Characterization of laser ablation as a means for doping helium nanodroplets

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(Received 19 February 2003; accepted 4 June 2003)

Helium nanodroplets are doped with metal atoms by means of laser evaporation. The material is evaporated directly in front of the helium nozzle by a pulsed laser. In comparison with conventional pickup from an oven we deduce that the droplets can be loaded with more than one atom per droplet on average. Conditions and efficiencies for loading are evaluated. Furthermore, metal ions can be attached to helium droplets by this method, allowing isolation of charged particles at temperatures below 1 K. In this way we can directly measure size distributions of helium nanodroplets which are compared to results using other techniques. © 2003 American Institute of Physics.

[DOI: 10.1063/1.1602943]

I. INTRODUCTION

Helium nanodroplet isolation (HENDI) has been developed as a powerful tool for spectroscopic studies of atoms and molecules at very low temperatures. In these studies the peculiar properties of liquid helium are exploited to cool down attached species to temperatures below 1 K and to probe them with minimal perturbation in a matrix environment. The peculiarities are, on one hand, the superfluid state, leading to efficient cooling and frictionless motion, and, on the other hand, the inert, liquid and very diffuse condition of helium at that temperature which results in isotropic, very weak interaction. To date, most studies have concentrated on frequency domain microwave, infrared, as well as electronic spectroscopy. Furthermore, photoelectron spectroscopy, real-time spectroscopy and ion imaging have already been applied and various new experiments are on the way. In all the experiments the beam of helium droplets has been generated in a supersonic expansion from a cold nozzle (typical temperatures: 6–25 K). A crucial point in all these studies is the availability of dopant material. Since coexpansion of helium and the dopant is not an option because of the cryogenic temperatures of the nozzle, the helium droplets have to be loaded further downstream. Loading is achieved upon inelastic scattering with the dopant gas and commonly referred to as the pick-up technique. This technique requires a certain density of molecules in the gas phase. In many studies the gases have been directly let into the doping region. Materials that have to be evaporated in an oven to generate the required vapor pressures were for the first time utilized in experiments involving alkali metals. To date, the use of a pick-up oven has been extended to a variety of metals as well as to organic molecules (see Table I in Ref. 3). In a recent task, another cornerstone with respect to the variety of dopants has been achieved by picking up radicals in a pyrolysis source.

At elevated pick-up pressure, more than one atom or molecule is collected by the droplet and hence clusters and complexes can form. Clusters up to a couple of thousand atoms have been grown by successive pick-up. In this way, the evolution of properties to relatively large size clusters or complexes can be probed. Finally doping successively different constituents allows one to design specific complexes which could not have been formed in any other way.

With a pick-up region of 10 cm, an equivalent partial pressure of $10^{-5}$ mbar is enough to dope the droplets with one chromophore on average. Although this pressure is very low, many atoms and molecules cannot be evaporated by conventional heating or it is at least impractical to do: either temperatures are to high (e.g., a great many metals) or the molecules are too fragile to survive heating (e.g., most of larger organic compounds). For both types in principle this problem can be circumvented by laser evaporation/desorption. The use of laser evaporation for the generation of intense cluster beams has a long history as a standard technique particularly in studies on metal clusters. However, in the combination with helium droplet beams it has not been clear whether laser-ablated particles can be utilized to be captured by the fragile droplets. The relatively high kinetic energies are generally too large to dissipate by evaporative cooling. Ghazarian and co-workers introduced laser evaporation combined with a pulsed helium droplet source (PDS) operated in the vapor above liquid helium. They reported pick-up by helium droplets of neutral and charged copper atoms as well as electrons from a laser plasma generated on a rotating disk at cryogenic temperatures. At first glance their approach seems to be very similar to the experiments presented here. However, so far helium beam spectroscopy has used nanodroplet beams expanded in high vacuum, and this shows crucial differences: in Ghazarian et al.’s experiments helium droplets are even produced when setting source conditions (stagnation pressure, temperature) to values under which droplet formation was not observed when operating a PDS under high vacuum conditions. The authors interpretation is that droplet formation occurs by postexpansion condensation in the chamber filled with helium at pressures on
the order of 10 Torr. The mechanism is not well understood at present and results in beam velocities less than 50 m/s. Droplet sizes were not given but they are probably substantially larger than the commonly used 10,000 helium atoms per droplet for spectroscopic measurements. The aspects of energy distributions and energy dissipation are based on very different mechanisms: In one case continuous scattering with background helium gas is crucial for droplet formation; laser-ablated particles are expected to thermalize in the helium vapor before they attach to droplets. In the other case nanodroplets are isolated in vacuum with only evaporative cooling to thermalize dopants.

