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Formation and properties of metal clusters isolated in helium droplets

Josef Tiggesbäumker\textsuperscript{a} and Frank Stienkemeier\textsuperscript{b}

Received 9th March 2007, Accepted 1st May 2007
First published as an Advance Article on the web 12th July 2007
DOI: 10.1039/b703575f

The unique conditions forming atomic and molecular complexes and clusters using superfluid helium nanodroplets have opened up an innovative route for studying the physical and chemical properties of matter on the nanoscale. This review summarizes the specific characteristics of the formation of atomic clusters partly generated far from equilibrium in the helium environment. Special emphasis is on the optical response, electronic properties as well as dynamical processes which are mostly affected by the surrounding quantum matrix. Experiments include the optical induced response of isolated cluster systems in helium under quite different excitation conditions ranging from the linear regime up to the violent interaction with a strong laser field leading to Coulomb explosion and the generation of highly charged atomic fragments. The variety of results on the outstanding properties in the quantum size regime highlights the peculiar capabilities of helium nanodroplet isolation spectroscopy.

I. Introduction

When atoms agglomerate and form molecules and even larger particles, the bond formation modifies the properties of the aggregate and a new and sometimes unexpected behavior may evolve which differs not only from the properties of isolated atoms but also from the corresponding bulk material. The study of such clusters and their properties lead to the field of cluster physics. The size-dependent evolution of electronic, optical and chemical properties has already been addressed in a paper by Kawabata and Kubo\textsuperscript{1} in the 1960s. As a prominent example of cluster properties, the reddish color of ancient glass windows results from the absorption of small silver and gold particles embedded in the glassy material. In this particular case the change in the transmission characteristics results from the excitation of the surface plasmon which is shifted and broadened due to the chemical interface. Mie\textsuperscript{2} and also Debye\textsuperscript{3} calculated the change of the optical response of small particles within the framework of classical electrodynamics, extending the work of Rayleigh.\textsuperscript{4} Zsigmondy\textsuperscript{5} was one of the first to study the influence of a matrix on the absorption. For a detailed discussion of the optical properties of small particles we refer the reader to the books of Bohren and Huffman,\textsuperscript{6} and Kreibig and Vollmer.\textsuperscript{7}

To some extent the change in the ground state and response properties has been predicted by applying classical approaches. A number of scaling laws has been found in order to explain the size-dependent shift of a physical behavior, see for example the review of de Heer.\textsuperscript{8} For example, the ionization potential ($I_P$) increases with the inverse of the small particle radius when compared to the bulk work function and approaches the atomic value at a low number $N$ of atomic constituents.\textsuperscript{9} On the other hand, at rather low $N$ the classical laws are no longer valid and thus at the nanoscale, quantum effects have to be taken into account. In this way, specific electronic properties for each single cluster size lead to distinct aspects of the properties of clusters.

In order to study the unique properties of clusters, the agglomeration of metal atoms in helium nanodroplets has been found to be an alternative route to forming metal clusters of well defined composition. Moreover, helium nanodroplet isolated clusters at temperatures in the millikelvin range are expected to open versatile new studies in the direction of e.g. nanoscale magnetism or superconductivity. So far, most of the work done with helium nanodroplets concentrated on spectroscopic studies of atoms and molecules in the superfluid environment. The results have been reviewed in several publications.\textsuperscript{10–14} Besides understanding the properties of specific molecules or molecular complexes, the size limited superfluid properties and the interaction with the embedded entities have been of particular interest.\textsuperscript{15–18} The dynamics of doped helium nanodroplets have been reviewed recently.\textsuperscript{19}

In this article we summarize recent work done on metal clusters isolated in the helium nanodroplet environment. We start with particular aspects of using helium nanodroplet beams to form metal clusters and continue with special properties of the clusters residing in the helium environment. After introducing the formation of the metal clusters we discuss their optical as well as electronic properties. Finally, the excitation in the non-linear regime is presented with emphasis on the cage effect and the formation of a nanoplasma in a strong laser field.

II. Ion–helium snowballs

Before discussing the formation of larger entities in droplets we first concentrate on the response of the helium environment on the presence of a single impurity. The simplest solvation structure is expected to form around isolated embedded atoms. Compared to neutral atoms the influence of charged species on the surrounding helium is much stronger through
the ion-induced dipole interaction. In the following we will discuss this context in more detail. Due to the superfluid properties of bulk liquid helium the response forces could be both attractive as well as repulsive. Electrons are known to have a strong repulsive interaction with helium. Due to this repulsion and the extended de Broglie wavelength of a thermalized electron, an electron impurity resides in a bubble state leading to a region of low helium density in the vicinity of the negative charge. In liquid the electron bubble has a diameter of 34 Å.\(^{20-22}\) Electron attachment to helium droplets has been studied by several groups and is nicely reviewed in a paper by Northby.\(^{23}\) A minimum droplet size of about 13 nm (2 \(\times\) 10\(^5\) atoms) was found to be necessary in order to stabilize an electron inside a helium droplet. Only recently Denifl et al.\(^{24,25}\) formed droplet anions upon free electron attachment. A positive charge, on the other hand, leads to local enhancement of the helium density by electrostriction, often called snowball formation. We note that this has impact on the movement of ions in the superfluid. A number of experiments concentrate on the corresponding mobility measurements,\(^{26,27}\) e.g. to determine the critical Landau velocity for the generation of rotons.\(^{28,29}\) Atkins\(^{30}\) has introduced a phenomenological model claiming that the presence of the ionic impurity enhances the local pressure up to approx. 4 bar, independent of the specific property of the atom. The resulting snowball consists of about 40 He atoms having a diameter of 6.5 Å. Experiments\(^{26,27,31,32}\) show that the mobility of the alkaline earth metals increases when compared to He\(^+\) and decreases for the alkalis, the latter in accordance with the model of Atkins. Abundance spectroscopy on ion snowballs formed in the ionization of metal atoms in droplets could in principle help to clarify the behavior. Moreover, ion-induced electrostatic interactions are of fundamental interest in catalysis\(^{33}\) and also has relevance e.g. in biology\(^{34}\) and aerosol physics.\(^{35,36}\) The formation of ion–snowball complexes in helium droplets have been studied using different ionization techniques. Surprisingly, after electron impact ionization (EII) of atoms and clusters, only the monomer shows notable intensity of attached helium atoms.\(^{37}\) This observation holds true even for ionization with nanosecond and femtosecond laser pulses, see Fig. 1. Possibly, energy dissipation from internal degrees of freedom (vibration, rotation) of a formed hot molecule or cluster ion boils off all remaining helium atoms. An additional contribution might stem from transient excitation of (MeHe\(_n\))\(^*\) —exciplexes which are formed within the multi-photon ionization process. The dependence of the snowball abundance on the kernel size, see Fig. 2, supports the assumption that snowballs are generated when single atoms are embedded. Possibly, fragment atoms from the photodissociation of small clusters also contribute. Applying EII, the embedded species is ionized via charge exchange with helium\(^{38,39}\) whereas with laser pulses the ionization of the dopant is direct. Snowball formation therefore gives information on the dynamics of the helium matrix upon charging of the dopant irrespective of the charging method.

The mass spectra of the ion–snowball complexes also show magic numbers which have been obtained in mass spectra of e.g. rare gas, metal, and alkali halide clusters.\(^{42-44}\) The enhancement in the distribution reflects the stability of the system and depends on the nature of the bonding. Fig. 1 shows the resulting mass spectrum of embedded lead atoms after ionization with femtosecond laser pulses. Up to 200 He atoms are attached to Pb\(^+\) showing a distinct shell structure. The actual position of the magic number depends on the charge state of the ion. Pb\(^+\)He\(_{17}\) appears prominent in the snowball distribution of the singly charged ion, whereas Pb\(^2+\)He\(_{12}\) is magic in the doubly charged ions. The latter could possibly be assigned to the formation of an icosahedral structure. For silver, Ag\(^+\)He\(_{17}\) is prominent in the spectrum. Although the first solvation shell might have an icosahedral structure, a shell closure at \(N = 54\) as predicted by theory\(^{44}\) is not observed in the spectrum. Instead Ag\(^+\)He\(_{32}\) and Ag\(^+\)He\(_{44}\) show up. Possibly the inner shell partly rearranges and the number of atoms in the first solvation shell decreases. The presence of shell closures at \(N = 10, 12\) and \(N = 32, 44\) suggests two different shell structure configurations to contribute with \((N = 10, 22)\) and \((N = 12, 30)\) atoms in each of the two shells. Possibly, the metal ion is in different electronic representation shell effects are clearly visible, indicating that ‘crystallization’ of helium atoms around the impurity takes place. The even–odd progression in the distribution of the Pb\(^2+\) snowballs results from the signal of helium clusters appearing on the same mass channel. Adapted from ref. 40.

**Fig. 1** Mass spectrum of droplets doped with lead atoms and ionized by femtosecond laser pulses. After the interaction with the infrared pulse (\(\lambda = 800\) nm) the complex fragments and forms ion snowballs (Pb\(^+\)He\(_N\), \(z = 1, 2, N = 1...200\)). Even in the logarithmic representation shell effects are clearly visible, indicating that ‘crystallization’ of helium atoms around the impurity takes place. The even–odd progression in the distribution of the Pb\(^2+\) snowballs results from the signal of helium clusters appearing on the same mass channel. Adapted from ref. 40.
states. An overview of all shell closures found so far is given in Table 1.

The reason for the enhanced abundance of specific complexes could be due to a geometrical packing of the atoms which is modified by the electronic configuration of the ion. Such a behavior is predicted by the ligand-field model which has been successfully applied to the formation of rare gas complexes around metal ions, $\text{Me}^+\text{RG}_N$ (RG: Ne, Ar, Kr, Xe). However, the results of the experiments do not support such a formation process. For instance, a closed-shell atomic configuration as well as a spherically symmetric state do not naturally induce a shell closing at $\text{Me}^+\text{He}_{12}$. In caesium a magic number is instead obtained at $N = 15$. In addition, a second shell closure should show up at $N = 18$. However, no evidence is found in the mass spectra. It seems reasonable that quantum effects of the helium environment have to be included. The superfluid properties of the matrix might be responsible for the fact that shell effects are not as prominent in the abundance distribution as in the ion–rare gas clusters of the heavier rare gas elements. More likely, the mass spectra reflects the He density around the impurity. Calculations have been performed on $\text{Li}^+\text{He}_N^{47-49}$, $\text{Na}^+\text{He}_N^{48,51}$, $\text{K}^+\text{He}_N^{48,51,52}$, $\text{Cs}^+\text{He}_N^{48}$, $\text{Be}^+\text{He}_N^{51,53}$, $\text{Mg}^+\text{He}_N^{47,49,54}$, and $\text{Mg}^{2+}\text{He}_N^{47,54}$. The closure of the first solvation shell is located at $N = 12$ for $\text{Be}^+$ and $N = 20$ and 9 for $\text{Mg}^+$ and $\text{Mg}^{2+}$, respectively. An interesting growth pattern is predicted for $\text{Mg}^+$: in contrast to $\text{Be}^+$ helium is first preferentially attached to only one side of the singly charged Mg ion (Fig. 3).

