Effect of kinetic energy on the doping efficiency of cesium cations into superfluid helium droplets

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We present an experimental investigation of the effect of kinetic energy on the ion doping efficiency of superfluid helium droplets using cesium cations from a thermionic emission source. The kinetic energy of Cs^+ is controlled by the bias voltage of a collection grid collinearly arranged with the droplet beam. Efficient doping from ions with kinetic energies from 20 eV up to 480 V has been observed in different sized helium droplets. The relative ion doping efficiency is determined by both the kinetic energy of the ions and the average size of the droplet beam. At a fixed source temperature, the number of doped droplets increases with increasing grid voltage, while the relative ion doping efficiency decreases. This result implies that not all ions are captured upon encountering with a sufficiently large droplet, a deviation from the near unity doping efficiency for closed shell neutral molecules. We propose that this drop in ion doping efficiency with kinetic energy is related to the limited deceleration rate inside a helium droplet. When the source temperature changes from 14 K to 17 K, the relative ion doping efficiency decreases rapidly, perhaps due to the lack of viable sized droplets. The size distribution of the Cs^+ -doped droplet beam can be measured by deflection and by energy filtering. The observed doped droplet size is about 5×10^6 helium atoms when the source temperature is between 14 K and 17 K. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4927471>]

INTRODUCTION

Doping of superfluid helium droplets offers the advantage of investigating isolated particles under cryogenic temperatures in a non-perturbing medium.^{1–6} The technology of doping neutral particles has evolved from volatile molecules to thermally labile biomolecules to radicals and clusters.^{7–13} The superfluid environment and the unique properties of the quantum fluid have also inspired generation and investigation of esoteric species.^{14–24} Even the possibility of producing nanomaterials with controlled properties in superfluid helium droplets has been explored.^{15,17,21,25} For example, in the mass spectrum of metal vapor-doped droplets, silver clusters are observed to contain up to 100 Ag atoms,^{15,17} and magnesium clusters can even reach several thousands of atoms.¹⁶ The photoabsorption of Ag clusters in helium droplets shows that the transition from compact to multicenter aggregates increases with the growth of droplet sizes.²¹ In the work of Gomez *et al.*²² silver clusters desolvated from helium droplets have been captured and imaged via electron microscopy. The authors have observed evidence of single and multiple vortices longer than 300 nm. To explore the dynamic properties of individual droplets, recently, Gomez *et al.*²³ have further recorded Bragg diffractions of neat and xenon-doped droplets via x-ray scattering from a free-electron laser.

Efforts have also been devoted in doping cations in helium droplets, partly motivated by studies of helium snowballs.^{26–36} Direct ionization of helium atoms or embedded

neutral molecules has proven the most straightforward approach.^{16,28,29,32,36–38} Schöbel *et al.*³⁷ have reported the mass spectrometry of pure helium droplets and droplets doped with krypton using electron impact ionization. Döppner *et al.*³² have ionized metal clusters embedded in helium droplets using a femtosecond laser and studied the size distribution of metal ion-helium clusters. For Mg^+He_N , the first solvation shell closes at $N = 19$ – 20 , and for Ag^+He_N , $N = 10$ and 12 . Using synchrotron radiation, Kim *et al.*²⁸ have reported an indirect mechanism of dopant ionization via excitation transfer or charge transfer from the surrounding helium atoms. Subsequently, the same group²⁹ has reported efficient cooling of fragments from photoionization and fragmentation of SF_6 in helium droplets. Following the lead of Ghazarian, Eloranta, and Apkarian in using laser ablation in the presence of cold helium vapor for injection of molecular species into a liquid helium beam,³⁹ Claas, Mende, and Stienkemeier have reported doping of alkali and alkaline metal ions from the plasma produced by a focused laser beam on a rotating and translating metal rod.⁴⁰ Since the ablation spot is close to the expansion and nucleation region of the droplet beam, the authors have attributed the unusually large size of the doped droplets and the temperature dependence of the droplet size to the nucleation effect of the ablated atomic and ionic species. Direct doping of cations in helium droplets has been reported by Bierau *et al.*⁴¹ using an electrospray ionization (ESI) source. Biological ions stored in a quadrupole ion trap have been doped in helium droplets when a pulsed droplet beam traverses the trap. Only heavy doped droplets with high kinetic energies can escape the trap to hit the detector. In the work of Falconer *et al.*,¹¹ sodium cations from a thermionic emission source have been

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introduced into the path of a helium droplet beam via an electric field, and $[\text{Na}(\text{H}_2\text{O})_n]^+$ cluster-doped helium droplets have been confirmed.

