Effective doping of low energy ions into superfluid helium droplets

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We report a facile method of doping cations from an electrospray ionization (ESI) source into superfluid helium droplets. By decelerating and stopping the ion pulse of reserpine and substance P from an ESI source in the path of the droplet beam, about 10^4 ion-doped droplets (one ion per droplet) can be recorded, corresponding to a pickup efficiency of nearly 1 out of 1000 ions. We attribute the success of this simple approach to the long residence time of the cations in the droplet beam. The resulting size of the doped droplets, on the order of 10^5 /droplet, is measured using deflection and retardation methods. Our method does not require an ion trap in the doping region, which significantly simplifies the experimental setup and procedure for future spectroscopic and diffraction studies. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4928689>]

INTRODUCTION

The invention of the superfluid helium droplet beam has triggered an avalanche of research activities involving microscopic superfluidity, optical spectroscopy, and ultrafast dynamics at cryogenic temperatures.^{1–9} Unfortunately, the superior advantages of superfluid helium droplets cannot be easily transferred to the investigation of ions, both negatively and positively charged. A particular concern for cations is the possible strong matrix effect due to the heavy snowballs—a term used to describe tightly bound many helium layers to a cation dopant.¹⁰ Studies of small cations formed upon ionization of neutral dopants have found evidence of metastable cluster ions,^{11–15} but upon electronic or even vibrational excitation of the putatively doped droplets, non-thermal ejection of a free cation from the droplets has been reported.^{16–21} Spectroscopic analysis has further revealed that for aniline, the helium matrix exerts minimal interference to the line shape and linewidth of the cation in the infrared.¹⁸ More recently, Filsinger *et al.* have embedded hemin⁺ from an electrospray ionization (ESI) source in superfluid helium droplets and reported non-thermal ejection of the dopant upon resonant excitation of the chromophore.¹⁹ In this case, the helium environment has caused a slight blue shift in the electronic transition, and the linewidth of the transition is narrower than that from the gas phase. Filsinger *et al.* have also reported that ejection involves more than one photon and the yield depends on the size of the droplet.¹⁹ So far, one can conclude that the bonding structure of a cation inside a droplet is far from uniform and simple, and that perhaps, there is a complete spectrum of variations in bonding structure and strength depending on the nature of the cation.

We have been interested in doping of cations in superfluid helium droplets not for spectroscopic studies but for electron diffraction of laser aligned protein ions.²² Our idea involves embedding protein ions into superfluid helium droplets for laser induced alignment and then electron diffraction of

aligned molecules for oversampling, phase retrieval, and structural refinement. The ultracold rotational temperature inside a droplet is ideal for effective field induced orientation.^{23–25} However, a unique requirement of our experiment is the size of the doped droplets: although as a light atom, helium has a small diffraction cross section, when more than 1000 helium atoms surround a dopant, diffraction from the helium atoms can overwhelm the signal from the dopant. For this reason, we need to not only maximize the number of cation doped droplets but also minimize the resulting size of the doped droplets for diffraction.

An advantage offered by ion doped droplets, as compared with neutral doped droplets, is the net charge of the doped droplets: one can use electric fields to manipulate and measure charged particles. In a previous study, we have generated cesium cations from a thermionic emission source and measured the size distribution of the resulting doped droplets.²⁶ An anticorrelation between the doping efficiency and the kinetic energy of the incident ions has been observed. Based on the calculation of the droplet size distribution under different nozzle temperatures, we have attributed the increase in doping efficiency at low nozzle temperatures to the increase in the number of viable sized droplets. The adverse effect of the kinetic energy on doping was attributed to the limited deceleration of a fast moving ion inside a droplet, resulting in many fast ions directly penetrating through the droplet.