Calculations of alkali ions surrounded by helium show the evolution of solvation shells. The number of atoms in each shell depends on the chosen ion, see Table 1. For example, for the alkalis the number of atoms in the first solvation shell $N$ increases from $\text{Li}^+$ to $\text{Cs}^+$ in correlation with the size of the ion. The calculations show that there is He atom exchange within the inner solvation shells pointing out the unique properties of the superfluid helium matrix. In the first shell the

<table>
<thead>
<tr>
<th>Reference</th>
<th>Ion radius/pm</th>
<th>Shell closures</th>
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<tr>
<td>Group Ia</td>
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<tr>
<td>$\text{Li}^+$</td>
<td>cal. 48</td>
<td>78</td>
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<tr>
<td>$\text{Na}^+$</td>
<td>cal. 48</td>
<td>98</td>
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<tr>
<td>$\text{K}^+$</td>
<td>cal. 50</td>
<td>133</td>
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<tr>
<td>$\text{Cs}^+$</td>
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<td>165</td>
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<tr>
<td>Group Ib</td>
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<tr>
<td>$\text{Ag}^+$</td>
<td>exp. 41</td>
<td>113</td>
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<tr>
<td>Group IIa</td>
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<tr>
<td>$\text{Be}^+$</td>
<td>cal. 51</td>
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<td>$\text{Mg}^+$</td>
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<td>$\text{Mg}^{2+}$</td>
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<td>Group IIb</td>
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<td>exp. 41</td>
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<td>$\text{Cd}^+$</td>
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<td>exp. 41</td>
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<tr>
<td>$\text{Pb}^{2+}$</td>
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helium density is strongly enhanced compared to the density of a neat droplet by about an order of magnitude, i.e. 0.2 Å⁻³ and quasi-crystallization occurs. The second solvation shell shows properties of the quantum liquid and is superfluid up to a temperature of 1.25 K. According to the measurements, more than two solvation shells can be identified to form around the impurity ions. For example, for magnesium ions attachment of up to 125 helium atoms has been obtained, indicating the presence of a third shell.55

III. Generation of helium droplets

The generation of beams of helium nanodroplets in the size range up to 10⁷ helium atoms per droplet is an established technique which has been described and summarized in several papers and review articles.14,19,58,59 To date, metal clusters have only been attached to ²⁴He droplets from continuous expansion sources. Hence we restrict this section to the properties of such a source. In short, helium at stagnation pressures P₀ from a few up to 100 bar is expanded at low temperatures (6 K ≤ T₀ ≤ 40 K) from a small nozzle (diameter D: 2 μm < D < 20 μm). In this way, a beam of droplets traveling under high vacuum conditions is condensed in an isentropic, supersonic expansion (subcritical regime). Dependent on the expansion conditions the amount of condensation changes and thus by varying P₀ and T₀ the average droplet size can be set to the desired value. At nozzle temperatures below ≈ 15 K the expansion enters the supercritical regime where droplets are formed from the fragmentation of the liquid state.59 In terms of mean droplet size this transition has been determined to be around 15 000 helium atoms per droplet (D = 5 μm). In the supercritical regime the mean droplet size ᴅ strongly increases when lowering the nozzle temperature. Within a few Kelvin, the value of ᴅ increases by orders of magnitude. The supercritical size distributions have been measured to follow linear-exponential distributions.60

\[ P_N(N) = \frac{1}{N} \exp - \left( \frac{N}{N} \right) \]  

In contrast, in the subcritical regime the size distribution follows log-normal functions

\[ P_N(N) = \frac{1}{\sqrt{2\pi N\delta}} \exp \left( -\frac{(\ln N - \mu)^2}{2\delta^2} \right) \]  

where \( \delta \) the width of the distribution, \( \mu \) maximum of the distribution, and \( \bar{N} = \exp(\mu + \delta^2/2) \) the mean droplet size.61

This difference directly affects the doping of the droplets discussed later. The width of the size distributions are comparable to the value of \( \bar{N}^{-1.66,62} \) which could have a relevant impact in experiments. At a given \( \bar{N} \), droplets of much smaller as well as much larger size are abundant in the molecular beam. Even more important, one always has to take into consideration that the droplet size does not change linearly when decreasing

the nozzle temperature. The absolute intensities of larger droplets, in particular in the supercritical regime are orders of magnitude lower when compared to conditions where small mean droplet sizes are formed. In this way the droplet size which is asymptotically reached in the subcritical regime at low source temperatures plays a special role: even at nozzle temperatures assigned to the supercritical regime, the majority of formed droplets may still have a size given by the asymptotic limit. On the other hand, since the experimentally measured droplet size distributions show that this asymptotic limit does not depend on the stagnation pressure, it can only be modified by changing the nozzle diameter. We explicitly found this effect when studying the line broadening of the e.g. 2p \( \leftrightarrow \) 2s transition in atomic lithium.63,64 The width of the absorption line is expected to increase with the curvature of the surface, i.e. the droplet size. When recording the absorption profile as function of nozzle temperature the line width converges at low nozzle temperature. However, depending on the nozzle opening a different value is obtained. Broad line widths measured with a larger nozzle could not be reproduced with smaller ones, even performing the experiments at much lower source temperatures. This shows that one has to be careful in the assignment of the droplet size and even more careful when using the often referenced scaling laws for estimating droplet sizes.55–67

IV. Metal cluster formation in droplets

A strength of the helium droplet isolation spectroscopy is the ability to efficiently load a huge variety of atoms and molecules into the droplets. In particular, clusters as well as complexes can be formed from many constituents, the properties of which might be of very different nature. For example, molecules can be mixed with metal clusters68,69 in order to study properties of metal adsorbate systems; on the other hand large organic or even biological relevant molecules have been studied in the cold environment.12,70,71 Doping is achieved by the pick-up technique72,73 where the dopants stick to the droplets with probability close to unity upon an inelastic collision.74 In practice one has to establish a vapor pressure of the order of (10⁻⁴ mbar) within the cell (typical length \( L_{D} \): a few centimetres) the droplet beam passes through. Volatile components are directly introduced whereas other materials are thermally evaporated in heated cells or even by laser evaporation.75 To generate clusters the density in the pick-up region has to be increased in order to collect the desired number of constituents. The probability of picking up a certain number of atoms is determined by the Poissonian statistics. The droplet beam described by eqn (1) or (2) therefore comprises a size-distribution of clusters. The latter is on the other hand changed by the doping process because the kinetic and internal energy of the picked-up atoms or molecules as well as the released binding energy of formed complexes or clusters is dissipated into the helium droplet. The droplets evaporatively cool, dispensing many helium atoms according to the injected energy. For droplets (\( \bar{N} \gtrsim 5000 \)) formed in the subcritical regime and small clusters with respective low binding energies (e.g. van der Waals complexes) shrinkage of the droplets can be neglected and, assuming a constant pick-up cross section, the Poissonian
statistics describes the doping process quite well. The statistical behavior in many experiments has been exploited to assign spectroscopic features to specific complexes or clusters by recording intensities as a function of the density in the pick-up cell.\textsuperscript{14,76} The resulting Poissonian distribution
\begin{equation}
P_k(N_k, n_d, \sigma_d) = \frac{(L_c n_d \sigma_d)^k}{k!} \exp(-L_c n_d \sigma_d)
\end{equation}
with \(n_d\) the density of dopant particles, \(\sigma_d\) the droplet pick-up cross section, \(L_c\) the effective length of pick-up region, has an initial incline proportional to \(n^k\) and equally spaced maxima when going to higher \(k\). Such a behavior has been confirmed for molecular complexes and the assignment of a density dependent curve to a specific \(k\) proved to be essential to assign the signal to a certain size.

\subsection*{A. Simulation of particle growth in droplets}
When forming larger complexes the resulting clusters as well as droplet size distributions may substantially change due to the energy dissipation mechanism. In order to model the doping process, one can numerically simulate the cluster formation process.\textsuperscript{63,64} Based on an initial droplet size distribution, the density and the temperature of the dopant atoms and the binding energies of the enclosed aggregates, the terminal size distributions of droplets carrying a specific cluster size can be calculated. A few key features are presented in the following. The simulations were performed for alkali metal atoms, because of their surface location and weak binding to the droplets. In addition, the desorption mechanism was incorporated in the calculations.\textsuperscript{63,64} We note that in particular for these systems even a small contribution from energy dissipation gives rise to a pronounced modification of the size distribution.

In Fig. 4 the formation of sodium trimers and their corresponding helium droplet sizes are plotted as function of the density of dopant atoms. Clearly, at higher pick-up rates, the size distribution has substantially decreased from the mean size of 5000 which they had before doping (bottom bar in Fig. 4). Moreover, at rather low pick-up densities the maximum of the doped droplet distribution is shifted to a larger size because of the enhanced pick-up cross section of these droplets.

The initial distribution of droplet sizes on the other hand significantly alters the pick-up probabilities. As a consequence the density dependent intensities (Poissonian distributions) deviate drastically from the functional form given in eqn (3). Fig. 5 (lower panel) models such distributions of lithium monomers. The black curve has as input a linear-exponential droplet distribution as present in the supercritical regime; for the simulation of the red curve a log-normal distribution was chosen as initial condition. For comparison, the upper panel plots experimental results of lithium monomer doped helium droplets at different nozzle temperatures. In the supercritical regime at \(T_0 = 15\ K\) the underlying linear-exponential droplet size distribution clearly determines the measured curve which is far from being Poissonian. For the experimentalist these results show that when optimizing signals by e.g. varying pick-up densities, one has to recognize that the droplet beam conditions in terms of e.g. size distributions may also substantially alter and the interpretation in comparison with theory has to be performed for the right parameters. The other way round: changing the droplet beam conditions alters the pick-up probabilities and thus modifies the cluster size distribution. With respect to the pick-up density dependent distribution one

\begin{figure}[ht]
\centering
\includegraphics[width=\textwidth]{fig4.png}
\caption{Probability of finding a sodium trimer in a droplet of size \(N\) dependent on the density of atoms in the pick-up cell. Droplets were assumed to initially have a log-normal distribution with a mean size of 5000, which is represented by the bar on the bottom. The left panel plots the Na\textsubscript{3} intensity integrated over all droplet sizes. The dotted line indicates the mean droplet size \(N\). The distributions are normalized.}
\end{figure}

\begin{figure}[ht]
\centering
\includegraphics[width=\textwidth]{fig5.png}
\caption{Upper panel: measured laser induced fluorescence intensity of lithium monomer doped helium nanodroplets as a function of pick-up density at selected nozzle temperatures. At \(T_0 = 15\ K\) droplet formation results from supercritical expansion leading to a linear-exponential cluster size distribution. Lower panel: calculated intensity distributions dependent on the pick-up density using as input a linear-exponential \((N = 100\ 000)\) and a log-normal distribution \((N = 5000,\ FWHM = 4000)\) of droplet sizes, respectively.}
\end{figure}
can summarize: if the droplets are in a size range where shrinkage from the energy dissipation is significant, the maxima for each \( k \) are no longer equidistant but move together at low pick-up pressures. The exponent \( k' \) of the initial incline \( (nk'_0) \) becomes smaller (!) compared to the size of the cluster \( k_0 \). The formation of larger cluster sizes is, as expected, strongly suppressed. All these characteristics have been proven in experiments.64

In order to demonstrate how strongly this effect could modify the resulting cluster size distribution, Fig. 6 plots a calculated sodium cluster size distribution in comparison to the one expected from the Poissonian statistics. Under the chosen parameters the initial droplet size distribution is small enough that energy dissipation and desorption processes determine the resulting cluster sizes. The pronounced structure obtained as a function of size stems from the binding energy of the sodium clusters which is not varying monotonically with increasing cluster size. Obviously, the expected formation of cluster sizes mainly around \( k = 4 \) is largely suppressed.