Most results of ion-doped droplets have focused on the size distribution of the ion-doped droplet beam. The deflection and acceleration experiments of Bierau *et al.*⁴¹ have demonstrated that doped droplets containing the protein cytochrome C (CytC) have on average 10^{12} helium atoms per ion, and when the charge of CytC shifts from +9 to +17, the droplet size slightly increases. In the work of Falconer *et al.*,¹¹ although no direct measurement of doped droplets has been observed, based on simulation and mass spectrometry, the authors have estimated a mean size of 3×10^5 helium atoms per droplet.

An open question related to doping of charged species in superfluid helium droplets is the effect of kinetic energy on the ion doping efficiency. Superfluid helium droplets have been considered scavengers for neutral closed shell species with a pickup efficiency of near unity.⁴² In many experiments involving doping of neutral molecules, the thermal energy of the gaseous molecules is below 0.1 eV with a velocity less than 500 m/s. Ions on the other hand typically have kinetic energies over 10 eV with velocities over 5000 m/s, and many head-on collisions with helium atoms inside a droplet are probably necessary to decelerate and stall the fast moving ions. In this work, we present our investigation of the effect of kinetic energy on the ion doping efficiency of superfluid helium droplets. We use a thermionic source of cesium cations Cs^+ as dopant because of its high ion abundance and its ease in operation; both factors contribute to the reproducibility and high signal-to-noise (S/N) ratios of the experimental result. We introduce a relative ion doping efficiency to reveal the anti-correlation between the kinetic energy of bare ions and the number of doped droplets, and we offer a tentative model for the observed effect. Within the temperature range of 14 K to 17 K (limited by our experimental apparatus), we have also discovered that the final size distribution of the doped droplets is independent

of the source temperature, although the ion doping efficiency decreases with increasing source temperature.

EXPERIMENTAL SETUP

The experimental setup is shown in Fig. 1. Superfluid helium droplets were generated in the source chamber labeled A, and the droplet beam passed through the ion source region and arrived ultimately at a copper target detector. The droplet source chamber and the chamber for regions B and C were separated by a skimmer, while the two regions B and C were separated by a copper plate with a 1 cm central hole. The droplet source chamber was pumped by two diffusion pumps (Varian VHS-6 and Edwards Diffstack 160 mm) and was usually at $4 \times 10^{-7}/4 \times 10^{-6}$ Torr when the pulsed valve was off/on. The ion source and analysis chamber (regions B and C) were pumped by a turbo molecular pump (Varian V551) and were typically at $7 \times 10^{-7}/4 \times 10^{-6}$ Torr when the pulsed valve was off/on.

We used a pulsed valve (Parker Hannifin Corp, Series 99) to produce superfluid helium droplets by supersonic expansion of ultrapure (99.999%) helium at about 30–50 bars into vacuum. The pulsed valve had a homemade nozzle with a diameter of 500 μm . It operated at 10 Hz with a duration of 130–145 μs powered by its own driver (Parker Hannifin Corp, IOTA One). The nozzle was cooled by a closed-cycle helium cryocooler (APF cryogenics, HC-4 MK1), and it could be set at any temperature above 13 K. The helium droplet beam was further collimated by a 5 cm long skimmer of 2 mm in diameter (Beam Dynamics) located 12 cm downstream from the nozzle.

Cesium ions were produced by heating a tungsten filament coated with a zeolite paste as detailed by Draves *et al.*⁴³ The filament was a tungsten coil of 3.0 cm in length and 2.0 mm in diameter, and the wire itself was 0.25 mm in diameter. The coil was shaped into a semicircle surrounding the droplet beam, and its side view is shown in Fig. 1(I) and the end view

FIG. 1. Experimental setup. In part (I), (A) droplet source chamber: superfluid helium droplets were generated by a pulsed valve and collimated by a skimmer. (B) Doping region: cesium ions were produced from a thermionic emission source and were accumulated in the coil shaped grid to overlap with the droplet beam for doping. (C) Analysis region: a metal target was directly in-line with the droplet beam for detection of only charged (doped) droplets. We placed the ion source and the detector in two different positions (Position 1 and Position 2) to determine the velocity of the pure droplet beam. Light blue dots/drops represent pure helium droplets, dark purple dots represent cesium cation, and dark centered light blue drops represent doped droplets. Part (II) shows the end view of the ion source/doping region, part (III) shows a simulated trajectory of one ion emitted from the top of the filament traversing the doping region multiple times, and part (IV) is the side view of the same trajectory. The starting position of the ion is noted by a dark purple dot in part (III).