In this report, we describe a simple approach of doping ions from an electrospray ionization source into superfluid helium droplets. Compared with the literature reports, our method does not require an ion trap to enhance the interaction between the droplet beam and the incident ions. Instead, a stopper electrode decelerates the incident ions to maximize the doping efficiency. This unique design extends our investigation of doping efficiency to the extremely low kinetic energy regime for the incident ions, below the lower limit of 20 eV from our previous work on cesium cations.²⁶ We report similar numbers of doped droplets and similar size distributions as those reported from an experiment with an ion trap.¹⁹ The simplicity of our setup, on the other hand, makes it straightforward

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to integrate with future spectroscopic or diffraction experiments. More importantly, the simple geometry allows qualitative modeling of the doping process.

EXPERIMENTAL

Figure 1 shows the schematic of the experimental setup. The droplet source was described in detail in a previous publication.²⁶ It consisted a pulsed valve (Parker Hannifin Corp, Series 99) with a nozzle diameter of $500\ \mu\text{m}$ cooled down to a minimum of 15 K using a closed-cycle helium cryostat (APF cryogenics, HC-4 MK1). The helium droplet beam was collimated by a 5 cm long skimmer of 2 mm in diameter (Beam Dynamics) located 12 cm downstream from the nozzle. Ultrapure (99.999%) helium at about 30–50 atm was released into vacuum to generate the superfluid helium droplets. The ion source was adapted from a reflectron mass spectrometer with electrospray ionization (Bruker Daltonics, BioTOF), and the reflectron component was removed for this experiment. In addition to the ESI source, the apparatus also included a quadrupole mass selector and a collisional cooling ion trap with nitrogen as the cooling gas. A pulsed voltage gate at the exit of the ion trap released the ions into the path of the droplet beam. The average kinetic energy of the released ions was controlled by the bias of the ion trap, and it was mostly in the range between 25 and 30 eV.

In the doping region, the ion beam passed through the droplet beam just once, but the ions were slowed down, stopped, and perhaps even returned by the bias voltage on the collector/stopper electrode. The electrode was wired to an operational amplifier and a mega-ohm resistor, so that the absolute ion count from the ion trap could be obtained when the electrode was not intentionally biased. During the experiment, the bias on the electrode was adjusted to maximize the number of doped droplets.

Downstream from the droplet source, two different setups were used for two different types of measurements, similar to our previous report on cesium cations.²⁶ In the first experiment, two planar electrodes with one grounded and the other biased between -3 and $+3$ kV were used to deflect the doped droplets away from the detector. In the second experiment, a retardation electrode was used instead of the deflectors, with the intention

of stopping low energy (small doped droplets) thereby resolving the size of the doped droplets.

Further downstream from the analysis region was a Daly dynode detector, similar to the one used by Filsinger *et al.*¹⁹ A ground shield protected the high voltage dynode biased at -20 kV, and a channeltron facing the dynode recorded the secondary electrons emitted from the dynode. The system functioned in an analogue mode, and a voltage signal was representative of the number of charged particles hitting the dynode. To obtain the absolute number of doped droplets, we calibrated the gain of the Daly detector using a copper target wired with an operational amplifier and a giga-ohm resistor. Unfortunately, the ion count from the current experiment with an ESI source was too low to be observable on the copper target, so we resorted to cesium doped droplets using our thermionic source. Also shown in the source region of Fig. 1 is the thermionic emission ion source for cesium used in a previous experiment.²⁶ The huge number of cesium ions from this source was sufficient to generate more than 10^4 doped droplets per pulse, large enough for the copper target to respond with voltage pulses in the millivolt range. We first recorded the voltage pulse, for example, 183 mV, from the Daly dynode, and then replaced the dynode assembly by the copper target and recorded a voltage trace on a calibrated oscilloscope. The voltage trace was then converted into a current trace, and integration of the current trace yielded the number of ion-doped droplets of 10^4 . We then assumed that a voltage pulse of 183 mV on the Daly dynode should correspond to 10^4 ion-doped droplets. The linearity of the correlation was checked throughout the response range of the copper target. We also tried the integrated peak from the pulse of the Daly dynode and concluded that the peak area was directly proportional to the peak intensity throughout the response range of the dynode. Although we took the liberty of extending the linear conversion between the voltage pulse of the Daly dynode and the number of doped ions to a lower range in the cases of reserpine and substance P, we believe that our numbers should be trustworthy within an order of magnitude.