V. Metal cluster mass spectra

A. Alkali metal clusters

Alkali atoms play a special role when attaching them to helium droplets because they are not dissolved in the bulk helium liquid. In contrast, when forced into bulk liquid helium, they form bubble-like states because of the Pauli repulsion. As a consequence, in helium nanodroplets alkali atoms reside at the surface in dimple-like structures. The bonding to the helium droplet surface is quite weak; for all the alkalis binding energies have been calculated to be on the order of 10 cm\(^{-1}\) (1 meV).77,78 Consequently, the release of binding energy upon bond formation or energy from laser excitation processes can easily detach the atoms or molecules from the droplet. Since the probability of desorption directly correlates with the binding energy of the molecule or cluster formed, weakly bound systems are preferentially transported by the helium droplet beam. Various experimental studies of alkali dimer-doped helium droplets have confirmed such a mechanism.79–82

In monovalent systems spin pairing results in much larger binding energies compared to molecules or clusters having parallel spin orientations of the valence electrons. Hence, high-spin configurations are expected to be strongly enhanced on helium droplets. One indeed finds that the signal from dimers in triplet states is enhanced by a factor of 50.81 Moreover, in the case of alkali trimers only quartet states have been assigned to date (see later). The central questions as far as the formation of larger alkali clusters are concerned have always been: (a) Can one form larger entities attached to helium droplets despite the fragile desorption mechanism? (b) Are, as in the case of dimers and trimers, the larger clusters selected in high-spin states?

Question (a) has been proven directly in experiments by recording mass spectra of alkali-doped helium droplets at enhanced pick-up densities,53,83,84 As an example Fig. 7 shows the resulting size distribution of sodium clusters attached to helium nanodroplets and ionized by femtosecond laser pulses. A striking feature is the pronounced structure of electronic shells leading to an even–odd alternation and distinct shell closures. Magic numbers are identified e.g. at \( n = 9, 21 \), assigning the ensemble of clusters to a fragmentation pattern of the ionic system with e.g. \( \text{Na}_9^+ \), having \( N_e = 8 \) electrons filling the 1p shell. Hence the mass distribution is governed by fragmentation upon the ionization step in the detector and does not represent the size distribution upon pick-up. Recent measurements63 clearly detect potassium cluster size distributions extending to more than 70 atoms. Measuring fragmentation patterns one would like to assign native cluster sizes by evaluation of pick-up density dependent distributions of selective masses. Due to the desorption mechanism, these distributions are found to be strongly distorted as shown by
the model calculations in the preceding section. Only if one is able to obtain a complete series where the masses unambiguously match, is an assignment of unknown spectral features reliable.

As far as question (b) and the formation of high spins is concerned, so far no direct proof of the electronic configuration has been achieved and a clear-cut answer cannot be given. Comparing the formation of clusters attached to helium droplets of different alkalis, one finds that the formation of larger rubidium and caesium clusters (Rb: \( n > 5 \), Cs: \( n > 3 \)) is somehow suppressed.\(^8^3\) It was argued that because of the just introduced selection of weakly bound species, only high-spin clusters survive the formation in helium droplets. The missing larger Cs and Rb clusters desorb because the higher spin–orbit interaction depolarizes high spin states and the released binding energies of the covalently bound clusters multiplies desorption. The validity of this mechanism is supported by energetic considerations. Extended studies have been performed by doping the droplets with different alkali atoms using a series of pick-up cells each containing another metal. An inspection of the mass distribution reveals that all combinations of bimetal clusters (e.g. Na\(_n\)Cs\(_n\)) containing more than three or five Cs or Rb atoms, respectively, also do not agglomerate on helium droplets,\(^8^5\) confirming the measurements of ref. 83 and the presence of discrimination in some way. The given line of argument implies that the larger sodium and potassium clusters formed should only consist of weakly bound high-spin states. Since the probability of forming clusters that have all the spins of the valence electrons in parallel goes with \( (n + 1)/2^l \), it was argued by the authors that the observed clusters are unlikely to be made of high spins only. Vongehr and Kresin\(^8^6\) modeled the cluster formation and deduced analytical expressions to answer this question. They found a strongly non-Poissonian behavior describing the cluster growth and proposed that distinct features in the pick-up density distributions should be looked at to distinguish high-spin from low-spin formation. In particular the tails at higher pick-up pressures were calculated to be significantly elevated for high-spin systems. To shed light on the structure and energetics of such systems, density functional studies have been applied by Andrea et al.\(^8^7\)

Putting the different binding properties of sodium clusters into our calculations modeling the pick-up properties,\(^6^3\) one can directly determine the fraction of high-spin clusters carried by the ensemble of helium droplets, see Fig. 8. As already obtained in the preceding section the distinct influence of the initial droplet size distribution becomes evident. In small droplets, where shrinkage is significant, the strongly enhanced abundance of high-spin dimers and trimers are indeed reproduced by the calculations. For the large droplets, a significant increase compared to the pure spin statistics is still present but the fraction of high-spin states remains comparable to all the other spin configurations. Certainly a neat high-spin distribution is not present. Moreover, the total number of formed clusters is notably suppressed. By increasing the droplet size in order to avoid shrinkage, alkali clusters are formed whose spin configuration deviate insignificantly from the statistical considerations. This means that the formation of an intense undiluted high-spin cluster distribution of larger size appears not to be likely. This still does leave open a conclusive picture explaining the experimental findings, in particular the missing abundance of larger rubidium and caesium clusters.

Another issue that has not been addressed so far is the location of the clusters: surface vs. interior. All the dimers and trimers were clearly proved to reside in dimple states on the surface of the helium droplets. At some larger cluster size one would expect the alkali clusters to submerge. To date, no experimental technique has been proven to distinguish between an interior and a surface location of the cluster complex (see next section). Here theory should be able to give new input, calculating the total binding clusters of the droplets.

### B. Coinage metal clusters

Dopant atoms have been classified in terms of their solvation properties in helium droplets. The alkalis, e.g. (see. section V A), stay on the surface whereas most of the other atoms submerge into the droplets. The dimensionless Ancilotto parameter \( \lambda_A \) gives a good estimate whether a surface location is energetically more favorable (\( \lambda_A < 1.9 \)) for the atom than an inside position (\( \lambda_A > 1.9 \)).\(^8^8\)

\[
\lambda_A = \frac{1}{2^{l/6}} \frac{\rho_{\text{He}}}{\sigma_{\text{He}}} \frac{\rho_{\text{eq}}}{\sigma_{\text{eq}}} \tag{4}
\]

where \( \rho_{\text{He}} = 0.022 \text{ Å}^{-2} \): the helium density, \( \sigma_{\text{He}} = 2.3 \times 10^{-5} \text{ eV Å}^{-2} \): the helium surface tension, \( r_{\text{eq}} \): the impurity–helium equilibrium distance, and \( \rho_{\text{eq}} \): the corresponding potential depth. Calculating \( \lambda_A \) for the Ib metals gives values far above 1.9 and thus these atoms are expected to enter the helium matrix and form clusters inside the droplets. By applying resonant 2-photon excitation (R2PI) in combination with pulsed electric field ionization, Federmann et al.\(^8^9\) have indeed found that silver atoms submerge.
Table 2  Compilation of temperature values \( T_{\text{cell}} \) necessary to generate a vapor pressure of \( 10^{-4} \text{--} 10^{-3} \text{ mbar} \) in the scattering cell \((L_c = 5 \text{ cm}) \) in order to maximize the number of pick-up events for metal cluster formation in helium nanodroplets. For a 1 cm long oven a partial pressure of \( 10^{-3} \text{ mbar} \) is necessary to achieve similar pick-up rates. Corresponding temperature values are given in parenthesis. Values taken from ref. 92

<table>
<thead>
<tr>
<th>La</th>
<th>( T_{\text{cell}}/^\circ\text{C} )</th>
<th>Ha/b</th>
<th>( T_{\text{cell}}/^\circ\text{C} )</th>
<th>Ib</th>
<th>( T_{\text{cell}}/^\circ\text{C} )</th>
<th>IIIa</th>
<th>( T_{\text{cell}}/^\circ\text{C} )</th>
<th>Vlb</th>
<th>( T_{\text{cell}}/^\circ\text{C} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>390 (450)</td>
<td>Mg</td>
<td>315 (360)</td>
<td>Cu</td>
<td>1000 (1120)</td>
<td>Al</td>
<td>1020 (1070)</td>
<td>C</td>
<td>2050 (2200)</td>
</tr>
<tr>
<td>Na</td>
<td>180 (230)</td>
<td>Cd</td>
<td>170 (210)</td>
<td>Ag</td>
<td>820 (900)</td>
<td>Ga</td>
<td>900 (980)</td>
<td>Si</td>
<td>1350 (1470)</td>
</tr>
<tr>
<td>K</td>
<td>115 (155)</td>
<td>Zn</td>
<td>235 (280)</td>
<td>Au</td>
<td>1120 (1225)</td>
<td>In</td>
<td>735 (810)</td>
<td>Ge</td>
<td>900 (1250)</td>
</tr>
<tr>
<td>Cs</td>
<td>55 (105)</td>
<td>Hg</td>
<td>-10 (10)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Pb</td>
<td>530 (610)</td>
</tr>
</tbody>
</table>

For the generation of clusters in droplets a sufficient vapor pressure of \( 10^{-4} \text{--} 10^{-3} \text{ mbar} \) within the pick-up cell is necessary. For the coinage metals the required temperature \( T_{\text{cell}} \) in the pick-up cell is much higher when compared to the alkalis; see Table 2 for selected elements. A double layer radiation shield surrounding an \( \text{Al}_2\text{O}_3 \) ceramic which is heated by a tantalum wire can be used to reach the required conditions inside the collision cell.\(^9^0\) Due to the large binding energy release per atom of up to more than 2 eV\(^9^1\) the droplets disproportionately shrink. In addition, the momentum transfer in the pick-up process leads to a net scattering of the embedded complex off the molecular beam axis. Due to these circumstances only small clusters of gold are formed. \( \text{Cu}_N \) and \( \text{Ag}_N \) have been found to be present with larger sizes and clusters containing up to \( N = 160 \) constituents have been detected for silver.\(^9^2\) As for the alkalis, see section VA, the mass spectrum of photoionized silver clusters shows shell effects, e.g. a prominent shell closing at \( \text{Ag}_{91+} \) \((N_e = 58)\). The enhanced abundance of the odd-sized species suggests that the intensity distribution results from the stability of the charged cluster and thus the systems undergoes fragmentation after ionization.