in Fig. 1(II). For illustration, light blue dots/drops represent pure helium droplets, dark purple dots represent cesium cation, and dark centered light blue drops represent doped droplets. Under normal working conditions, a current of about 2.8 A was passed through the filament, and the total emission current was 2.8 μ A. Concentric with the filament on the end view (Fig. 1(II)) is the ion collector, a copper grid (referred to as the grid in the following) of 2 cm long and 1 cm in diameter, and its side view is shown in Fig. 1(I). The grid was biased negative relative to the filament, thereby facilitating the oscillation of cesium ions through the space inside the grid at a constant and defined kinetic energy. In Fig. 1(III), a simulated trajectory of one ion emitted from the top of the filament (the initial position of the emitted ion is indicated by a dark purple dot) is shown viewed from the end, and in Fig. 1(IV), the same trajectory is shown from the side. The grid was connected to an operational amplifier and a megaohm resistor, which converted the ion current into a voltage signal. We could treat this current to be representative of the total number of available ions for doping, although the true number of ions inside the grid was unknown. Both the grid and the filament could be independently biased, and the current on the grid increased with the bias voltage on the grid. Typically when the grid was at -100 V and the filament was at 10 V, the voltage signal was about 1.5 V, corresponding to an ion count of 10^{13} ions/s on the grid.

The copper target detector measuring 4 mm $\times$ 10 mm was not biased intentionally and was directly attached to an operational amplifier and a gigaohm resistor, converting a single charge into a voltage pulse. The copper target was only sensitive to charged species; hence, neutral undoped droplets generated no detectable signal. The ion source and the detector could be placed in two different positions as labeled “Position 1” and “Position 2” in the figure, so the group velocity of the droplet beam could be determined by monitoring the different arrival times of the doped droplets on the target. In the analysis region C, a set of electrodes could be used to deflect the charged particles away from the detector, with the intention of resolving the kinetic energy of the charged species. For this purpose, the copper target was placed at Position 2 while the ion source remained at Position 1.

EXPERIMENTAL RESULTS

Doping of cesium ions into helium droplets

Doping of cesium ions into helium droplets was confirmed by varying the experimental conditions. When only the filament and the grid were in operational conditions, no ions could be detected on the copper target. When the pulsed valve was turned on but was kept at room temperature, there were still no ions arriving at the detector. Only when we cooled down the nozzle below 20 K, could there be any observable ion signal. The ion signal disappeared when the ion source was turned off.

Figure 2 shows the time profile of the detected doped droplet signal under different nozzle temperatures recorded at Position 2 in Fig. 1. Both the magnitude and timing of the ion signal depend on the temperature of the droplet source. From

FIG. 2. Arrival times of doped helium droplets with varying nozzle temperatures, from 13.2 K to 17.0 K. With increasing nozzle temperature, the ion signal decreases and shifts to an earlier time. Shoulder peaks are visible under all different nozzle temperatures; they were results of the rebound of the pulsed valve. The ion detector was in Position 2 during this experiment.

13.2 K to 17.0 K, the arrival time of the ion signal shifts by 0.24 ms and the total signal decreases by over 50%.

Without any acceleration field along the flight path, the arrival time of the doped droplets was determined by the group velocity of the neutral droplet beam. Although the response time of our gigaohm resistor was limited, with sufficient distance between the two measuring points (Positions 1 and 2 in Fig. 1), we could still use the onset of the ion signal to measure the velocity of the droplet beam. In Fig. 1, Position 1 was 37 cm away from the pulsed valve, and Position 2 was 74 cm away from the pulsed valve. From the difference in the arrival time between the two positions, we determined that the droplet speed was 371 m/s at 13.2 K and 422 m/s at 17.0 K. In comparison, the theoretical speed of an ideal helium gas from a supersonic expansion should be 375 m/s at 13.2 K and 419 m/s at 17.0 K, in general agreement with our measurements.

Effects of fringe fields and space charges

Fig. 3 shows the total number of ion-doped droplets and the total number of ions hitting the grid at different grid voltages. In calculating the number of ions hitting the grid, we took the duty cycle of the droplet beam into consideration, so the DC ion current on the grid was chopped to 140 μ s to match the duration of the pure droplet beam. We calculated the total number of ion-doped droplets by changing the voltage signal from Fig. 2 to a current through the gigaohm resistor and then integrating the peak area for the number of charges. While the number of bare ions hitting the grid grows with the grid voltage following a power law-like behavior, the number of doped droplets also increases but with a clear “bend”—an abrupt change in the rate of increase—when the grid voltage reaches -150 V. Fig. 3 also shows that with increasing source temperature, the number of doped droplets also drops. At 16 K when the grid voltage is -100 V, the number of doped droplets is less than half of that at 14 K.