It is worth noting that in all cases of direct ion doping,^{19,27} including our own, the probability of picking up more than one ion is negligible. This is because of the space charge limit of 10^7 ions/ cm^3 , which is equivalent to a doping pressure of 10^{-9} Torr. For droplets with sizes of 10^6 atoms/droplet, the probability for a first encounter with one ion is less than 0.1%; hence, a second encounter is statistically impossible.

Two standard samples in mass spectrometry from Sigma Aldrich were used, with molecular weights of 609 g/mol for reserpine and 1348 g/mol for substance P. Reserpine is an indole alkaloid used as an antipsychotic and antihypertensive drug, and substance P is a neuropeptide containing a chain of 11 amino acid residues. The former only ionizes into a singly charged cation (denoted as R^+ in the following), but the latter has two possible ions, and only the doubly charged ion (denoted as sP^{2+}) was chosen because of its higher abundance from the ESI source. Both samples were dissolved in 1:1 water acetonitrile solution with a final concentration 1.8×10^{-4} M, and to increase the ionization yield, we also added two drops (~ 0.1 ml in total) of 1% formic acid into the ~ 2 ml solution, with a resulting pH value between 4 and 5. At a flow rate of

FIG. 1. Experimental setup showing the arrangement of the electrospray ionization source, the superfluid helium droplet source, and the analysis region of the doped droplets including the Daly dynode detector. The cesium source was temporarily used to calibrate the gain of the Daly dynode, and it was removed for the doping experiment of the ions from the ESI source.

200–700 $\mu\text{l/h}$, the total number of ions released from the ion trap arriving at the collector electrode was $\sim 10^7$ ions/pulse.

RESULTS

With this relatively simple setup for doping, we were surprised when we first released the reserpine ions from the ESI source and directly observed doped droplet signal on the Daly detector. The source temperature of the droplet beam was kept at 15 K. The collector/stopper electrode was unbiased, and the connected resistor was showing a total ion count of $\sim 10^7$ ions/pulse. The signal on the Daly dynode showed a dependence on the relative timing of the droplet beam and the ion exit gate, and no signal could be detected when the relative timing was shifted by $\pm 150 \mu\text{s}$ away from the optimal condition. We then varied the voltage on the stopper electrode, and Fig. 2 shows the change in the number of doped droplets with the voltage on the stopper electrode. Fast increase in the number of doped droplets is observable when the voltage on the stopper electrode is increased from 40 to 50 V, after which the rise slows down and reaches a peak value. Above 70 V, the doped droplet signal drops precipitously, and no doped signal is observable when the voltage reaches 80 V. Overall, the addition of a deceleration voltage on the stopper electrode has an effect of more than doubling the count of doped droplets, from less than 4000 at no bias to over 10 000 doped droplets at 70 V.

Fig. 3 shows the results from the deflector experiment where doped droplets were driven out of the system by an increasing deflection voltage. The two types of ions R^+ and sP^{2+} have similar mass-to-charge ratios, but substance P is about twice as heavy as reserpine with twice the number of atoms and twice the heat capacity. At 15 K, the total number of doped droplets of R^+ is almost twice that of sP^{2+} , both on the order of thousands per pulse. Based on the ion count recorded at the stopper electrode, the resulting doping efficiency is just below 1%. This value is about a fraction of that (5%) from our previous work on doping of cesium ions at a source temperature of 14 K.²⁶ Limited by the deteriorating performance of

FIG. 2. Dependence of the number of reserpine doped droplets on the voltage of the stopper electrode. The diamonds represent the experimental data, and the lines are calculations proportional to the residence time of the ions inside the droplet beam (see Discussion): the dashed lines correspond to ions with initial kinetic energies of 28 and 32 eV passing through the droplet beam once, and the dotted line corresponds to an initial kinetic energy of 40 eV and the ions are deflected back inside the droplet beam.