The role of the helium matrix in the ionization of the embedded cluster has to be discussed in more detail. Droplets are known to have a temperature of \( T_D = 0.37 \text{ K} \).\(^9^3\) Any excess energy as e.g. released in a bond formation is transferred to the matrix by thermal coupling. Hence the droplet cools down to \( T_D \) by evaporating helium atoms.\(^9^4\) As a rule of thumb about 1800 helium atoms are evaporated for each eV of released energy. This property is used in many experiments in order to study small molecules in droplets. For example, beam depletion by optical excitation as a standard experimental tool is sensitive only to a significant loss of helium atoms from the droplet due to the transition into the excited state. In contrast, in order to form larger particles, one usually uses nanodroplets having several hundreds of thousands of He atoms. Upon optical ionization the excess energy is rather low, typically a few eV. This would lead to a loss of only a few thousand helium atoms from the droplet. One would therefore expect to detect a broad distribution of \( \text{Me}_N\text{He}_M \) clusters in the mass spectrometer. Instead, the resulting mass distributions show up with almost no helium atoms attached to the metal core, see Fig. 7. We emphasize that a similar result is obtained when electron impact is used for ionization, see e.g. ref. 95. Thus, in the ionization process the whole matrix is stripped off. This is intriguing since due to electrostatic considerations a positive charge would be located in the center of the droplet, as pointed out by Lehmann and Northby.\(^9^6\) The reason for this behavior is still under debate and a satisfying explanation cannot be given to date. As mentioned above, the additional degrees of freedom in many-body particles may contribute to the desorption of helium atoms.

C. Divalent metal clusters

1. Magnesium. One of the remarkable properties of metals is the high electron density in the valence band which results in a large thermal and electrical conductivity, as well as a high reflectivity in the optical and infrared wavelength region. A special class of materials are metal atoms having a closed electronic valence shell and a small energy gap to the first excited state, i.e. the divalent metals. These elements are characterized by a \textit{nonmetal to metal transition} (NMM) as a function of the interatomic distance.\(^9^7\)\(^9^8\) In clusters, NMM can be studied as a function of size, see ref. 99 for a recent review. With increasing number of atoms the fully occupied s-band and the empty p-band of the divalent metal widen and overlap at a certain size \( N_c \), inducing the NMM transition. In this simplified picture possible contributions from hybridization are neglected. Mercury has been thoroughly studied by the group of Hensel\(^1^0^0\) and later by others.\(^1^0^1\)\(^1^0^4\) In the measurements of Rademann \textit{et al.} a critical size of \( N_c = 70 \) was found for NMM based on the value of the size-dependent ionization potential and a comparison with the predictions of the metal sphere model.\(^1^0^6\) Later Chesnovsky and co-workers\(^1^0^3\) used photoelectron spectroscopy on mass-selected cluster anions to determine the HOMO-LUMO band gap and found a much larger value of about \( N_c = 400 \pm 30 \), indicating that \( N_c \) is sensitive to the applied method. Due to the high reactivity of the divalent metals NMM was not studied in other systems until recently. For example, the group of Castleman studied magnesium and found that their source mainly produces \( \text{MgO} \) clusters.\(^1^0^5\) Magnesium complexes can be formed in helium droplets without any evidence for oxidation making this technique quite interesting for this purpose. Instead of measuring the band gap or the ionization potential the phase transition is determined by mass spectrometry. In particular, the mass distribution is analyzed with respect to clusters showing metallic properties, i.e. shell effects, indicating the NMM transition. The mass spectrum of \( \text{Mg}_N \) (see Fig. 9, top) obtained after nanosecond multiphoton ionization shows a highly structured distribution. An enhanced intensity of certain cluster sizes (e.g. \( \text{Mg}_{10} \)) as well as distinct gaps (e.g. at \( \text{Mg}_{22} \)) are present, hinting at a huge difference in the stability of the complexes. Changing the experimental conditions, i.e. the excitation wavelength as well as the laser intensity, the cluster size and the diameter of the droplets doesn’t modify the overall structure in the spectra.
localized, closed shell spherical clusters would appear at specific reasonable assumption that both valence electrons are delocalized. Metal clusters like sodium (see Fig. 7) and silver. Under the condition obtained for simple spectra are well-known from the spectra obtained for simple systems. The chosen method, thus correlated to a fundamental property of fs-excitation (not shown here) reveal that the structure found in the size range. From the analysis of the spectra the critical size for NMM is determined giving a value of \( N = 20 \). Adapted from ref. 122.

Furthermore, experiments performed with different ionization sources, \( i.e. \) EII, see Fig. 9 (bottom) for comparison as well as fs-excitation (not shown here) reveal that the structure found in the mass spectra is to a large degree independent of the chosen method, thus correlated to a fundamental property of the system.

Some of the peaks which appear enhanced in the distribution are well-known from the spectra obtained for simple metal clusters like sodium (see Fig. 7) and silver. Under the reasonable assumption that both valence electrons are delocalized, closed shell spherical clusters would appear at specific numbers \( N = 1/2N_e \) depending on the energy position of the \((n, l)\) shells and the width of the HOMO–LUMO gap.\(^{107}\) This would result in an enhanced stability of particular cluster sizes leading to the appearance of magic numbers. In addition to the findings in the alkali systems, extra shell closings appear with cluster size due to level crossing of the \((n, l)\) shells.\(^{108}\) Such behavior is already known from calculations on fermionic \(^3\)He-clusters.\(^{109,110}\) A typical example is \( \text{Mg}_{40} \) having \( N_e = 80 \) electrons which cannot reasonably be explained by the standard jellium model.\(^{107}\) According to the calculations only closures at \( N_e = 70 \) and 92 are expected.\(^{111}\) Serra et al.\(^{112}\) have performed calculations on magnesium clusters within LDA using pseudopotentials and found some evidence for level crossings and the appearance of additional magic numbers.

With femtosecond laser pulses a higher charging of the clusters can be achieved and the abundance distribution of the doubly charged clusters was analyzed with respect to magic numbers.\(^{106}\) Isotopic distributions have to be evaluated to extract the abundance of the doubly charged species. The mass spectrum of \( \text{Mg}_{30}^{2+} \) shows a shell structure pattern having enhanced intensities at sizes \( \text{Mg}_{14}^{2+}, \text{Mg}_{18}^{2+}, \text{Mg}_{21}^{2+}, \text{Mg}_{30}^{2+}, \text{Mg}_{36}^{2+}, \text{Mg}_{41}^{2+} \) and \( \text{Mg}_{47}^{2+} \). These clusters have a total number of valence electrons of \( N_e = 20, 58, 70, 80, \) and 92, all in accordance with the predictions of the level interchange shell model.

The exceptionally low abundance of certain clusters obtained in the mass spectra\(^{106}\) like \( \text{Mg}_{32}^{2+}, \text{Mg}_{37}^{2+}, \text{and Mg}_{37}^{2+} \) turns out to be due to an interplay between an electronic and a geometrical effect. According to calculations performed by Ahlrichs et al.\(^{113}\) the structure of the closed-shell clusters is spherical and rather compact. They can be regarded as the building blocks on which additional atoms are adsorbed. The additional atoms are weakly bound and a quite low excess energy is sufficient to induce fragmentation leading to the distinct drop of intensity beyond some of the closed-shell systems.

As a result of the findings that the abundance distribution is governed by the delocalized electron density, an estimate for the value of \( N_e \) can be given. The smallest cluster size which shows evidence for complete delocalization appears to be \( \text{Mg}_{10} \). However, no signatures of metallic-like behavior is found up to \( \text{Mg}_{20} \). Beyond this particular cluster size all features in the spectra can be explained by the level interchange shell structure model. Therefore, the critical size for the NMM in \( \text{Mg}_N \) can be assigned to \( N_e = 20 \). Bowen and co-workers studied the evolution of the band gap in \( \text{Mg}_{20}^{2+} \) and found \( N_e = 18 \)\(^{114}\) also in accordance with the metal cluster signatures obtained in the corresponding mass spectra. The rather low value of \( N_e \) in \( \text{Mg}_N \) is also consistent with calculations using the Car–Parrinello method.\(^{115–117}\) \( \text{Mg}_9 \) and \( \text{Mg}_{10} \) were identified as clusters showing signatures of complete delocalization. An enhanced intensity of \( \text{Mg}_{17} \) as predicted by the simulations is missing in the experimental data. Kumar and Car\(^{118}\) analyzed the evolution of the band gap and estimated the transition to metallic behavior to about \( N_e = 22 \). Both the experiments on the Mg-cluster anions and the Car–Parrinello molecular dynamic calculations on \( \text{Mg}_N \) in this respect support the findings obtained in the droplet experiments.

2. Cadmium and zinc. The cluster size dependence of the NMM can also be studied for elements which appear in the same column of the periodic table as mercury, \( i.e. \) Cd and Zn. As for magnesium, the abundance distribution of these clusters show evidence for NMM in the small size regime.\(^{106}\) For \( \text{Cd}_N \) (see Fig. 10) similar values for \( N_e \) are obtained in experiments\(^{119}\) and density functional calculations.\(^{120}\) Clusters with 10, 18, 20, 35, 46, and 69 atoms show up as enhanced intensities in the mass spectra. All of these sizes correspond to magic numbers within the jellium model.\(^{107}\) In comparison to \( \text{Mg}_N \) some pronounced features could not be explained by
Atoms have been detected, see Fig. 10 for Cd cell, large clusters of Mg, Cd, and Zn with more than 2000 atoms have been studied by Katakuse et al. In this restricted size range similar magic numbers were assigned. Although these clusters are believed to have internal temperatures of several thousands of Kelvin, having lots of energy for weaker bound clusters to fragment, the structure in the abundance distribution is not as pronounced as in the spectra of the embedded clusters. For the latter it is not clear that the clusters formed in the ultracold environment are natively in a metallic state but switch upon electronic excitation, i.e. within the photoionization process. Note that due to the even number of delocalized valence electrons one cannot clearly distinguish whether a magic cluster reflects the stability of the neutral or the ion. The group in Rostock currently explores the possibility of magic clusters which can be attributed to closed-shell electronic configurations; e.g. see the enhanced abundance of Cd$_{32}$ ($N_e = 64$) in Fig. 10. The structure of the larger clusters seems to be more affected by their geometry. For example, the geometry of Cd$_{44}$ could be interpreted to be a decahedron.

Sputtered cadmium as well as zinc cluster cations up to $N = 70$ have been studied by Katakuse et al. In this restricted size range similar magic numbers were assigned. Although these clusters are believed to have internal temperatures of several thousands of Kelvin, having lots of energy for weaker bound clusters to fragment, the structure in the abundance distribution is not as pronounced as in the spectra of the embedded clusters. For the latter it is not clear that the clusters formed in the ultracold environment are natively in a metallic state but switch upon electronic excitation, i.e. within the photoionization process. Note that due to the even number of delocalized valence electrons one cannot clearly distinguish whether a magic cluster reflects the stability of the neutral or the ion. The group in Rostock currently explores the possibility of a photoinduced NMM in the divalent systems.