The bias on the grid in the ion source affected not only the number and movement of bare ions, but also those of doped

FIG. 3. Dependence of both the number of doped droplets (left axis, filled symbols) and the number of ions hitting the grid (right axis, open squares) on the grid voltage at different source temperatures.

droplets, both as a trapping field and in terms of fringe fields at the exit of the grid downstream from the doping region. The group velocity of the pure droplet beam was 388 m/s at a source temperature of 14 K, and at a grid voltage of -180 V, a doped droplet had to consist of at least 5.7×10^4 helium atoms to have enough kinetic energy to escape from the negative trapping field of the grid. Downstream, some escaped doped droplets would be affected by the fringe field of the grid thereby veering too far off-axis along the path to the target. Using Lorentz-EM (Integrated Engineering Software, Winnipeg, Manitoba, Canada), a software package specially designed for magnetic analysis and for analysis of charged particle trajectories in the presence of electric and magnetic fields, we simulated this fringe effect and obtained a cutoff size of $\sim 10^5$ helium atoms per droplet, below which a doped droplet would fail to arrive at the target. Experimentally, the actual cutoff size was probably even bigger, at $\sim 10^6$ atoms/droplet, because of unaccounted loss mechanisms in the simulation, such as the non-ideal vacuum level and stray fields due to other electrodes or even turbomolecular pumps. As the grid voltage increases, the cutoff size also increases. In the meantime, from Fig. 3, the number of bare ions traveling into the grid seems to also increase. The increase in the number of doped droplets, however, slows down at the “bend” when the grid voltage is more than -150 V.

One possible explanation of the “bend,” i.e., the change in slope for the doped droplets at -150 V, is the space charge limit. In Fig. 3, the number of ions hitting the grid is on the order of 10^{10} , and given the fact that the volume inside the grid is a few cubic centimeters, this value is way above the space charge limit of $10^7/\text{cm}^3$.⁴⁴ The actual number of ions inside the grid should then be much smaller, at most on the order of 10^7 . Once the space charge limit is reached, further increase in the negative bias of the grid has the effect of expanding the retention region, determined by the negative potential of the grid, further out to the vacuum chamber (fixed at ground potential). The ultimate effect is therefore an increase in the volume of the “ion trap,” determined by the dimension of the grid and its extended field upstream and downstream along the droplet

beam. However, this effect should be rather limited given the available physical space for expansion, so the increase in the number of bare ions for doping with increasingly more negative bias on the grid would be at a much lower rate after the system reaches the space charge limit. On the other hand, the cutoff size will increase with increasing bias, preventing small doped droplets from reaching the detector. The change in the number of doped droplets is then determined by the balanced effect of the cutoff size and the doping volume. The “bend” in Fig. 3 could be the point where the space charge limit is reached, and the slow rise after -150 V is the predominant effect of the increasing doping volume with increasing grid bias.

If we assume that the total number of bare ions in the doping region is limited by the space charge limit to 10^7 ions at a grid bias of -150 V, the absolute ion doping efficiency, defined as the ratio of the number of ion-doped droplets and the number of total ions available for doping, should be on the order of 5% at a source temperature of 14 K when the number of doped droplets is 5×10^4 . On the other hand, if the “bend” is not representative of the space charge limit, then the actual ion doping efficiency should be higher since the number of ions inside the doping region is smaller.

Droplet size distribution

Deflector test

To determine the size distribution of the doped droplets, we first used a set of deflectors to steer the doped droplet beam away from the detector, similar to the method of Bierau *et al.*⁴¹ As the voltage on the deflector increases, small doped droplets are driven away from the detector, thus a correlation between the detected doped droplets and a lower size limit can be established at each deflection voltage. In Fig. 1, the deflector electrodes were 40 mm long and were separated by 40 mm. These electrodes were positioned 38 mm downstream from the ion source, and the detector (4 mm along the deflection direction) was located 60 mm downstream from the deflectors. These geometric parameters and the voltage on the deflector determine a lower size limit for the detected doped droplets. During the experiment, one of the deflector electrodes was grounded, while the other was biased from -2200 V to 2200 V. The left of Fig. 4 shows the number of doped droplets arriving at the target under different deflection voltages (bottom axis), and the top axis shows the corresponding lower size limit for the detected droplets. At -300 V, the signal drops to 54% of that without the deflection voltage. The corresponding lower size limit for the doped droplets arriving at the detector is 4.3×10^6 helium/droplet.

The source temperature of the pulsed valve determines the average size of the droplet beam, which in turn affects the doping efficiency. After doping, we anticipate that perhaps the size distribution of the resulting doped droplet should also reflect this difference. To emphasize the size distribution at different source temperatures, on the right of Fig. 4, we plotted the normalized ion signal by setting the maximum ion intensity under a fixed nozzle temperature to unity. Surprisingly, all traces overlap. We therefore conclude that within the

FIG. 4. Deflection of doped droplets. Left panel: absolute number of doped droplets arriving at the target under different deflection voltages. Right panel: normalized ion signal by setting the maximum ion intensity under a fixed nozzle temperature to unity. The black dashed line is the integrated result from a log-normal distribution of pure droplets at 14 K using parameters obtained from Fig. 5.

temperature range of 14 and 17 K, the doped droplets had a similar size distribution, independent of the initial nozzle temperature.