FIG. 3. Change in the number of doped helium droplets with increasing deflection field.

the cryostat, unfortunately, we could not consistently lower the source temperature to below 15 K for more measurements, as we did in the cesium experiment. At this stage, we can only qualitatively state that from cesium to reserpine to substance P, with the increase in the complexity and weight of the dopant, the doping efficiency seems to be decreasing.

The voltage on the deflectors determines a lower size limit for the detectable ions if all droplets travel with the same velocity; hence, the horizontal axis of Fig. 3 can be converted to the size limit based on the experimental geometry. Differentiation of the ion signal vs. the droplet size limit should produce the size distribution of the doped droplets. In Fig. 4, we have fitted the resulting size distribution using the log-normal function,²⁸

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

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 fitting results are similar

FIG. 4. Log-normal fitting of the droplet size distributions of R^+ and sP^{2+} doped droplets. The fitting parameters using Eq. (1) are also shown in the figure.

FIG. 5. Retardation experiment showing the change in the number of doped droplets as a function of a retardation field. A single exponential fitting of the experimental data is also shown.

for both ions, on the order of 10^6 for the mean and 2×10^5 atoms/droplet for the most probable size. These sizes are about 1/10 of those from the experiment on cesium.²⁶

In another effort, we grounded the deflection electrodes and biased the retardation electrode. The retardation electrode was made of a copper sheet with a central mesh (50×50 mesh plain and 0.001 in. in wire diameter) for ion transmission. Only doped droplets with sufficient kinetic energy can overcome the retardation field and reach the detector. Fig. 5 shows the change in the ion count as a function of the retardation voltage. The smaller initial ion count than that from the previous deflection experiment (Fig. 3) is reflective of the fluctuation level of the ESI source on a day-to-day basis.

Although in theory, both the retardation and the deflection experiments should reveal the same size distribution, attempts to fit the data from the retardation experiment to a log-normal distribution were unsuccessful. Instead, we used a single exponential function to fit the experimental data, and the resulting average size from the fitting was on the order of 10^5 /droplet. This value is about half to a third of that from the deflection experiment. The discrepancy, as we speculated in the experiment of cesium,²⁶ is probably related to the different functional modes of the deflection and the retardation experiment. In the deflection experiment, smaller droplets were steered away from the path of the larger droplets, while in the retardation experiment, smaller droplets were turned back towards the incoming larger droplets. At this stage, however, we do not have a good explanation for the discrepancy.

The average droplet sizes from this experiment and that from our previous experiment with cesium ions²⁶ are more than one order of magnitude larger than those from typical subcritical supersonic expansions.²⁹ One reason is probably related to the design of the pulsed valve, which has been considered to generate unusually large droplets based on reports from Bierau *et al.*²⁷ and Filsinger *et al.*¹⁹ Another reason, which applies to all types of sources, is that smaller droplets do not have a high enough pickup efficiency to be doped and hence detected. The resulting measurement based only on charged droplets necessarily shifts to larger sizes. At 15 K and 50 atm for the pulsed valve, the source is close to the isentrope dividing subcritical and supercritical expansions; hence, the final fitting result for

the droplet size using log-normal and exponential functions could go awry. In fact, the profiles of Fig. 5 are statistically better represented by bi-exponential functions, and the slower decay component dominates both profiles, corresponding to an average size of $\sim 5 \times 10^5$ atoms/droplet for both reserpine and substance P. Attempts to fit the profiles of Fig. 4 using exponential functions have also been successful, resulting in an average size of 9×10^5 and 6×10^5 atoms/droplet for reserpine and substance P. Although numerically different, these fitting results are in reasonable agreement, and the basic conclusion from this experiment remains the same, i.e., the average size of ion doped droplets is on the order of 10^5 atoms/droplet for reserpine and substance P. Unfortunately, limited by the much lower level of signal at higher source temperatures and the achievable lowest temperature of the cryostat (15 K), experiments in other temperature ranges were unsuccessful. Variations in the stagnation pressure from 10 atm to 50 atm did not produce substantial improvements at any of the achievable temperatures, since unlike temperature, pressure for a pulsed valve plays a complicated role, and its effect on the droplet size was limited in our case.