Fine-tuning the droplet size at nozzle temperatures around 9.0–9.2 K and the vapor pressure conditions in the pick-up cell, large clusters of Mg, Cd, and Zn with more than 2000 atoms have been detected, see Fig. 10 for Cd$_N$ and ref. 106 for Mg$_N$. In the size range above $N = 147$ the abundance distribution is no longer dominated by electronic shell effects but instead by the geometry of the system. This second transition results from the gradual decrease of the homolayer–LUMO gap in the larger clusters, scaling with $N^{-1/3}$. As the gap narrows electronic shell closings only lead to a slightly enhanced stability of the system and the ground state energy could be lowered more effectively by a different geometrical packing. In particular, the distribution of Mg$_N$ shows signatures of shells of atoms, resulting from a five-fold symmetry structure of the complexes. Enhanced intensities at $N = 147, 309, 561, 923, 1415$ are obtained which nicely agrees with the magic numbers predicted for an icosahedral packing

$$N_k^{iso} = \frac{10}{3} k^3 - 5k^2 + \frac{11}{3} k - 1$$

where $k$ is the shell index. In Cd$_N$, see Fig. 10, the abundance distribution shows a different structure. Although $N = 307$ appears as a pronounced mass intensity, indicating an icosahedral, other enhanced intensities, e.g. $N = 158, 168, 178, 205, 258, 360$, cannot be reasonably explained by e.g. capped icosahedrals. Similar findings have been obtained for Zn$_N$.

VI. Optical and electronic properties

Optical spectra of clusters offer the possibility to test time-dependent many-body theories. By comparison of the calculated optical response with the experimental data one can determine basic properties of the system like the ground state geometry. Since the calculations are mostly performed at $T = 0$ it is advantageous to keep the temperature in the measurements as low as possible. However, taking spectra at higher $T$ can reveal possible contributions of certain isomers on the optical response. Detailed information about the optical properties is available for mass-selected cluster ions. Usually beam depletion, which is sensitive to the absorption process itself, is applied. R2PI is, in principle, suitable for gaining information about optical excited states. Despite the finite size of the metal clusters, however, the density of states is quite high even for small clusters and the lifetime of excited states is expected to be only in the picosecond range. For a long time was common belief that only ultrashort laser pulses can overcome this bottleneck and allow for R2PI. For example, in silver and gold particles a dephasing time in the range of a few femtoseconds has been determined. Therefore R2PI studies on metal cluster systems are so far mainly restricted to the properties of metal dimers and trimers (e.g. ref. 134 and 135).

A. C$_{60}$

Fullerenes, e.g. C$_{60}$, C$_{70}$, C$_{84}$ can be produced in large quantities. A temperature of only 640 K is sufficient to generate a vapor pressure of about $10^{-5}$ mbar, enough to efficiently dope helium droplets. In this way one circumvents the capability of the helium droplets to grow clusters from picked-up atoms.

The exceptional stability of carbon clusters with 60 and 70 atoms was first observed in measurements at Exxon and later identified as buckminster fullerene structures by the group of Smalley. Close et al. succeeded in storing C$_{60}$ into helium droplets. The absorption spectrum recorded in the 595–635 nm range by the beam depletion method showed a vibrational structure of narrow lines which are comparable to gas phase data. Since the lowest vibrational excitation in C$_{60}$ is located 257 cm$^{-1}$ above the fullerene ground state, even modest cooling would be sufficient to avoid vibrational hot bands. The advantage of a helium environment compared to matrix spectroscopy is demonstrated when comparing spectra to data taken in a neon matrix. Whereas the line...
positions in helium only shift by about 5 cm\(^{-1}\) compared to the gas phase,\(^{142}\) the spectral shift in neon is found to be eight times larger.\(^{144}\) Moreover, the crystalline matrix broadens the absorption lines substantially, thus losing much of the fine structure information.

B. Alkali clusters

Alkali atoms, molecules and clusters were the first targets at the time when electronic laser excitations and corresponding fluorescence detection methods were introduced in combination with doped helium nanodroplets.\(^{79,145–147}\) Even the first published electronic spectrum of alkali molecules already contained a strong absorption feature that could not be assigned at that time but it was suggested that "the measured intensity may be due to a process involving three or more Na atoms".\(^{145}\) Later on the spectra were assigned to a Na trimer transition in the quartet manifold and for the first time it became clear that the cold helium environment can be utilized to form weakly bound aggregates that can not be isolated by other means. The almost exclusive formation of high-spin states of alkali trimers has been introduced above and to date, quartet sodium, potassium and rubidium as well as caesium trimers have been spectroscopically identified.\(^{80,148–151}\) As shown by these results, aggregates of alkalis in high-spin states represent ideal species for the optical study of fundamental chemical dynamics processes including non-adiabatic spin conversion, change of bonding nature, and unimolecular dissociation.

The laser induced fluorescence (LIF) spectrum of the sodium trimers (cf. Fig. 11) was assigned to the \(2^4E' \rightarrow 1^4A'_2\) transition from the lowest quartet state based on multi-reference configuration interaction calculations.\(^{80}\) The doublet transition \(2^3A'_1 \rightarrow X^3B_2\) of \(\text{Na}_3\) lies in the same spectral region but is completely masked by the quartet spectrum, underlining the strong preference for high-spin species. Similar to \(\text{Na}_3\),\(^{79,81}\) the spectrum of the corresponding trimer exhibits an intrinsic asymmetric, blue shaded broadening on the order of \(\approx 30\) cm\(^{-1}\), due to the repulsive interaction with the bubble-like helium solvation structure. The quantitatively similar amount of broadening already suggests that the trimers are as well bound to dimple-like textures on the surface of helium nanodroplets. The widths of absorption lines impede rotational resolution for a detailed structural analysis but provide the vibrational structure. Aiding \textit{ab initio} calculations, in this way potential parameters were obtained fitting the vibronic structure.\(^{148}\) The nonadditive contributions to the interaction energy were found to be quite large. About 80\% of the van der Waals binding energy of \(\text{Na}_3\) in high-spin states were quantified to be due to nonadditivity. This work was extended later to the \(1^1E\) excited state and also to \(\text{K}_3\) (transitions: \(2^4E' \rightarrow 1^4A'_2, 1^4E' \rightarrow 1^4A'_2\)).\(^{152}\)

The spectrally resolved emission spectrum (Fig. 11) reveals three channels of fluorescence. The direct de-excitation channel to the lowest quartet state of the trimers clearly resolves the vibrational structure of the quartet ground state. The potential surface was modeled to fit the observed emission lines in perfect agreement.\(^{148}\) Other competing channels are the atomic \(n^2P_{3/2,1/2} \rightarrow n^2S_{1/2}\) fluorescence and emission of singlet alkali dimers \((\text{B})^1\Pi_u \rightarrow (\text{X})^1\Sigma_g^+\), cf. Fig. 11). The energy of these fluorescence photons are higher with respect to the energy of the initial excitation. Hence following the transition, the molecule converts its potential energy partly into electronic energy. The detection of singlet dimers among the products of the excitation shows that the quartet sodium trimer is undergoing a non-adiabatic spin flip process to cross into the doublet manifold of \(\text{Na}_3\). The following dissociation leads to atomic and singlet dimer fragments, where electronic excitation can be localized on either product. A further inspection of the fluorescence signal resulting from the dissociation products reveals that the emission is occurring in the gas phase after desorption from the helium droplet. Previously observed emission spectra from the \(3^3P_{3/2,1/2} \rightarrow 3^5S_{1/2}\) transition of Na on helium droplets were found to exhibit broad fluorescence extending from 16 960 to 13 000 cm\(^{-1}\).\(^{153}\) This red fluorescence is not present in the emission spectrum of the atomic Na produced in the dissociation of the doublet \(\text{Na}_3\).

The occurrence of a complex photo-induced dynamics, i.e. spin flip, internal energy redistribution, predissociation and desorption has triggered dynamical studies on the alkali trimer molecules. Reho \textit{et al.}\(^{152}\) employed reverse time-correlated photon counting in order to study the intersystem crossing and dissociation dynamics of potassium and sodium quartet
trimers. In these experiments selected vibronic states are populated and the occurrence of fluorescence from the different decay channels is measured time-resolved. The spin-flip process occurred in 1.4 ns for the 0–0 transition of Na3+, decreasing to approximately 380 ps at the access point to the doublet manifold in the excited state. The measured times indicate that the quartet trimer is undergoing many vibrational oscillations before the valence electrons may undergo a spin-flip transition. Using the same experimental technique the vibrational relaxation upon electronic excitation can be quantified. Relaxation times are found to be on the same time scale but somewhat slower compared to the spin-flip process. Absorption spectra of Rb and Cs trimers have also been observed.\textsuperscript{151,154} The larger masses impede the resolution of the vibrational structure of the bands and hence only broad Franck–Condon contours appear in the spectra. Since theoretical support for these systems is far less elaborated compared to the lighter alkalis, even the assignment to specific electronic states is rather speculative.

Concluding the spectroscopy of alkali trimers, we note that studies are restricted so far to the weakly bound quartet states, that were not at all characterized before the helium droplet studies started. The results in connection with \textit{ab initio} calculations provide a conclusive picture in the framework of molecular states revealing structures and the photo-induced dynamical processes.

Potassium clusters (\(N > 3\)) formed on helium nanodroplets have been probed by means of resonance enhanced photoionization to spectroscopically study their electronic properties.\textsuperscript{63} One can indeed find resonances in the expected energy range around 2.5 eV using nanosecond VIS- and UV-photons for excitation and ionization, respectively. This method is quite sensitive to the detection of long-lived states. Unfortunately fragmentation upon the ionization of the clusters inhibits an assignment to specific cluster sizes and the pick-up dependent distributions clearly point to a mixture of many cluster sizes around \(N = 15\). Taking into account that several electronic configurations and possibly different isomers are involved, such measurements appear less promising without other means to preselect cluster sizes.