According to Ref. 45, the size distribution from a continuous superfluid helium droplet source can be modeled using a log-normal function when the nozzle temperature is higher than 14 K,

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

where $P_N(N)$ is the probability of a droplet consisting of N helium atoms, and the parameters σ and μ are the standard deviation and the mean of $\ln N$. The size distribution of the doped droplets could be obtained by differentiating the number of doped droplets arriving at the detector by the corresponding minimum droplet size (the top axis of Fig. 4). In Fig. 5, black squares represent the resulting differentiation from the experimental data at 14 K (Fig. 4), and the continuous trace is a log-normal fit to the experimental data. The mean size from this fitting was 7×10^6 helium/droplet. Similar treatments of

FIG. 5. Size distribution of doped droplets at a source temperature of 14 K.

data from other source temperatures also resulted in similar size distributions and mean sizes. The resulting values of σ and μ were about 0.77 and 15.45. These values were then used to calculate the number of doped droplets at each deflection voltage by integrating Eq. (1) from the lower size limit determined from the experimental geometry to infinity, and the result is shown by the dashed line of Fig. 4 labeled as “Int. 14 K.” This trace overlaps with our experimental data. Although it is known that in the range of the current source temperatures (≥ 14 K), neutral helium droplets follow a log-normal function, and apparently, the doping process did not alter this size distribution substantially. However, the consistency in size and distribution within our temperature range also implies that the size distribution of the doped droplets was insensitive to the initial size distribution of the neutral droplet beam. This could be due to the small limited temperature range of our cryostat, and the fact that we were only fitting the tail part of a log-normal distribution. In the work of Filsinger *et al.*,⁴⁶ a similar conclusion was obtained within the temperature range of 14 K to 18 K.

Energy filter experiment

Another possible approach to determine the size distribution of doped droplets is to introduce an energy filter using a biased mesh. If the doped droplets move at a constant group velocity, different sizes will have different kinetic energies, and only ions with sufficient kinetic energies can pass through the biased retardation electrode. For this purpose, we replaced the deflector electrodes with a planar electrode that had a circular hole of 38 mm in diameter. The hole was covered with a fine mesh of 50×50 mesh plain and 0.025 mm in wire diameter. To further shield the copper target from the field of the retardation electrode, another coarse mesh of 16×16 mesh plain and 0.25 mm in wire diameter was placed 2 mm in front of the copper target. The planar electrode and detector were positioned 142 cm downstream from the ion source.

Fig. 6 shows the variation of the ion signal as a function of the voltage on the retardation electrode when the source

FIG. 6. Doped droplets passing through a retardation electrode. The trace with open circles was obtained with a grid voltage of -200 V, and the trace with open squares was with a grid voltage of -100 V.

temperature was 14.5 K. We performed the experiment under two different voltages on the grid of the ion source, -200 V and -100 V, and in both cases, the trend was the same. The uncertainty of each data point is about 10%, so the “bend” in the experimental data at a retardation voltage of 1500 V when the grid voltage was -200 V is most likely due to a variation in the experimental condition. From Fig. 6, even when the retardation voltage reaches 3500 V, there are still more than 28% of the doped droplets reaching the target, and the corresponding droplet size is 1.1×10^6 helium/droplet.

A mean size of doped droplets can be obtained from Fig. 6. When the grid in the ion source was biased at -200 V, the ion signal dropped to 54% of its peak value at a retardation voltage of 1500 V. Assuming a group velocity of 390 m/s for each droplet, each helium atom in the droplet has a kinetic energy of 3.18 meV, and to obtain a total kinetic energy of 1500 V, the corresponding size of the doped droplet is 4.4×10^5 helium/droplet. Thus, we conclude that about 54% of the doped droplets were larger than 4.4×10^5 helium/droplet.

The average size of doped droplets from this retardation experiment was about one tenth of that from the deflector experiment (Fig. 4). One factor for this discrepancy could be the position of the detector: in this experiment, the detector was placed 68 cm further downstream from the ion source. Continued evaporation due to collisions with ambient molecules in the flight path would result in a decreased droplet size. At a vacuum level of 4×10^{-6} Torr and a source temperature of 14 K, the average radius of a droplet was about 17 nm, and the average collision rate was 3×10^5 /s. If each collision consumed about 42 helium atoms by evaporation, the total loss of helium atoms after a path length of 68 cm was 2.2×10^4 . This value was too small to account for the one order of magnitude decrease in droplet size from this energy filter experiment. Another possibility was the additional collisions between the small doped droplets stopped in the path of the larger droplets at the retardation electrode (the fine mesh). Since this effect was size dependent, particularly detrimental to large sized droplets, it could play a significant role in reducing the average size of the droplet beam from this retardation experiment.