DISCUSSION

A major difference of the current experiment from the work of Bierau *et al.* and Filsinger *et al.* is the missing ion trap for doping.^{19,27} Our experiment demonstrates that even without a trap, we can generate doped droplets near 10^4 /pulse, comparable with that from Bierau *et al.*²⁷ An ion trap typically ensures a high ion concentration—close to the space charge limit—for doping, thereby it is favored for increasing the number of doped droplets. However, the operation of an ion trap requires filling of the trap with ions and collision gas and pumping of the collision gas prior to droplet doping. This filling and pumping procedure interrupts the continuity of the experiment. Moreover, depending on the trajectories and the kinetic energies of the ions in the trap, the number of crossings between an ion and the droplet beam and the overall effective interaction time are difficult to model.

The lack of any type of ion trap in the doping region of the current design does not allow oscillatory trajectories of the incident ions in and out of the droplet beam. In the meantime, it also eliminates any potential trap for doped droplets along the path of the droplet beam. Falconer *et al.* used a biased ion collector to pull the sodium ions into the path of the droplet beam for doping.³⁰ In our own work on doping of cesium ions, a biased grid was used to trap the ions in the doping region, and the incident ions were able to traverse the region ~ 15 times.²⁶ However, the biased ion collector or grid can also trap small doped droplets, as discussed in both previous publications.^{26,30} The effect of a potential trap at 20 eV is elimination of doped droplets with less than 10^4 helium atoms from reaching the detector. In our current experiment with the doping region biased slightly positive for the incoming cations, essentially all doped droplets can reach the detector. Upon doping, about 10^4 helium atoms need to be evaporated to absorb a kinetic energy of 25 eV. If half the momentum of the incident ions is transferred to the doped droplet along the same transverse direction perpendicular to the droplet beam—an

over exaggeration, the maximum gain in transverse velocity is 30 m/s. Given the distance between the doping region and the detector of 20 cm, the exit ions in the most extreme case would be off axis by 1.5 cm. The diameter of the hole on the shield for the Daly detector is 2.5 cm; thus, almost all doped droplets can be detected, without discrimination against small droplets.

Effect of residence time on doping efficiency

A possible reason for the success of this simple setup is the low kinetic energy of the incident ions for doping. We simulated the electrostatic potential of the doping region 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. When the voltage on the stopper electrode was 60 V, given the geometry of the doping region, ions with a kinetic energy of 30 eV would be returned near or just pass the center of the doping region. We therefore suspect that perhaps the doping efficiency was related to the residence time of the ions in the droplet beam. Our droplet beam had a duration of 200–300 μ s, and the ion beam from the exit electrode of the ion trap was ~ 150 μ s. It is therefore reasonable to assume that to the incident ions, the droplet beam was pseudo-continuous. We then performed a crude calculation on the residence time of the ions in the path of the droplet beam based on the geometry shown in Fig. 6. For simplicity, we assumed that the droplet beam was in the midpoint between the stopper electrode and the exit electrode of the ion trap (a slight deviation from our true experimental setup), and the distance between the two electrodes was $l = 18$ cm. The width of the droplet beam was assumed to be $d = 5$ mm. By further assuming that when the exit gate opened (grounded), the electric field across the doping region was uniformly determined by the voltage on the stopper electrode V_s , we can calculate the residence time t_1 of the ion beam passing through the droplet beam with an initial kinetic energy E_0 ,

$$t_1 = \frac{l}{V_s} \sqrt{\frac{2m}{q}} \left(\sqrt{\frac{E_0}{q} - \frac{l-d}{2l} V_s} - \sqrt{\frac{E_0}{q} - \frac{l+d}{2l} V_s} \right), \quad (2)$$

where m and q are the mass and charge of the ions. As the stopper voltage increases, some ions will be stopped and returned and perhaps even re-enter the region of the droplet beam, as shown by traces b–d in Fig. 6. If the turning point is outside the droplet beam and the ion re-enters the droplet beam (trace b), then the residence time should be simply twice of t_1 . If the turning point is within the width of the droplet beam (trace c), the residence time of the ion inside the droplet beam can be calculated by

$$t_2 = \frac{2l}{V_s} \sqrt{\frac{2m}{q}} \left(\sqrt{\frac{E_0}{q} - \frac{l-d}{2l} V_s} \right). \quad (3)$$

