom on average [panel (a)] the spectrum shows a single maximum centered at 279 nm. At a higher doping with two Mg atoms per droplet, an additional structure at 282.5 nm appears [panel (b)]. Increasing the mean number of Mg atoms to 4 [panel (c)] the peak at 279 nm vanishes and the absorption around 282.5 nm becomes dominant.

(3 cm^{-1} [9]), we expect that a shallow local minimum develops, trapping the Mg atoms in a metastable state. Multiple Mg-atom-filled bubbles in a single droplet would grow into a three-dimensional structure. This aggregate resembles a foam, with one Mg atom in the center of each bubble.

The experimental apparatus is described in Refs. [11,12]. Briefly, helium droplets are generated in a supersonic nozzle source cooled by a liquid helium cryostat to 9–16 K. The droplets are loaded with Mg atoms from a vapor (pressure in the order of 10^{-5} mbar) produced by a heated oven. The impact kinetic energy is dissipated by evaporation of He atoms (about 80 He atoms per Mg atom). By varying the expansion conditions of the helium or the vapor density in the pickup region, the distribution of the number of Mg atoms per droplet can be adjusted. The ultracold and chemically inert droplets transport the embedded atoms into the ionization region of a high-resolution reflectron time-of-flight spectrometer. Here, the cluster beam interacts with tunable nanosecond light pulses or femtosecond pulses from a Ti:sapphire laser system with a regenerative amplifier. With resonant two-photon-ionization (R2PI), optical properties of the complexes can be explored. In addition, access to aggregation dynamics is obtained by the use of the femtosecond pump-probe technique.

In order to reveal the spectral signature of the metastable complexes, we study the change of the $3^1P_1^0 \leftarrow 3^1S_0$ transition of embedded magnesium atoms [13,14] under various source conditions. Figure 2 depicts the spectra of droplets containing 6000 He atoms on average doped with different

numbers of magnesium atoms. Generally, there are two contributions to the spectra. For the lowest pickup pressure (i.e., in the limit of a single Mg atom per droplet), the absorption peaks at about 279 nm. When increasing the number of embedded atoms, an additional signal evolves between 282 and 283 nm and shows an asymmetric broadening to the blue. The structure at 282.5 nm only appears if the droplet contains more than one magnesium atom. We emphasize that this behavior is not restricted to the chosen droplet size. We observe the same change when the Mg vapor pressure is held constant and the number of dopant atoms is increased by using larger droplets. Thus, there is a clear impact of the number of Mg atoms in the droplet on the spectral signature.

In previous laser-induced fluorescence (LIF) studies, Reho *et al.* [13] and Moriwaki and Morita [14] found a spectrum similar to panel (b) in Fig. 2. Reho *et al.* explained the double-peak structure by the lifting of the degeneracy of the $3^1P_1^0 \leftarrow 3^1S_0$ transition due to dynamic quadrupole deformations of the bubble cavity around the excited atom. The present studies do not support this assumption as droplets doped with one Mg atom show an absorption around 279 nm only. We assign this peak to an isolated magnesium atom embedded in helium. In comparison to the free atom the absorption is shifted by about 90 meV (6 nm) and has a width of roughly 50 meV (3.5 nm). This is compatible to the calculated spectra of Mella *et al.* [16], especially when considering the trend with the droplet size in their calculations. One should note that in the LIF experiments no direct information about the size of the fluorescing species can be obtained, whereas the R2PI technique employed here enables the detection of the absorption signal on all final ion channels. Furthermore, Moriwaki and Morita had no control over the possible formation of larger complexes, as they have used the technique of laser evaporation directly in liquid helium.

Since the R2PI spectra in Fig. 2 are detected on the Mg monomer channel, an *ad hoc* assumption to explain the structure at 282.5 nm would be to assign the peak to the magnesium dimer that may fragment in the ionization process. If true, one would expect to see this resonance behavior also in the Mg dimer mass channel. Indeed, the dimer shows an enhanced count rate in that region. But interestingly, *all* small clusters up to at least Mg_{15} have virtually the same spectrum. Figure 3 exemplarily compares the spectra recorded on the monomer with those of selected Mg clusters. They all peak at 282.5 nm. This observation clearly indicates that Mg atoms are the absorbing species even in the aggregates which appear as Mg clusters in the mass spectra. Obviously, during excitation the magnesium atoms are still separated from each other, showing only a weak interaction proven by the slight shift to 282.5 nm. Upon excitation magnesium cluster formation is initiated and the metastable foam collapses to a compact cluster. From mass spectroscopic studies with the same setup, it is known that the resulting species exhibits metallic binding as evidenced by pronounced electronic shell effects [17].