DISCUSSION

Size distribution of doped droplets

The size distribution of ion-doped droplets has been measured by Bierau *et al.*⁴¹ in 2010. The authors used a pulsed helium droplet beam to catch a protein cytochrome C in different charge states and singly charged protonated phenylalanine (Phe) produced by electrospray ionization. The ions were trapped in a linear hexapole ion trap coaxial with the droplet beam. The authors reported 10^4 ion-doped droplets per pulse with a duration of 200 μ s. Using electrostatic deflection, they fitted a log-normal distribution for the resulting doped droplets, with mean sizes 10^{12} helium atoms for CytC +17 and 10^{10} for Phe. These unusually large sizes, compared with those from Slipchenko *et al.*,⁴⁷ were attributed to the large nozzle diameter of 800 μ m of the pulsed valve. Subsequently, the group replaced the pulsed valve with a different model and measured the size distribution of hemin⁺-doped droplets

via an acceleration experiment.⁴⁶ The resulting median size of the doped droplet was reported to range from 1.6×10^6 to 8.3×10^4 helium atoms when the source temperature was varied from 6 K to 18 K.

Falconer *et al.*¹¹ employed a different approach to dope cations into superfluid helium droplets, although no direct characterization of the size distribution of the doped droplets was reported. After traversing a pickup chamber filled with sodium cations generated from a thermionic source, a droplet would pick up a Na⁺ ion and several neutral H₂O molecules to form a $[\text{Na}(\text{H}_2\text{O})_n]^+$ cluster inside. The doped droplet was desolvated along the flight path before the bare cation was deflected into a mass spectrometer. Based on the mass distribution of $[\text{Na}(\text{H}_2\text{O})_n]^+$ and pickup statistics, the authors derived a mean droplet size by fitting the probability curve using a log-normal and linear-exponential distribution function. At 13 K, the resulting mean droplet size was about 3×10^5 helium atoms. They also pointed out that based on their simulation, only doped droplets with greater than 10^6 helium atoms would be able to escape the potential well of the grid at -200 V. This cutoff size was one order of magnitude bigger than the mean droplet size, so the explanation was that only the tail of the droplet distribution was being sampled in the experiment.

Using laser vaporization of alkali and alkaline metal rods near a cryogenic nozzle, Claas, Mende, and Stienkemeier have observed ion-doped droplets due to surface plasma formation.⁴⁰ However, the authors proposed that the formation mechanism of ion-doped droplets was related more to the seeding of ions as a nucleation center during condensation of helium atoms near the exit of the nozzle than to the migration of ions into already formed droplets. For this reason, the authors observed a variation in droplet size when the source temperature changed from 19.6 K to 23 K. Moreover, the observed size of nearly 5×10^4 atoms/droplet at a source temperature of 19.6 K was substantially larger than the corresponding theoretical value.

Our droplet size is in general agreement with those from Bierau *et al.* and Falconer *et al.*^{11,46} Limited by the capacity of our cryostat, we can only vary the source temperature in the range of 14 K to 17 K, and our resulting doped droplet sizes are similar in all cases, with an average value of 7×10^6 helium atoms. The discrepancy of our value from that of Claas, Mende, and Stienkemeier can be attributed to the different mechanisms of droplet formation.⁴⁰ On the other hand, our observation of the decrease of doped droplets with increasing nozzle temperature as shown in Fig. 3 agrees with that of Claas, Mende, and Stienkemeier. Our design of the ion source is the same as that of Falconer *et al.*,¹¹ but the additional grid in the doping region has been observed to triple the doping signal. More importantly, the bias on the grid offers control over the kinetic energy of the incident ions, which allows observation of the effect of kinetic energy on the ion doping efficiency.

Relative ion doping efficiency

To determine the absolute ion doping efficiency, we need to take the ratio of the total number of doped droplets and the

total number of ions in the doping region. The absolute number of doped droplets is affected by the temperature of the droplet source and by the grid voltage of the ion source. Without a bias voltage on the grid of the ion source, only thermal ions were present around the region of the filament, and no doping was observable when the source temperature of the droplet beam was above 14 K. As the bias on the grid increased, more ions were pulled into the region of the droplet for doping, and more doped droplets were observable. However, the number of ions in the doping region was limited by the space charge effect while the measured current on the grid was not.