In a simple-minded approach, we can assume that the number of doped droplets is directly proportional to the residence time of the ions in the droplet beam. We then introduce two adjustable parameters α_1 and β_1 to represent the scaling of the ion signal (I) with the residence time and a base line. Scenarios a and b can then be fitted using

$$I = \alpha_1 t_1 + \beta_1. \quad (4)$$

The dashed lines in Fig. 2 show the result obtained when $\alpha_1 = 7.7 \times 10^8$ and $\beta_1 = 2500$. The short dashed line was obtained by assuming $E_0 = 28$ eV, while the long dashed line was by assuming $E_0 = 32$ eV. As the stopper voltage increases from 40 to 50 V, ions with higher and higher kinetic energies begin to spend more time in the doping region, resulting in increased signal. This simple model has reproduced the rise edge of the doped droplet, and it also demonstrates that with only 4 eV of extra kinetic energy from 28 to 32 eV, the position of the sharp rise shifts by 8 V. We can therefore deduce that the width of the peak is related to the energy spread of the ion beam.

It is worth noting that this crude fitting made no distinction between traces a and b (Fig. 6), and it should only be treated as a qualitative interpretation of the experimental result. When the kinetic energy is reduced close to zero at the turning point, stray fields start to play an overwhelming role, and intrinsic divergence of the ion beam will also diminish the number of returned ions. The effective resident time of the returned ions should be much shorter than that of the entering ions. In fact, the agreement between calculation and experiment seems to imply that perhaps none of the returned ions had a chance to interact with the droplet beam.

A similar argument can be used for the calculation of traces c and d: we used $\alpha_2 = 1/2\alpha_1$ but a different β_2 value ($-12,500$) to simulate the effect of deflection of the stopper electrode using the modified formula,

$$I = \alpha_2 t_2 + \beta_2. \quad (5)$$

The dotted line in Fig. 2 was obtained by assuming $E_0 = 40$ eV. This value can be considered the cutoff energy when all ions are deflected away from the droplet beam, as shown by trace d (Fig. 6). Although the majority of the ions released from the ESI source have energies in the range of 28 and 32 eV, a high energy tail up to 40 eV is not totally out of reason. We therefore

FIG. 6. A simplified geometry of the experimental setup for modeling the residence time of ions from the ion trap in the droplet beam. The arrows labeled a–d represent four different possible ion trajectories depending on the initial kinetic energy of the ions and the bias on the stopper electrode.

consider that 40 eV is the upper limit in the energy distribution for the ions released from the ion trap.

Crude as it is, this calculation has reproduced all the essential features of Fig. 2. When the stopper voltage rises to above 50 eV, the residence time of low energy incident ions dramatically increases, resulting in much more effective doping and a sharp rise in the resulting number of doped droplets. As the stopper voltage further increases to 60 eV, lower energy ions can no longer penetrate into the droplet beam, resulting in a fast drop in the doped droplet signal, but in the meantime, higher energy ions begin to have longer resident times in the droplet beam, causing a moderate increase in the total number of doped ions. At even higher voltages on the stopper electrode, even the high energy tail of the bare ions can no longer penetrate into the droplet beam, and no more doped droplets can be generated. The net result of the above process is the peak of Fig. 2. The width of the peak is determined by both the energy spread of the droplet beam and the intrinsic rise and fall of even a mono-energetic ion beam within the finite width of the droplet beam.