In this article we demonstrate that also helium nanodroplet beams (HeN, \( N \approx 10,000 \)) expanded in vacuum can be loaded from a laser ablation process. We find that doping of helium droplets by laser evaporation (DLE) is as efficient as pick-up from an oven. In addition to evaporation of neutral metals, helium nanodroplets have been loaded directly with ions, thereby enabling the study of ionic species at millikelvin temperatures. In this way, spectroscopic studies of specific ions at low temperatures can be performed which are particularly relevant with respect to astrophysical observations. Finally, the extension to laser desorption of biological relevant molecules which has been commonly used in other studies is apparent.

Because of the power densities required, laser evaporation can only be performed using pulsed lasers. Compared to continuous wave (cw) pick-up from an oven, one might consider this a drawback. However, since in many experiments pulsed lasers and time-of-flight methods are used, and a PDS already was adopted to form a nanodroplet beam in high vacuum, a pulsed method for doping is especially suited for an increasing number of future studies.

**II. EXPERIMENT**

The experimental setup for laser evaporation combined with helium nanodroplets has been tested in different machines using various lasers. Figure 1 gives an overview of the arrangement for doping and the different detectors used in our experiments although not all the components shown in Fig. 1 have been combined in that order in a fixed apparatus.

The molecular beam machine for generation of helium droplets has been used mainly for spectroscopic studies and is described in detail elsewhere. In short, helium gas (stagnation pressure \( P_0 \): 30–100 bar) expands through a cold (temperature \( T_0 \): 15–26 K) nozzle 5 \( \mu \)m in diameter. The droplet size can be varied by changing the expansion conditions \((T_0, P_0)\). Behind the first skimmer (diameter: 400 \( \mu \)m, distance: 20 mm) is an oven that provides the vapor for pickup of the chromophores in a separate vacuum chamber. The cylindrical oven with 3 mm entrance and exit orifices is heated via radiation from a coaxial heater with tantalum coils. The oven was filled with sodium, for which we precisely know the doping conditions from spectroscopic measurements, i.e., the average number of sodium atoms per droplet. Further downstream under ultrahigh vacuum (UHV) conditions several detectors have been used

1. A time-of-flight arrangement in which after pulsed extraction and a field free region ions can be mass analyzed by means of time correlated detection in a multichannel plate detector.
2. A quadrupole mass spectrometer in which neutral species are ionized by electron bombardment.
3. A Langmuir–Taylor surface ionization detector which can accurately measure the number of alkali and alkaline earth doped helium droplets.

The setup for doping the droplets by means of laser evaporation was installed directly in the droplet source chamber. Apart from the fact that in this way a doped helium droplet beam can be produced with only one vacuum chamber, there is another crucial reason choosing this option. In order to carry dopants, the helium droplets have to dissipate the kinetic energy upon impact by evaporation of helium atoms. The total energy a droplet of 10,000 helium atoms can dissipate by complete evaporation is 6 eV. Since the atoms from a laser plasma have large kinetic energies, the probability of ejected particles being trapped in a droplet is low. Having the laser-evaporated atoms directly in front of the nozzle allows two extra processes: on one hand the ejected atoms with high kinetic energy can be “ precooled” during scattering processes with the high density of the outer beam of helium atoms. This major part of the expanded helium is skimmed upon entry into the second chamber in order to establish the good vacuum conditions required downstream. On the other hand, the laser evaporated material can directly serve as a seed and enhance condensation of droplets. The measured cluster size distributions presented later indicate that the latter process appears to be important.

The dopant material is evaporated from a target rod which is oriented perpendicularly with respect to the droplet beam. No housing or shielding was installed. The rod carries out rotational and translational motion in order to evenly spread ablation over the rod. We used rods 3–5 mm in diameter. The position (distance from the nozzle and distance from the droplet beam) can be varied during operation. The optimal position was found to be 6 mm below the beam axis.
and 10 mm away from the nozzle, although there is no substantial dependence of the measured intensities on the exact position. For the ablation a frequency doubled Nd:YAG laser ($\lambda = 532$ nm) and alternatively an excimer laser ($\lambda = 308$ nm) was focused ($f = 300$ mm) onto the target material. The energy per pulse was of the order of 20 mJ. The optimum energy is material dependent and not very crucial.\textsuperscript{39} Repetition rates up to 50 Hz have been used, limited only by the lasers available.