To avoid the above difficulties, we define a relative ion doping efficiency by setting the ratio of doped droplets to the ions on the grid to unity at a kinetic energy (grid voltage) of -20 V and a source temperature of 14 K. This choice of the kinetic energy corresponds to the lowest bias when doped droplets were observable at all source temperatures between 14 K and 17 K. The left side of Fig. 7 shows the relative ion doping efficiency at different kinetic energies and different source temperatures. At a fixed source temperature, the size distribution of the droplet beam is fixed. With the increase in grid voltage, the absolute number of doped droplets increases, but the relative ion doping efficiency actually decreases. With the increase in source temperature, the droplet distribution shifts to smaller sizes, and the relative ion doping efficiency also decreases. However, if we renormalize the maximum of each trace, as shown on the right side of Fig. 7, all traces overlap. This result implies that lowering the source temperature uniformly increases the ion doping efficiency in the temperature range of 14 K and 17 K, with no effect on the final size distribution of the doped droplets.

The decrease in the relative ion doping efficiency from 14 K to 17 K can be explained from the following numerical analysis. The binding energy of each helium atom is about 5 cm^{-1} in a droplet. To cool down a single Cs^+ ion with a kinetic energy of 400 eV, it would take more than 10^6 helium atoms

with a minimum droplet radius of 20 nm. To further escape the potential well of the grid at -400 V, the cooled ion has to retain another 10^6 helium atoms (see discussions of Fig. 3). The total number of droplets in this size range from a pure droplet beam can be obtained by integrating Eq. (1) in the appropriate size range. If we assume the same gas flux, the theoretical number of droplets at 17 K is about 1.8 times of that at 14 K. This means that if all droplets larger than 10^6 have the same probability of doping, we should observe 1.8 times more doped droplets at 17 K than at 14 K. Even if we take into consideration the higher gas flux at lower nozzle temperatures, based on the ideal gas law, the $\sim 20\%$ increase in gas flux at 14 K can only reduce the ratio to 1.4. On the other hand, if we change the lower limit of integration from 10^6 to 10^7 , the calculation reveals that the total number of droplets for pickup at 17 K is only 1/4 of that at 14 K. This value agrees with our experimental observation where the number of doped droplets at 17 K is about 1/3 of that at 14 K. We thus conclude that the actual pickup cross section of a droplet is probably less than half ($10^{1/3}$) of its geometrical cross section, and that the lower relative ion doping efficiency at higher nozzle temperatures is most likely due to the lack of viable sized droplets.

Effect of kinetic energy on ion doping efficiency

The decrease in ion doping efficiency with increasing grid voltage shown in Fig. 7 demonstrates the adverse effect of kinetic energy of the bare ions for doping. However, the situation is complicated by the fact that bare ions can oscillate in and out of the grid during the doping process. In Fig. 1, the grid of the ion source attracts the emitted Cs^+ ions into the field free central region where the droplet beam traverses. Without collision with a droplet, a cation can pass through the grid and move towards the chamber wall before turning back. We have simulated this oscillatory motion under different grid voltages using Lorentz-EM, and parts (III) and (IV) in Fig. 1 show a typical trajectory of one ion emitted from the top of the filament. Within the duration of the droplet beam ($140\text{ }\mu\text{s}$), the number of round trips of a Cs^+ ion passing through the centre of the grid is 15, a value essentially independent of the grid voltage. Upon further inspection, we realize that higher energy ions are more prone to be affected by fringe fields because of their deeper penetration into the outside region of the grid. Even though they have a higher frequency of oscillation, their stable oscillatory periods are limited. We therefore conclude that the rapid decrease in the relative ion doping efficiency with grid voltage on the left of Fig. 7 is indeed the adverse effect of kinetic energy.

The decrease in ion doping efficiency with increasing kinetic energy is a clear indication that the capture rate of cations upon collision with a sufficiently large helium droplet can be much lower than unity. If we assume that the “bend” in Fig. 3 at a bias of -150 V is related to the space charge effect, we could ignore the drop in the ion doping efficiency beyond -150 V, because the number of available ions for doping remains more or less constant instead of increasing as shown in Fig. 3. However, a clear drop in doping efficiency between -20 V and -150 V is still evident. When the kinetic energy varies from 20 eV to 100 eV, the velocity of the cesium

FIG. 7. Relative ion doping efficiency at different kinetic energies and source temperatures. The left panel is normalized relative to the efficiency at a source temperature of 14 K and a kinetic energy of -20 V, and the right panel is normalized for each source temperature. The solid line on the left panel is a fitting result assuming an inverse relation between the ion doping efficiency and the energy of the incident ions (Eq. (2)).

ions varies from 5000 m/s to 10 000 m/s, and the ion doping efficiency drops by 60%.