To directly observe the transition to a compact Mg cluster and measure the time scale for the cluster formation, a femtosecond pump-probe setup is used. The first pulse excites the system and initiates the collapse, whereas the second

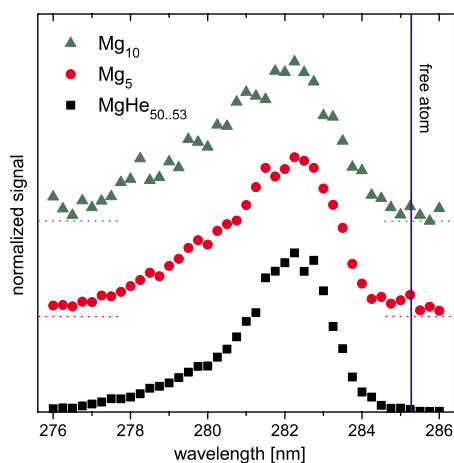


FIG. 3. (Color online) R2PI spectra of helium droplets consisting of 40 000 atoms doped with an average of 8 Mg atoms for different mass channels. The high similarity to the monomer spectrum recorded at the same conditions implies that all species originate from the same atomic precursor.

pulse probes the time-delayed formation of the clusters. Figure 4 shows as a representative example the result for Mg₅. A distinct rise of the cluster signal is observed over several picoseconds, reaching a plateau after roughly 30 ps. Obviously the delayed cluster formation is in accordance with the anticipated collapse of the metastable, loosely bound Mg complex into compact clusters. As an interesting consequence, the whole binding energy of the cluster is released during the collapse, transiently creating a very hot system, which cools by evaporation of Mg atoms and the surrounding helium. This may explain the richly structured mass spectra of large Mg clusters [17], which show a strong fragmentation even when ionizing at threshold with very low laser pulse energies.

With the observation of the collapse, we now turn to the interesting questions concerning the geometrical arrangement of several Mg atoms inside a single droplet and the forces between them. For randomly distributed atoms in the

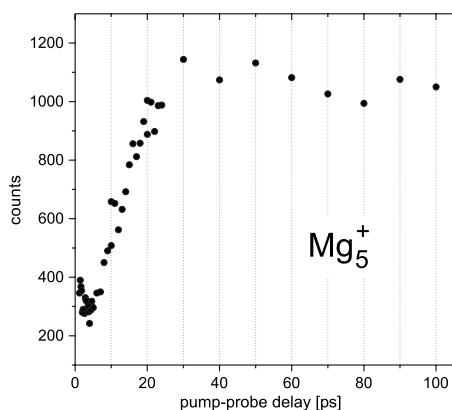


FIG. 4. Femtosecond pump-probe signal at 800 nm with a highly Mg doped He droplet. The signal of clusters (here, Mg₅) only rises after a considerable delay and stabilizes beyond about 30 ps. The time scale for the cluster formation can be estimated to be roughly 20 ps.

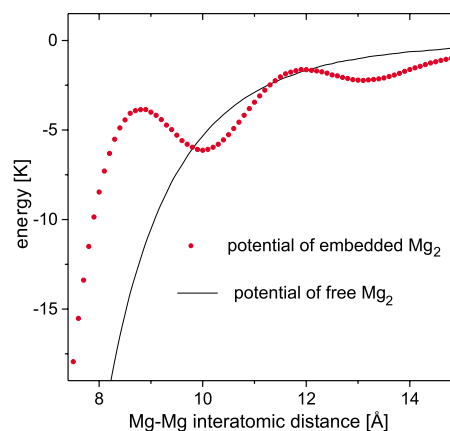


FIG. 5. (Color online) Long-range Mg-Mg potential energy curves of a dimer embedded in helium (dots) and in the gas phase [9] (solid line). The result for the embedded dimer is shifted by the solvation energy in helium to enable an easy comparison. One clearly sees the modulation induced by the helium solvation layers, leading to several shallow local minima, the deepest located at about 10 Å distance.