III. RESULTS AND INTERPRETATION

A. Doping neutral atoms

The performance of DLE is illustrated in Fig. 2. We used sodium as the dopant material because the efficiency of doping can be quantified in comparison with well defined pickup from the oven. For the measurements shown in Fig. 2 the oven temperature was set to conditions where a maximum of singly doped helium droplets is present in the beam. In this case, in a statistical, successive pick-up process 58\% of all droplets carry one metal atom. The correct behavior was checked by recording the Poisson distributions\textsuperscript{17} by spectroscopic identification by means of laser-induced fluorescence. In this way, fragmentation processes which play a role on mass separation after the ionizing process, and might bias measured intensities, are avoided. The constant background represents doping from the heated oven; the peaks labeled A, B and C rise from the laser ablation process (power density: $10^8$ W/cm$^2$, nozzle temperature: $T_n = 19$ K, stagnation pressure: $P_0 = 70$ bar).

Peaks A and C are separated by using mass selection in the quadrupole mass spectrometer after electron impact ionization. The signal was recorded by setting the quadrupole filter to mass 8 amu. Lower trace: Time-of-flight signal of mass 24 giving the intensity of magnesium-doped droplets.

FIG. 2. LT surface ionization signal of sodium-doped helium droplets as a function of time. The constant background represents doping from the heated oven; the peaks labeled A, B and C rise from the laser ablation process (power density: $10^8$ W/cm$^2$, nozzle temperature: $T_n = 19$ K, stagnation pressure: $P_0 = 70$ bar).

FIG. 3. Upper trace: Droplet beam intensity measured in the quadrupole mass spectrometer after electron impact ionization. The signal was recorded by setting the quadrupole filter to mass 8 amu. Lower trace: Time-of-flight signal of mass 24 giving the intensity of magnesium-doped droplets.

Even larger for the droplets in the initially doped pulse. This demonstrates that doping is very efficient and even clusters or complexes of molecules can be isolated in helium nanodroplets by this means. Furthermore, when choosing high laser pulse energies, it may already be that a significant amount of clusters form before pickup during cooling within the gas of helium atoms and attach to the droplets afterwards. In this way the formation of selected conformers that have been observed upon formation in helium droplets\textsuperscript{26–28} can be circumvented.

Dip B indicates that the ablation of atoms in the source chamber leads to a decrease in the flux of doped droplets. The lower intensity measured can be caused by several reasons: on one hand, scattering of particles with high kinetic energies leads to destruction of the droplets. In this way a lower number can be doped in the oven afterwards. The higher the kinetic energy of an ablated atom, the faster the atom interacts with the droplet beam. In this way dip B is shifted towards earlier times compared to peak A. On the other hand, droplets can be doped with charged particles from the ionizing plasma. A charged droplet cannot reach the ionizing surface of the LT detector because of the electric fields. Hence, the appearance of charged droplets reduces the intensity plotted in Fig. 2. Finally, ion-seeded cluster growth (discussed below) increases the droplet size but reduces the total number of droplets.

Peak C corresponds to velocities of 1500–8000 m/s which is much more than the droplet beam velocity but complies with typical particle velocities from an ablation plasma. Hence we interpret peak C as ablated atoms which are scattered in the beam direction and enter the detector without being picked up by a droplet. We only observe these atoms at power densities beyond 0.1 GW/cm$^2$. Apparently, high densities of ablated atoms are required for this process to occur.