A detailed modeling of the ion doping efficiency is beyond the scope of our current work. However, a crude analysis of the situation might shed some light on the experimental observation. When an approaching ion has a sufficiently high velocity, its trajectory can be considered ballistic, and the charge-induced dipole interaction can be ignored at first. The helium atoms inside the droplet can be considered stationary in a lattice separated by an interatomic distance of 3.5 Å. In a head-on collision between a cesium ion (atomic mass = 133) and a free helium atom, the Cs⁺ loses 6% of its velocity. It thus takes nearly 40 such collisions to reduce the velocity of a Cs⁺ from 5000 to 500 m/s—a velocity in the range of thermal neutral molecules for doping. If the mean free path of a Cs⁺ is 3.5 Å, the overall time of the 40 collisions for speed reduction is about 13 ps and the overall distance travelled by the ion is 14 nm—almost halfway through a droplet of 10⁶ atoms. If side-on collisions are included and we average over the whole range of impact parameters, the effect of deceleration is even less effective: each collision results in a loss of energy (instead of velocity) of 6%. We therefore suspect that many fast ions can directly penetrate through the droplet simply because of the slow deceleration of helium atoms inside the droplet. Following this logic, the ion doping efficiency should be inversely proportional to the energy of the incident ions. The solid line in the left panel of Fig. 7 shows a fitting of all the data at 14 K using the function,

$$y = \frac{a}{E} + b, \quad (2)$$

where y represents the relative ion doping efficiency, E is the kinetic energy of the ions, and a and b are fitting coefficients. The model is only qualitatively acceptable, and other factors such as the space charge limit and the limited range of effective impact parameters are therefore not to be neglected.

Doping of closed shell neutral molecules has been considered to follow the Poisson distribution determined by the geometric cross sections of the helium droplets.⁴² However, studies on refractory metal atoms and the open shell oxygen molecules have revealed much lower pickup efficiencies or smaller pickup cross sections of helium droplets.^{48,49} Although atoms of refractory metals and alkali and alkaline metals are all open shell, refractory metals are typically heated to much higher temperatures thereby having much higher thermal energies for doping. We suspect that, perhaps, the high velocity of refractory metal atoms is partially responsible for the lower sticking probability with helium droplets. In several photofragmentation studies of doped droplets, the inability of the helium droplet in trapping the newly formed energetic fragments has also been documented and simulated using a ballistic model.^{50,51} Effect of the kinetic energy on the trapping efficiency has also been explored based on the same principle as our current work with ions. Different from our case of ion doping, on the other hand, neutral molecules have a much weaker interaction with the helium environment. It is therefore surprising that even with the strong ion-neutral interaction, the ballistic model is still qualitatively acceptable, under the current experimental conditions.

Our proposal of a fast ion directly passing through a droplet upon collision is unrelated to the superfluidity of the droplet and unrelated to the ion-neutral attraction inside the droplet. This crude model is therefore only applicable to fast ions; at some point along the deceleration path, the intermolecular interactions will become too important to ignore. Our current investigation is limited to kinetic energies above 20 eV due to practical issues with the thermionic source and the temperature range of our cryostat. In an ongoing experiment, we have used an electrospray ionization source to extend the investigation to essentially zero kinetic energies, and the results will be reported in the future. Unlike the doping process of neutral species, with special care in the experimental design, the doping process of ions has advantages in controlling the kinetic energy and in measuring the absolute number of ions and ion-doped droplets. Hence, studies of ion doping are of a particular value in revealing the detailed physics inside superfluid helium droplets.

CONCLUSIONS

We have characterized the cation doping process into superfluid helium droplets using cesium cations from a thermionic emission source. By performing two different types of measurements including deflection and energy filtering, the size distribution of Cs⁺-doped droplet beam was measured. Our experimental data could be fitted by a log-normal distribution, with a mean size of 5×10^6 helium atoms, more or less independent of the source temperature between 14 K and 17 K. At a fixed source temperature, we observed increased number of doped droplets with increasing grid voltage, but the rate of increase had a sudden drop at a grid voltage of −150 V, perhaps due to the space charge effect. The absolute ion doping efficiency was difficult to measure, but it should be on the order of 5% based on the space charge limit in the doping region and the number of doped droplets. When the source temperature was changed from 14 K to 17 K, a rapid decrease in the relative ion doping efficiency was observed, and the reason was attributed to the lack of viable sized droplets in the droplet beam. The relative ion doping efficiency decreased with increasing kinetic energies of the bare ions. We suggest that for fast moving ions, the ion doping efficiency was far from unity, and many ions simply penetrated through the droplet without being captured due to insufficient deceleration inside the droplet.

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