C. Silver clusters

Metastable electronic excited states in metal and semiconductor clusters with lifetimes in the ns range are rare. Gantefor \textit{et al.} studied Ag\(_6\)\textsuperscript{−} and found evidence for surface states.\textsuperscript{155} Heath and co-workers reported on long-lived states in Si\(_N\) and Ge\(_N\) clusters.\textsuperscript{156} Duncan \textit{et al.} studied the optical response of Ag\(_N\) with emphasis on the trimer.\textsuperscript{157} An excited state was found at about 365 nm. In measurements on mass-selected silver clusters deposited in Ar matrices, laser induced fluorescence has been observed for Ag\(_4\) and Ag\(_8\) as well as Ag\(_{8}\).\textsuperscript{158–160}

Optical spectra of silver clusters embedded in helium droplets were first recorded by Federmann \textit{et al.}\textsuperscript{161} and later by Diederich \textit{et al.}\textsuperscript{72} R2PI by tunable nanosecond laser pulses was used to study the optical resonances. The method is therefore sensitive to long-lived intermediate states, \textit{i.e.} lifetimes in the nanosecond range. The spectrum of the silver trimer was measured between 3.3 and 3.9 eV covering the region which was studied before in the gas phase.\textsuperscript{157,162} Spectral lines from the embedded clusters show a considerable broadening. Additionally, sharp peaks are obtained, most likely due to trimers which have already been desorbed from the droplets. Similar results have been obtained recently in the optical spectra of Ag\(_2\) attached to droplets.\textsuperscript{162} The appearance of broad features instead of sharp lines in the optical spectra of metal clusters differs from the well-resolved vibronic progressions obtained for molecules.\textsuperscript{164} The enhanced broadening reflects the stronger interaction of the helium environment with the more extended wavefunctions of the delocalized valence electrons in the metals, \textit{i.e.} the spill-out effect.\textsuperscript{107}

1. Optical properties. An optical resonance of Ag\(_8\) at 312 nm was found in Göttingen\textsuperscript{161} when storing silver atoms in helium droplets, see Fig. 12. We note that experimental evidence for a long-lived state in the octamer was already present in the work of the Duncan group (see Fig. 4 in ref. 157) who recorded the multiphoton ionization mass spectrum of bare silver clusters at 317 nm. Due to the ultracold helium environment the width of the resonance at 312 nm is only about 56 meV. Compared to earlier measurements on Ag\(_7\)\textsuperscript{−} (ref. 165) and Ag\(_9\)\textsuperscript{−} (ref. 166,167) the line width is strongly reduced due to the low temperature. Bennemann and co-workers calculated the optical spectra of silver clusters and proved that the change in the absorption profile results from the different isomer abundance distributions present at different temperatures.\textsuperscript{124} Certainly, the number of isomers is strongly reduced in the droplets. However, in Ar matrices a substantial reduction in the line width is also present. The group of Bonačić-Koutecký has made quantum chemical calculations and determined the absorption spectra of silver clusters with up to eight atoms.\textsuperscript{168,169} For Ag\(_8\), the optical spectrum was found to agree well with that expected for a structure with \(T_d\) symmetry. This geometry was also calculated.
to be the lowest lying isomer in their calculation. The \(D_{2d}\) structure also shows a resonance in the spectral region of interest, however, the calculations predict a splitting of the absorption line which is not observed in the experiment. A similar result was obtained in time-dependent density functional (TDDFT) calculations by Yabana and Bertsch.\(^{170}\) Recently, this assignment was questioned.\(^{171,172}\)

Contributions from two different isomers were obtained for Ag\(_8\) clusters in an argon matrix.\(^{160}\) However, so far no signals from Ag\(_9\) as well as from Ag\(_{12}\) clusters have been obtained in droplets. Possibly, the rapid cooling and the rather different preparation method in droplets lead to the formation of isomers which might show no fluorescence. In the experiment of Sieber et al.,\(^{160}\) cluster ions are first formed in a sputter process and than embedded into the matrix. For the silver trimer as well as the tetramer the calculated ground state structures are planar\(^{168}\) and certainly this geometry is present in the matrix experiment. From the sequential growth process in droplets and starting with Ag\(_3\) one could expect that an additional atom would stick more probably on top of the triangle and thus a 3D structure might be more abundant. However, no optical spectra of such a Ag\(_4\) geometry are available from calculations as yet.

The mass spectrum taken at the octamer resonance with slightly larger laser fluence shows signals from fragments (Ag\(_7^+\), Ag\(_8^+\), Ag\(_9^+\) and Ag\(_{10}^+\)) which are not expected from the absorption of only two photons. Odd-sized metal cluster ions dissociate by the loss of a neutral dimer whereas even-sized ones only lose a monomer unit.\(^{173}\) The opposite is true for the neutral clusters. The presence of the odd-sized cluster fragments indicates that Ag\(_8\) mostly decays after the ionization with the second photon and not in the excited neutral state. A typical value for the dissociation energy is about 2 eV.\(^{174}\) Therefore, to explain the fragmentation pattern, absorption of a third photon by the system is necessary. Ag\(_{8}^+\) probably heats up after the ionization due to structural rearrangement. The optical spectra of highly excited Ag\(_N\) are known to have considerable photoabsorption cross section (about 1 A\(^2\) per s-electron) at 300 nm\(^{131,175}\) which would explain the strong signals from the octamer fragments.

The narrow line width of the resonance of Ag\(_8\) allows the investigation of the influence of rare gas atoms on the optical properties, comparable to bulk matrix isolation spectroscopy.\(^{176-178}\) In the gas phase, Duncan and co-workers\(^{179,180}\) studied the attachment of a single rare gas atom (RG = Ar, Kr, Xe) on Ag and Ag\(_3\). LIF spectroscopy was also performed on AgAr.\(^{181}\) In droplets the influence of the additional dopants can be studied as a function of the thickness of the rare gas shell between the metal core and the helium droplet. In principle one can perform an experiment in a nanomatrix of given size. In the experiment the vapor pressure in the pick-up oven is tuned to conditions where the octamer is most abundant. Since the binding energies of the metal clusters are much larger compared to RG–RG and Ag–RG, it is not required to separate the doping regions in order to have a well defined order of pick-up. Therefore, rare gas atoms are directly introduced into the pick-up chamber containing the oven for metal doping. By controlling the partial pressure the number of picked-up rare gas atoms can be controlled. The total number is limited corresponding to the binding energies to be dissipated by the droplet. Under conditions for optimal generation of silver octamers, i.e. 200 000 He atoms per droplet on average, 135 Ne atoms, but only about 15 Xe atoms, can be attached to the cluster. Fig. 13 shows the result of such an experiment where a different number of Xe atoms is layered around the octamer. The resonance is measured by R2PI taking the signal of Ag\(_8\) as a reference. Note that the experiment is performed on a distribution of RG atoms attached to the cluster. In addition, even for the same number of RG dopants the geometric structure of the nanomatrix may vary. Therefore, inhomogeneous contributions to the line broadening due to different sizes and structures of the surrounding RG atoms are expected. A shift of the center of gravity of the resonance line by about 5 nm is found for Ag\(_8\)Xe\(_N\), being the largest compared to the other rare gases. With krypton the displacement is smaller (approx. 2 nm). Argon induces almost no spectral shift. Compared to the corresponding argon matrix experiment neither the spectral shift of 8 nm nor the broadening can be reproduced. This indicates that either more than two layers of Ar (N = 46) are necessary or that the additional helium layers and their solvation structure substantially contribute to the optical spectrum in droplets. Attaching neon to the octamer, the resonance shifts to higher energies which might be due to the higher

![Fig. 13 Optical spectrum of Ag\(_8\)Xe\(_N\) (N = 3, 8, 15) embedded in helium droplets. The influence of the higher polarizability of xenon compared to helium shifts the resonance towards the lower excitation energies. Dashed line: optical spectrum of Ag\(_8\) obtained in pure helium droplets. Reprinted with permission from T. Diederich, J. Tigges-büntiker and K.-H. Meiwes-Broer, J. Chem. Phys., 2002, 116, 3263. © 2002, American Institute of Physics.](image-url)
negative electron affinity\(^{182}\) when compared to helium. Interestingly, measurements in a Ne matrix show a red-shift of the resonance.\(^{183}\) Only recently Gervais et al.\(^{184}\) calculated the influence of the size of an argon nanomatrix on the optical spectrum of sodium clusters. Assuming Na and Ag clusters to have a similar net shift in helium, the almost zero displacement of the silver octamer resonance in an argon nanomatrix can be understood. Two strong but competing effects contribute. The polarizability induces a red-shift which is 1.1 eV for Na\(_{42}\)Ar\(_{42}\), whereas the Pauli pressure of the matrix leads to a comparable blue-shift of the resonance.

2. Electronic properties. Apart from the optical properties one gains information about the density of states of the embedded system and possible dynamics by analyzing the corresponding electron spectrum. Single photon photoelectron spectroscopy on mass-selected anions have proven to be widely successful to determine electronic properties of clusters.\(^{99,185–189}\) Because photoemission is a vertical process, the method gives information about the density of states of the neutral in the geometry of the anion. For neutrals, mass-selection has to be achieved. Conventionally, the photoelectron spectrum is obtained by using the coincidence technique. This has been successfully applied by Rademann and co-workers\(^{100,119}\) in an experiment on mercury and cadmium clusters. However, the event rate has to be much lower than unity in order to guarantee a unique assignment of the electron to a certain cluster size. Resonant ionization in combination with photoelectron spectroscopy (R2PES) allows for a more efficient measurement. A powerful method for overcoming the limitations in low density targets is the magnetic bottle technique\(^{190}\) where all electrons from the interaction process are guided in a bottle-shaped magnetic field towards the detector. The kinetic energy of the electrons is determined by their time-of-flight. Due to the low helium droplet beam velocity\(^{191}\) of 60–450 m s\(^{-1}\) no Doppler broadening contributes to the line width thus giving a resolution of the instrument of about 5 meV for 1 eV electrons.

Additionally, the analysis of the kinetic energy of the electrons emitted from the cluster allows the study of the influence of the helium environment on the photoemission process. Loginov et al.\(^{192}\) have recently addressed this problem by recording the electron spectrum of aniline embedded in nanodroplets of different size. In this experiment they found a loss in the energy of the electrons due to collisions with the surrounding He atoms. As a benchmark experiment for metal clusters the photoelectron spectrum of Ag\(_3\) was recorded by R2PES.\(^{193}\) The Ag trimer has been chosen for several reasons. The R2PI spectrum of Ag\(_3\) in the photon range of 3.3–4.1 eV is well-known\(^{161}\) and no other Ag\(_x\) show optical resonances in this photon energy regime. The trimer also has a quite low ionization potential of 5.73 eV in the gas phase,\(^{194}\) which is easily accessible by a single photon from conventional laser systems. The R2PES spectrum is recorded using a photon energy of 3.65 eV, which is slightly above the low energy onset of the resonance. A broad asymmetric structure having a line width of about 200 meV close to the photoemission threshold is obtained. No other excited states are observed, although the chosen photon energy would allow for the detection of more deeply bound electronic levels. Using a two-color excitation scheme, the lifetime of the excited state was determined to 6 ns. The ionization potential \(I_p\) of Ag\(_8\) in droplets was determined to 5.73 eV which agrees rather well with the value found in the gas phase. Due to the polarizable medium one would expect a shift of the ionization threshold. Possibly, the trimer in the excited state leaves the droplet before the final ionization step. In the experiment, however, we observe a dependence of the photoelectron spectrum on the chosen droplet size which hints at an ionization inside the droplet. The difference in the matrix-shift of the ionization potential with respect to the photoelectron experiment on aniline in droplets can be explained by the more attractive interaction with the environment in the case of molecules. In contrast, bubble-like states are present when metal clusters are enclosed and hence matrix contributions are reduced. This effect is even more pronounced in the excited state and leads to only a slight shift of the threshold for metal clusters. The broad asymmetric line shape indicates a scattering mechanism. Unfortunately no gas phase photoelectron spectrum for comparison has been recorded up to now. Although the geometry of Ag\(_8^-\) is known to be linear and Ag\(_3\) has a triangular shape, a direct comparison with the corresponding anion spectrum is useful. The line width of the features obtained for Ag\(_8^-\) appears to be sharper than for the neutral cluster.\(^{195}\) Moreover, the peak is more asymmetrically broadened to higher binding energies. Interaction of electrons with the helium environment thus cannot be excluded. Another possibility turns out to be the formation of an electron bubble. Such a process takes place on a time scale of picoseconds.\(^{21,196}\) At typical electron kinetic energies of 1.0 eV the electron drift time through the droplet is much shorter when compared to the bubble formation time and should therefore only contribute for very large droplet sizes. An observed broadening of the lines in the spectra at low nozzle temperatures might indicate such an effect.