To analyze the width of the observed features, peaks A and B can be separated by using mass selection in the quadrupole mass spectrometer. In Fig. 3 the time-of-flight intensities are plotted when ablating magnesium. The lower trace
is recorded on the atomic mass of magnesium (24 amu) and gives the number of magnesium atoms carried by helium droplets. The detection of bare dopant masses is a well known feature of this detection method: decomposition of droplets upon electron impact is caused by the relatively large electron energies. A reliable measure for the droplet beam intensity is the signal for mass 8 amu (Ref. 40) (upper trace in Fig. 3). In this way dip B comes out separately. We observe typical depletion of about 20%. However, depending on the laser power and focusing conditions, complete depletion of the droplet beam can be achieved. The width of the observed features is comprised of different origins: (a) the velocity spread of the helium beam (0.5%–1%)29 and the corresponding time-of-flight broadening lead to a width at detector distance of ≈30 μs. (b) The length of the section of the helium droplet beam that is able to capture ablated atoms defines an initial width of the doped pulse. The region is limited by the nozzle skimmer distance, and corresponds to 50 μs of flight time. (c) The duration of ablating particles is mainly determined by the laser pulse width and because of that is negligible. However, by varying the focusing conditions, widths from 50 to 120 μs have been recorded for magnesium atoms. This means that the droplets can pick up atoms for quite a long time and that this duration significantly contributes to the widths observed. In order for that to happen, the ablated atoms must undergo many scattering processes before being picked up. The fact that the scattering and deceleration of captured atoms take a significant amount of time can already be deduced from the shift of features A and B. (d) The results using LT surface ionization (Fig. 2) are additionally broadened by the response time of the detector of ≈50 μs.

The absolute positions of the peaks depend on the velocity of the droplet beam and can be varied by changing the helium expansion conditions, i.e., the nozzle temperature $T_0$ and the stagnation pressure $P_0$. In Fig. 4 the measured time of flight (position of the maximum) is plotted versus the nozzle temperature. Comparison with the calculated times assuming the theoretical terminal velocity of a supersonic expansion ($v = \sqrt{5kT_0/m_\text{He}}$)30 confirms that doped atoms are carried by the droplets without significantly deteriorating the properties of the droplet beam. In Fig. 5 the dependence on the helium stagnation pressure is shown. At higher pressures more energy is put into the forward direction of the expanding atoms. We also got similar curves for the surface ionization signals of ablated sodium as well as for the depletion signals. Hence the features observed can unambiguously be correlated with the droplet beam.

B. Doping ions

The generation of a plasma by focusing the laser onto the target material leads inevitably to a certain degree of ionization of the evaporated material. Ions produced in this way have been utilized in several experiments for, e.g., the generation of beams of metal cluster ions.20,21 The isolation of ions in helium droplets has several interesting perspectives. Charged atoms such as, e.g., alkaline earth atoms, are interesting with respect to interaction with a helium environment.31,32 In particular, the formation of “bubble” and “snowball” structures has been an issue.33 On the other hand, the isolation of cluster ions as well as of molecular ions opens up the possibility of studying these entities at millikelvin temperatures.

We probed the abundance of helium droplets loaded with ions in a time-of-flight detector which extracts ions perpendicular to the droplet beam in a pulsed electric field (cf. Fig. 1). Since we observed features having different beam velocities for the neutral metals (peaks A and C in Fig. 2), ions can also be detected at different arrival times in the detector. Again, we observe at early times ions of evaporated material which directly enter the detection region without being attached to droplets. In the case of magnesium as the target material, we observe only bare Mg monomer ions in the time-of-flight spectra. By shifting the extraction pulse farther delayed from the laser pulse, positively charged helium drop-
lets can be identified in the time-of-flight spectra. We observe broad, asymmetric mass distributions. In Fig. 6 measured curves for three different nozzle temperatures are shown. The resolution of the detector is $m/\Delta m = 9.5$ and the error in the absolute mass scale is less than 10%. The time-of-flight data are converted into units of the number of helium atoms. These can be compared with mass distributions of helium droplets obtained by other techniques. One should note here that the size distribution of droplet beams is a crucial property in many experiments. The determination of cross sections$^{17}$ or interpretations of relaxation mechanisms and absorption line broadening$^{34}$ are only two examples where absolute cluster sizes are a prerequisite for interpretation of the data. In general the problem of measuring size distributions is that all standard mass selection techniques (e.g., time of flight, quadrupole filters, magnetic sector fields) require charged particles. On the other hand, a technique for charging helium droplets without severe fragmentation is hard to realize. Toennies and co-workers looked for alternative techniques to determine droplet size distributions.$^{35,36}$ For example, a scattering deflection method was applied which, in turn, is for other reasons experimentally challenging. The results are up to now the important reference for all experimental studies. The distributions obtained follow log–normal functions and the corresponding mean cluster sizes associated with defined expansion parameters ($P_0, \bar{T}_0$) are given. For the conditions in our measurements mean cluster sizes of 4000, 6000 and 10 000 are deduced for nozzle temperatures of 23, 21 and 19.6 K, respectively.$^{36}$