The implications of the fitting parameters in Eqs. (4) and (5) are worth considering. In Eq. (4), the value of β_1 corresponds to the existence of doped droplets without any residence time ($t_1 = 0$), i.e., when the droplet beam is infinitely thin ($d = 0$ mm). This signal accounts for 2/3 of the overall number of doped droplets when the stopper electrode is grounded. Increase in residence time further increases the number of doped droplets to a degree that it almost quadruples the final yield. This enhancement effect should be intimately related to the pseudo-continuous nature of the droplet beam. In Eq. (3) for t_2 , the factor two implies that the residence time for the return trip is considered to be identical as that of the incoming trip; hence, it is an overestimation of the overall residence time. In Eq. (5), this overestimate is eliminated by using $\alpha_2 = 1/2\alpha_1$. In essence, this approach is assuming that the return trip does not contribute to further doping, regardless of the position of the turning points as represented by traces b or c. The negative β_2 value, on the other hand, represents other unaccounted loss mechanisms when the turning point is inside (trace c) or prior to encountering the droplet beam (trace d). This is somewhat understandable since in the cases of traces c and d, the velocities of the ions are dramatically reduced once outside the ion trap. Stray fields and collisions with ambient residual gases and helium from the droplet beam can steer the ions away from the droplet beam.

In our previous work on doping of cesium cations,²⁶ we reported that the doping efficiency of Cs^+ rose dramatically with decreasing kinetic energy of incident ions. However, the conditions of the cesium experiment prevented us from investigating the doping efficiency below 20 eV. Since the cesium ion source was continuous, the residence time of the ion beam inside the droplet beam was not a parameter in affecting the doping efficiency. Instead, the resident time of a fast ion inside a droplet was limited because of the high velocity of the incident ion. The small mass of a helium atom is ineffective in slowing down a fast moving cesium ion. The doping efficiency was therefore discovered to be inversely related to the energy of the ions. In essence, the two scenarios of doping, either with a continuous or a pulsed ion source, demonstrate the same common factor in

determining the doping efficiency: ions have to be decelerated inside the droplet or the droplet beam to be captured.

Ion size and droplet size

A major motivation of the current experiment is to prepare droplet cooled protein ions for laser alignment and electron diffraction. Our previous work has concluded that for phthalocyanine gallium chloride, there can be no more than 100 helium atoms for each carbon atom of the dopant molecule during diffraction.²² Otherwise, the background from the helium atoms would overwhelm the diffraction signal of the embedded molecules. Although reserpine and substance P both have more atoms to contribute to the diffraction signal, the current size of doped droplets is still too large. Methods of size reduction or non-thermal ejection will be necessary to strip the helium atoms before diffraction.

On the other hand, the most probable size from the current experiment at $10^5/\text{droplet}$ is an order of magnitude smaller than that from cesium.²⁶ Compared with cesium, reserpine and substance P have ~ 100 times more atoms, which require 10^3 helium atoms to remove the thermal energy of these ions. This amount of helium atoms is negligible compared to that required to absorb the kinetic energy of 25 eV of the bare ions. In this sense, the extra heat capacity of the compound ions is not the reason for the one order of magnitude decrease in size compared with droplets doped with Cs^+ . On the other hand, compound ions have larger collisional cross sections and lower velocities than light atomic ions, which could be beneficial for doping of smaller sized droplets. This argument would lead to increased ion count for doped R^+ and sP^{2+} than for doped Cs^+ under the same source temperature and the same number of bare ions. The number of Cs^+ ions in the doping region of our previous experiment was difficult to measure, but the actual numbers of doped droplets from this experiment using an ESI source are lower than that from the experiment with a thermionic cesium source under the same temperatures for the pulsed valve.²⁶ More investigations using a wider variety of ions are necessary to resolve this issue.

In summary, we have demonstrated a simple approach to effectively dope ions from an electrospray ionization source into superfluid helium droplets. Without employing an ion trap in the doping region, we eliminate the need of trap filling and collision gas pumping, making the setup much simpler to be integrated with subsequent experiments. The success of this simple approach can be attributed to the low kinetic energy of the incident ions. Using a crude model, we have calculated the residence time of the incident ions in the droplet beam and discovered a direct correlation between the residence time and the doping signal. The resulting doped droplets of R^+ and sP^{2+} are smaller than those of Cs^+ , but they are still too big for electron diffraction. The reason for the smaller sized droplets with the compound ions R^+ and sP^{2+} from an ESI source warrants further investigation.

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