For the Ag octamer the situation appears to be more complicated. An accurate value of the ionization potential cannot be given. From experiments in the gas phase the \(I_p\) was estimated to be between 6.4 and 7.9 eV,\(^{157,194}\) i.e. the ArF and F\(_2\) emission lines of an excimer laser system. In addition, the absorption spectrum of Ag\(_8\) overlaps with the one of the silver dimer.\(^{161}\) The droplet size dependence of the pick-up process, however, allows one to distinguish between both cluster sizes. At a nozzle temperature of 12 K the photoemission spectrum originates mainly from electrons from photoionized dimers whereas at 9.2 K mostly Ag\(_8\) is present in the beam. Fig. 14 shows the corresponding R2PES spectra at different helium droplet source conditions recorded at a photon energy of 3.964 eV. At low nozzle temperatures a couple of distinct features show up in the spectrum. These are signatures of excited states of triplet Ag dimers, as discussed in more detail in ref. 163. Lowering the source temperature, the intensity of the Ag\(_2\) features decrease and a new line shows up at a binding energy of about 7.0 eV which one can assign to emission from the octamer. The corresponding R2PI spectra support this assignment. Evidence for photoelectron–helium scattering is found in the spectrum at lower nozzle temperatures. When larger droplets enclose the metal cluster core the photoemission line broadens to higher binding energies, see Fig. 14 (bottom).
Due to the excitation scheme which benefits from the intermediate state, the electron spectrum could be modified by relaxation within the excited state. Indeed, one finds that the ionization threshold energy \( E_{\text{th}} \) scales only with \( h_\Omega \) instead of \( 2h_\Omega \) when scanning the laser frequency \( \omega_L \) over the optical resonance. At the low energy onset of the resonance the slope of \( E_{\text{th}} \) changes towards a value of two, indicating the transition to non-resonant multiphoton ionization. Possibly, at higher photon energies, within the resonance a vibrational excited state of only Ag\( _8 \) or a local Ag\( _8 \)-He cluster complex is populated which thermalizes through contact with the ultracold environment down to the bottom of the electronic state. Taking this into account an accurate value for the ionization potential of Ag\( _8 \) as well as quantum chemical calculations is shown.

Fig. 14 R2PE spectra recorded at a wavelength of 312.8 nm. With decreasing nozzle temperature photoemission from triplet dimers first dominates the spectra whereas at colder conditions a broad feature shows up (shaded region) which can be assigned to emission from the embedded Ag\( _8 \). For comparison the ionization potentials obtained by EI are shown. Reprinted Fig. 3 with permission from R. Radcliffe, A. Przystawik, T. Diederich, T. Döppner, J. Tigggesbäumker and K.-H. Meiwes-Broer, Phys. Rev. Lett., 2004, 92, 173403. © 2004 by the American Physical Society (http://link.aps.org/abstract/PRL/v92/e173403).

VII. Fragmentation dynamics

Upon interaction with laser radiation, molecules, clusters or complexes may undergo breaking or formation of bonds, i.e. chemical activity. In particular, the fragmentation of clusters is of interest when having them isolated in a matrix environment.

In liquids as well as in solid matrices there is a certain probability that the dissociating fragments collide with surrounding atoms. In this case the environment can act as a cage possibly suppressing fragmentation or advancing different reaction pathways. The cage effect has been known since the early 1930s through the work of Frank and Rabinowitch. Dihalogens have been studied intensively in solids and liquids. Since the development of intense sub-picosecond laser systems, experiments on the cage effect can be performed in real-time, see e.g. ref. 206 and 207. The caging of small molecules like I\( _2 \) embedded in clusters were investigated e.g. in the groups of Lineberger, Zewail and Neumark as a function of the cage-size. For the process of recombination the environment plays a crucial role, shifting the timescales of the dynamics by orders of magnitude or even inhibiting dissociation processes. Upon optical excitation the recombination time of the iodine dimer embedded in carbon dioxide, e.g. (I\( _2 \)(CO\( _2 \))\( _{10} \)) is about 1.3 ± 0.1 ps whereas in argon a value of 127 ± 4 ps for I\( _2 \)Ar\( _{20} \) was found.

Only a few studies concentrate on the cage effect of molecules and clusters in helium droplets. In contrast to the weak interaction of the helium with embedded molecules apparent from the superfluid properties, dissociation is expected to lead to a stronger response of the solvent because corresponding translational energies exceed by far the energies needed to break down superfluidity. In other words, the Landau critical velocity is much lower than the velocity of most of the dissociating fragments.

Nauta and Miller studied the HCN dimer and found evidence that the dimer rearranges after predissociation due to caging by the helium environment. In a photolysis experiment Braun and Drabbels studied the fragmentation of CF\( _3 \)I when exciting with 266 nm laser pulses. The velocity distributions of the fragments suggest a direct escape from the droplet without substantial energy transfer to the helium. Takayanagi and Shiga calculated the photodissociation of C\( _3 \)I in droplets by treating both helium and the chloride dimer quantum mechanically. In the regime where superfluidity does not need to be taken into account the simulations reveal that dissociation is almost not inhibited through the presence of the cage. In contrast to other environments the exchange of energy in collisions is not restricted to a local region in the vicinity of the dopant but transferred to the droplet as a whole, i.e. emphasizing the quantum properties of the matrix.

Stimulated by experiments on EII of neon clusters in droplets by Ruchti et al., the group of Halberstadt studied the fragmentation dynamics of Ne\( _{14} \) in droplets by introducing a Landau velocity dependent frictional force in order to simulate the influence of the helium environment. The results agree with the observed fragmentation without significant caging. In a recent study Ne clusters up to a size of \( N = 14 \) have been calculated and Ne\( _{12} \) is identified as the main fragmentation channel. The contribution of larger fragments, however, increases, e.g. the abundance value for Ne\( _{4} \) is found to be 0.05 for a cluster size of Ne\( _{14} \). Evidence for a cage-affected change in the fragmentation ratio has been observed in the EII of C\( _1 \)-C\( _6 \) alcohols and ethers, where an enhanced loss of hydrogen was found.
The fragmentation and possible caging of embedded metal clusters in large droplets ($D = 20 \text{ nm}$) have been studied for Ag$_N$ and Mg$_N$ using the pump–probe technique probing the dynamics of the photo-activated complex. Information about the metal cluster bonding conditions can be obtained as a function of the optical delay.

Fig. 15 (bottom) shows the result of such a pump–probe experiment. Ag$_{39}^{2+}$ and Ag$_{58,59}^{3+}$ were chosen, since they are particularly stable multiply-charged clusters. The probe pulse induced signal from the clusters recovers at larger optical delays, indicating that a fragmentation of the metal core is suppressed by the helium environment. The signal obtained by feeding in the pump-pulse only is given for comparison. Reprinted with permission from T. Döppner, T. Diederich, S. Göde, A. Przystawik, J. Tiggesbäumker and K.-H. Meiwes-Broer, J. Chem. Phys., 2007, 126, 244513. © 2007, American Institute of Physics.

The fragmentation and possible caging of embedded metal clusters in large droplets ($D = 20 \text{ nm}$) have been studied for Ag$_N$ and Mg$_N$ using the pump–probe technique probing the dynamics of the photo-activated complex. Information about the metal cluster bonding conditions can be obtained as a function of the optical delay.

Fig. 15 (bottom) shows the result of such a pump–probe experiment. Ag$_{39}^{2+}$ and Ag$_{58,59}^{3+}$ were chosen, since they are particularly stable multiply-charged clusters. Apart from a slight enhancement due to the second pulse no clear pump–probe effect is present up to several picoseconds, indicating that a fragmentation of the metal core is still intact. After 10 ps the pump–probe signal decreases considerably and shows a distinct minimum. The cluster signal then recovers on a 100 ps timescale. Additional information about the underlying process arises from the analysis of the snowball signal also monitored in the experiment, see Fig. 15 (top). For the snowballs a similar dynamic effect is obtained in the measurement but showing the opposite trend. Apparently snowball formation is favored in this time regime.

According to the results presented in section II, that signals of snowballs indicate the presence of isolated atoms, the dynamics in the pump–probe spectrum can be understood on the basis of the cage effect and a subsequent recombination of the photo-activated metal core. A possible scenario is presented in Fig. 16. After excitation of the metal core by the leading pulse the cluster is partly ionized and possibly heated up by additional absorption of photons. In the following atoms are evaporated from the hot particle, decreasing the cluster size. A typical timescale is several picoseconds in accordance with the experimental result. The decrease in the cluster ion signal indicates that such a process takes place.
Possibly the system decays completely into atomic fragments. The snowball signal increase at longer optical delays, giving evidence that isolated atoms are ionized on the way out of the droplet. Due to the much larger diameter of the matrix compared to experiments in small droplets the number of collisions are certainly sufficient to cage the fragments. Taking typical values from gas phase studies on Ag clusters as a reference, the energy of the atomic fragments is about 100 meV giving a velocity of 500 m s\(^{-1}\), i.e. a transient time through the droplet of about 100 ps. Note that this value exceeds the critical Landau velocity in the superfluid. By collisions with the matrix the recoil energy of the atoms is effectively distributed over the droplet leading to caging. Atoms which are still inside the droplets in this time regime form Ag\(^{+}\)He\(_N\) snowballs when ionized by the probe-pulse. The cage effect finally leads to the recovery in the Ag-cluster intensity and the decrease in the snowball signal. The situation is interesting in itself, since the system might transiently undergo the NMM. Thus, it seems feasible to study NMM as well as re-assembling of clusters in real time.

VIII. Coulomb explosion in strong fields

With respect to the work of Keldysh,\(^{227}\) the ionization in strong optical laser fields can be divided in three regimes, i.e. multi-photon ionization (MPI), tunnel ionization (TI) and barrier suppression ionization (BSI). The Keldysh parameter \(\gamma_k = \sqrt{I_0/\beta} \phi_p\) (\(\phi_p\) the ponderomotive potential induced by the laser field) separates MPI from BSI. For field strengths of \(I_0 = 10^{16}\) W cm\(^{-2}\) the electric field of the laser pulse is about \(10^{10}\) V m\(^{-1}\), which is comparable to the interatomic electric field of a hydrogen atom. The ionization dynamics in the intensity range above \(10^{12}\) W cm\(^{-2}\) is therefore highly perturbed and one expects strong non-linear effects. For atoms a quite accurate value of the BSI threshold intensity \(I_{th}\) can be given\(^{228}\)

\[
I_{th} = \frac{\pi^2 e_{th} I_0^2}{2a_0^6 Z^2} \quad \text{or} \quad I_{th} [\text{W cm}^{-2}] = 4.0 \times 10^9 \frac{I_0^2 [\text{eV}]}{Z^2} \tag{6}
\]

where \(I_0\) is the binding energy of the electron and \(Z\) the charge state after ionization. For e.g. the silver atom the threshold value is \(I_{th} = 1.32 \times 10^{13}\) W cm\(^{-2}\).