In contrast to that, our measured sizes are much larger. Included in Fig. 6 are log–normal fits with the parameters given in Table I. Mean sizes up to almost 50 000 helium atoms per droplet are deduced from our measurements. At first glance larger size distributions are surprising because a disturbance from the interaction with high energy atoms is expected to decrease droplet sizes by evaporative dissipation of the energy. One reason might be that only the larger droplets are able to pick up ions. We do not think this applies because it would mean that the cooling process determines the cutoff at small cluster sizes. Then one would expect this cutoff to be at small sizes (less than 1000) and independent of the nozzle temperature, in contrast to the results shown here. Moreover, in general these effects would not lead to log–normal distributions. It may well be that the measured higher intensities in the tail of the distributions can be explained in this way. The only way left to increase the droplets size is a mechanism where the ions serve as seeds to enhance condensation. Since condensation occurs only within a few nozzle diameters behind the nozzle, one would, in the first place, not favor doping by this means. Providing the former determination of neutral helium cluster sizes to be correct, our measurements show that laser-evaporated ions substantially assist the condensation of large helium droplets.

The absolute number of ion-doped helium droplets is much stronger depending on the expansion conditions compared to the formation of neutral clusters (Fig. 7). We find a roughly exponential increase in the number of charged droplets decreasing the nozzle temperature. The number of droplets decreasing the nozzle temperature. The number of droplets

![Image](https://example.com/figure6.png)

**FIG. 6.** Size distributions of ion-doped helium droplets deduced from time-of-flight spectra upon pulsed extraction perpendicular to the droplet beam ($T_0 = 19$ K, $P_0 = 80$ bar). The gray lines are log–normal distributions fitted to the measured data. The parameters are given in Table I.

![Image](https://example.com/figure7.png)

**FIG. 7.** Comparison of the nozzle temperature dependence of the yield of doped droplets. The number of charged droplets increases almost exponentially with a decrease in the nozzle temperature. The Mg and Na curves are normalized to fit the high temperature region of the ionic curve. DLE was recorded at $P_0 = 70$ bar, the sodium curve at $P_0 = 50$ bar.

<table>
<thead>
<tr>
<th>$T_0$ (K)</th>
<th>$\mu$</th>
<th>$\sigma$</th>
<th>$\bar{N}$</th>
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<td>19.6</td>
<td>10.692</td>
<td>0.5</td>
<td>47 700</td>
</tr>
<tr>
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<td>10.463</td>
<td>0.4</td>
<td>37 900</td>
</tr>
<tr>
<td>23</td>
<td>10.146</td>
<td>0.4</td>
<td>27 600</td>
</tr>
</tbody>
</table>

**TABLE I.** Parameters $\sigma$, $\mu$ and the mean size $\bar{N}$ of the corresponding fits in Fig. 6 using the log–normal distribution: $P(N) = 1/(\sqrt{2\pi}\sigma N) e^{-(\ln N - \mu)^2/2\sigma^2}$. A total error of 10% is estimated for $\bar{N}$, primarily due to experimental uncertainties.
lets doped with neutral atoms from the DLE process as well as “conventionally” doped droplets exhibit a plateau or even a maximum slightly below 20 K depending on the stagnation pressure applied. The strong increase of the ion signal can be rationalized as follows: the helium throughput increases at lower nozzle temperatures. In this way more helium atoms are present for precooling the hot atoms from the plasma. Since an enhanced increase is not present for the neutral atoms from the laser plasma, either the kinetic energy of the ions is much higher, or the “seeding” mechanism has a strong dependence on the number of available helium atoms.

As far as the absolute number of ion-doped droplets is concerned, Fig. 7 gives the number of registered charged droplets per laser shot. At a temperature of 19 K the amount is approximately 1% of the number of droplets carrying neutral atoms. However, focusing conditions as well as laser pulse energy substantially alter the yield of picked up ionized atoms. Since an enhanced increase is not present for the neutral atoms, no reason has come up to indicate that the diversity of probes cannot be combined with the helium isolation technique. Hence, many existing studies will be available at temperatures below 1 K.

ACKNOWLEDGMENTS

The first measurements were performed within a series of experiments at the Max-Born-Institute (Berlin) and the authors thank C. P. Schulz for his support and for the YAG laser. Financial support by the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

38 Here we assume that each evaporated helium atom takes away its binding energy of 4.9 cm$^{-1}$ (after Ref. 37).
39 Tenfold energy results in double yield for doping.
40 The He$^+$ is a pronounced fragment ion formed upon electron impact ionization of a helium droplet.