droplet, one would not expect two peaks in the absorption. Instead, the spectrum should merely broaden to the red with increasing number of Mg atoms per droplet corresponding to all possible spacings. The occurrence of distinct peaks rather implies a preferred distance between the Mg atoms. Therefore, a local potential minimum between embedded Mg atoms has to exist at distances substantially larger than the Mg₂ ground-state configuration. The most likely mechanism for creating such local minima is the van der Waals interaction between Mg and helium modifying the Mg-Mg potential energy curves. The general idea for the creation of a barrier was already given in the beginning. In order to obtain a quantitative estimate of the modified Mg-Mg potential, we start from the calculated helium density distribution around a single Mg atom [10] and construct the distribution around two atoms by superposition of the approaching bubbles. Such a density profile is shown in Fig. 1, which closely matches the result of a recent density function theory (DFT) calculation [18]. The energy of two embedded Mg atoms is then calculated at various distances as the sum of the Mg-Mg [9] and Mg-He [19] interactions. The resulting potential energy curve is plotted in Fig. 5. One can identify a modulation of the Mg-Mg potential which correlates with the diameter of the helium solvation layers. The closest and deepest metastable state is located at a distance of about 10 Å (cf. Fig. 1). The increased helium density between the Mg atoms acts as a barrier preventing the formation of a dimer molecule in the ground state. Additional embedded Mg atoms would behave similarly, thus giving rise to the formation of a larger metastable complex of Mg atoms. One has to bear in mind that this calculation is not meant to replace a more sophisticated treatment. The He-He interaction was neglected; its inclusion would likely reduce the height of the barrier. However, this could be balanced by the polarizable helium environment, which will weaken the Mg-Mg interaction by partial screening of the van der Waals forces [20]. Furthermore, any angular momentum of the impurity atoms will increase the bar-

rier. We note that very recently a DFT calculation for the system of two neon atoms in helium was published [21]. There, a local minimum at a distance of 6.7 Å and a very similar barrier height of about 3 K were obtained.

Whereas the details of the resulting potentials still have to be worked out, one can check the consequences of an increased interatomic distance of a Mg₂ molecule on the absorption spectrum $^1\Sigma_u^+ \leftarrow ^1\Sigma_g^+$. At 10.6 Å, the ground-state energy is virtually unshifted from the separated atom limit (2.5 cm⁻¹), whereas the excited state is noticeably bound by 405 cm⁻¹ or 50 meV [22]. This equals a shift from 279 to 282 nm as observed in our experiment when doping the droplets with more than one atom. In fact, there is a second possible transition to a $^1\Pi_u$ state which should exhibit a blueshift of about 185 cm⁻¹ [22] compared to a single atom. This is substantially less than the width of the atomic peak (about 400 cm⁻¹) and was not resolved. The measured absorption is therefore consistent with magnesium complexes at interatomic distances of about 10 Å. For larger complexes forming three-dimensional structures, the resonance dipole interactions of the Mg atoms responsible for the splitting will cancel out each other to a large extent. Likely, only a broadening will survive. Furthermore, the peak positions and shapes are also affected by the interaction with the surrounding helium, especially as the bubbles around the Mg atoms are distorted by the presence of other Mg atoms. We may note that the proposed foam represents a novel type of metal atom condensate. Of particular importance are many-

particle effects as they are obvious from both the atom density-dependent monomer peak position as well as the monomer signatures in the cluster spectra. E.g., similar to the situation in a (nearly) frozen Rydberg gas [23], a dipole excitation in one atom might resonantly move to the neighboring atoms, giving rise to a density-dependent peak shape. A closer study of the metal-atom-filled foam is an interesting future issue.

In conclusion, R2PI spectra of Mg-doped helium droplets have been measured at variable doping conditions. A clear relation between the number of dopant atoms in a droplet and the corresponding absorption spectrum could be established. The results hint at a metastable complex, where the Mg atoms are separated by 10 Å. A layer of helium resides between the atoms, resembling a foam. The Mg-Mg distance in the foam is about 3 times as large as those in Mg molecules or the bulk. Optical excitation leads to the collapse of the structure and the formation of transiently hot, compact clusters on a time scale of about 20 ps.

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