In particular, small particles show an exceptional dynamics. Although the rare gases are almost transparent in the visible, a dense rare gas cluster beam exposed to intense laser pulses show an absorption of nearly unity.\(^{229}\) Due to the strong coupling into the system the particles are completely destroyed and only the atomic fragments survive the violent interaction process. The resulting Coulomb explosion leads to highly charged ions having MeV recoil energies, energetic keV electrons as well as the emission of high harmonic photons and X-rays.\(^{230-242}\) Even nuclear fusion processes from deuterium clusters have been observed\(^{243-246}\) and predictions have been made for efficient d-d fusion from (D\(_2\)O)\(_N\) clusters.\(^{246}\) Molecular as well as plasma physics concepts have been applied to explain the strong ionization dynamics in small particles.\(^{247-253}\) The central idea turns out to be that the particle forms a nanoplasma and strong absorption proceeds via the excitation of the giant electron dipole resonance of a delocalized electron gas, i.e. the Mie plasmon \(\omega_R \approx \sqrt{n_i/3}\), where \(n_i\) is the ionic background density.\(^{254-256}\) So far, most of the studies concentrate on rare gas clusters. In order to profit from collective effects the van der Waals clusters have to be brought transiently into the metallic state. Metal clusters on the other side have already delocalized electrons in the ground state and a plasmon resonance has been proven to exist in systems with only eight atoms.\(^{8,126,127,131,132,165,166,257,258}\) Therefore small metallic particles are well-suited to investigating the light–matter interaction in detail. Much of the physics of the ionization process has been understood by pump–probe spectroscopy in connection with model calculations of the complex electron and ion dynamics via density functional theory.\(^{241,256-259,262}\) Recently, a novel electron acceleration mechanism has been identified.\(^{263}\) Charging of embedded clusters in a helium matrix also offers a possible route for studying the interaction of highly charged ions with helium.

The difference in the charging dynamics between atoms and small particles is already evident in an experiment where the laser pulse duration is changed. This can be achieved simply by detuning the compressor of the laser amplifier system. According to eqn (6) one would expect that the intensity turns out to be the crucial parameter. While this is justified for single atoms, in clusters a longer pulse width results in the generation of higher charged atomic ions,\(^{237,265,266}\) e.g. the ionization state of the atomic fragment ions of platinum clusters of up to \(Z = 20\) are four-fold enhanced compared to the single atom. Fig. 17 shows the result of an experiment where Ag clusters are embedded in large nanodroplets and exposed to a strong laser field. Highly charged atomic fragments are detected from the Coulomb explosion following the violent excitation process.

![Fig. 17 Fragment spectrum of silver clusters embedded in helium nanodroplets after excitation with a strong femtosecond laser pulse (4 \(\times\) \(10^{15}\) W cm\(^{-2}\)) showing the presence of highly charged ions Ag\(^{Z^+}\) up to \(Z = 11\). Compared to an experiment on single atoms the ionization efficiency is strongly enhanced. Due to the different intensities within the laser focus, signals from helium clusters, Ag\(^{+}\) snowballs as well as singly and multiply-charged clusters appear in the spectrum. From T. Döppner, J. Müller, A. Przystawik, J. Tiggesbäumer and K.-H. Meiwes-Broer, Eur. Phys. J. D., 2007, 43, 261–266. With the kind permission of Springer Science and Business Media.](image-url)
Using the dual pulse technique the ionization dynamics can be studied in more detail. For instance, with longer laser pulses it is not apparent whether the charging is driven by a constant heating of the system during the laser pulse or if resonances play a more pronounced role in the interaction process. Fig. 18 shows the result of an experiment on silver clusters with a size of about 100 atoms embedded in droplets (mean size of a few tens of nanometers). At short delay times when both laser pulses overlap (giving a four-fold increase in intensity) the signal of the higher charged atomic fragments is weak. This indicates that the laser intensity is too low to strongly ionize the atoms of the cluster via BSI. Field ionization contributes significantly only at the leading edge of the laser pulse. At larger laser separations the abundance of Ag\(_{Z+}\) ions vastly increases and peaks at about 500 fs. The maximum in the dual pulse spectrum shifts to lower delay times with increasing \(Z\). Analyzing the position of the maximum \(t_{\text{opt}}\) as a function of the atomic \(Z\) reveals a shift towards shorter optical delays. One also observes that the width of the curves narrow with ionization state which provides evidence that generation of highly charged ions is only efficient within a narrow time window. In this experiment \(t_{\text{opt}}\) gradually shifts from 610 fs for Ag\(_{3+}\) to 250 fs for Ag\(_{11+}\). This general behavior is also found at other laser intensities and target systems. By choosing an appropriate optical delay it is therefore possible to enhance the abundance of a certain atomic charge state. The expansion dynamics as well as the final atomic fragment charge state can be controlled in the experiment by the intensity of the pump and probe beam, respectively. A weaker leading pulse e.g. enlarges the time period to match the resonance condition whereas the strength of the second pulse determines the final charging of the clusters.

The width of the dual pulse curves obtained in the experiment (cf. Fig. 18) reflects the width of the metal cluster size distribution present in the droplets. It is also worth mentioning that the spatial intensity distribution within the laser focus plays a crucial role in the analysis. Experimentally, the laser intensity is controlled by moving the position of the focusing lens with respect to the nanodroplet beam axis. However, perpendicular to the laser beam clusters are not exposed to a homogeneous laser fluence. This has an effect both on the timescale of the initial expansion as well as on the final charging of the system. As an example, clusters in the outer region experiences a lower intensity compared to clusters on the laser beam axis. Therefore, the initial expansion is slower shifting the delay \(t_{\text{opt}}\) towards a larger value. Moreover, the reduced fluence decreases the final ionization state of the cluster. Currently we investigate this effect in more detail by applying the z-scan method.

In order to understand the strong dependence of the ionization of clusters on the time structure of the excitation pulse, the plasmon enhanced ionization model can be applied. The key in the basic understanding of the charging dynamics turns out to be the role of the collective electron resonance \(\omega_R\) in metallic systems, the resonance frequency of which is modified through the ionization process. Due to the high atomic density which is comparable to the bulk value, the plasmon energy is far above the photon energy (\(h\omega_R\)) of the driving infrared laser pulse and thus the resonance initially cannot contribute to the absorption process. In a simplified version of the model, the cluster is first exposed to the first laser pulse. In the intensity regime used in the experiments only tunnel ionization and BSI can lead to a sufficient initial charging of the cluster. Due to the Coulomb forces between the ions in the cluster, the system expands, shifting \(\omega_R\) towards lower energies. The critical radius at which the plasmon approaches \(\omega_L\) can be estimated from the bulk Wigner–Seitz radius taking the 1/3 red shift of the plasmon resonance in small particles into account. A second pulse fed into the system at a particular time can couple resonantly into the plasmon, vastly increasing the absorption cross section. As a result the system is heated by inverse bremsstrahlung and strong ionization occurs. This simplified picture of the strong non-linear dynamics is supported by semiclasical Vlasov and as well as time-dependent density functional simulations. Fig. 19 shows the result of a Vlasov molecular dynamics calculation where Na\(_{55}\) is exposed to a pair of ultrashort and intense laser pulses. Clearly the leading pulse only results in a quite weak ionization state of the cluster whereas the subsequent pulse increases \(Z\) by nearly an order of magnitude. The resonant nature of the enhanced coupling of the laser field to the system becomes evident when monitoring the dipole response of the electronic system which
clearly behaves like a driven harmonic oscillator, showing the typical passage through $\pi/2$ at resonance.

Finally the influence of the helium droplets on the dynamics of the Coulomb explosion has to be discussed. Caging can almost be neglected. Classical molecular dynamics simulations using an appropriate molecular potential reveal that a notable deceleration of the Coulomb explosion takes place on a timescale of tens of picoseconds, thus much longer than the relevant timescale discussed in the preceding section. The ionization potentials of metal clusters are in general much lower with respect to helium. In fact, the pulse intensities chosen in most of the experiments are only slightly above the BSI threshold for the silver atom which is an order of magnitude lower when compared to He. One would therefore not expect a large fraction of the helium environment to be directly ionized under these pulse intensity conditions. When assuming an ionization of the He matrix, the small mass of He would instead lead to a fast stripping from the metal core due to the repulsive Coulomb interaction. However, electrons emitted from He atoms might contribute to the charging dynamics, since they could be accelerated by the laser pulse due to the quiver motion in the laser field. As a consequence the probability for EII of atoms within the droplet can possibly increase, leading to an accelerated expansion. In this context we refer to work by the group of Apkarian concerning the electron dynamics in bulk liquid helium. Finally, electrons in the vicinity of the metal core will enhance the polarizability of the complex and the plasmon energy would shift to a smaller value, reducing the time delay in order to approach the plasmon resonance condition. A direct comparison between free and embedded metal clusters has not been performed for lead clusters. However, the results have to be taken with caution, because there might be a difference in the cluster size distribution.

Although the pulse intensity of $4 \times 10^{15}$ W cm$^{-2}$ is too low to reach the BSI threshold of $I_{0h} = 5.3 \times 10^{15}$ W cm$^{-2}$ for helium double ionization (see eqn (6)), a He$^{2+}$ signal can be detected. Even more, one experimentally obtains a clear pump-probe signal from electron charge transfer between helium and the highly charged metal fragment ions (e.g. M$^{Z+}$ + He$^{+} \rightarrow$ M$^{Z-1}$ + He$^{2+}$), which proves that the matrix is still intact at times when the metal cluster core is ionized at resonance. The particular influence of the helium nanodroplet environment, however, has still to be evaluated in more detail.

\section*{IX. Conclusions}

Although the field of cluster physics has been established for quite some time, many interesting fundamental properties of metal clusters are still to be investigated. The agglomeration of metal clusters in helium nanodroplets and isolation at temperatures below 1 K has opened a new route for studying geometric as well as electronic characteristics of metal clusters. We summarized results on the formation and the limitations of growing metal clusters in helium droplets and reviewed the work performed applying mass spectrometry and the detection of laser induced processes. The latter includes spectroscopic data as well as the interaction with strong laser fields. Many aspects in the reviewed studies already introduced structural properties as well as dynamics in metal clusters that gave peculiar insight to properties of the systems under study. However, the opportunities for using helium droplets to probe low temperature specific unique properties like e.g. superconductivity or magnetism on the nanoscale have yet to be exploited. We expect quite significant progress in this direction from future experiments which, of course, need further support from theoretical models and advanced calculations in order to finally give a conclusive picture of the physics and chemistry of nanoscale materials.

\section*{Acknowledgements}

Financial support by the Deutsche Forschungsgemeinschaft is gratefully acknowledged. In particular JT likes to thank support through Sonderforschungsbereich 652. Main parts of the Rostock helium droplet machine were constructed and build by Peter Toennies and his co-workers. We thank Oliver Bünemann, Thomas Diederich, and Tilo Döppner for providing us with unpublished results.

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