Controlled growth of helium nanodroplets from a pulsed source

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Factors affecting the size of liquid-helium droplets produced by a pulsed nozzle are described. The shape of the nozzle orifice is found to be important in allowing control of the size of the droplets. With an appropriate choice of nozzle geometry, the average droplet size is shown to be continuously variable over nearly two orders of magnitude by adjustment of the helium gas stagnation pressure and/or temperature. A scaling law similar to, but not identical with, that found for helium droplets produced by continuous supersonic expansion sources is found for the pulsed source. The pulsed nozzle described in this article has been used to make helium droplets ranging in size from a few thousand atoms up to nearly 10^5 helium atoms. © 2005 American Institute of Physics.

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INTRODUCTION

Continuous helium nanodroplet beam sources are now well established in many laboratories across the world. Liquid-helium droplets can be produced by forcing pre-cooled helium at high pressure through a pinhole aperture into a vacuum chamber. The additional cooling due to adiabatic expansion can bring about condensation leading to the formation of nanoscale droplets. Condensation is a statistical process and therefore a variety of droplet sizes will result, a log-normal distribution being the expected outcome.¹ The mean size of the droplet, consisting of $\langle N \rangle$ helium atoms, can be altered by varying the reservoir gas pressure and temperature. As one would predict, an increase in temperature and/or a decrease in gas pressure is found to produce a decrease in the average size of the helium droplets.

The first report of a pulsed helium droplet source appeared in 2002. In this seminal work Slipchenko *et al.* succeeded in producing repetitive pulses of helium droplets by modifying a commercially available pulsed valve such that it could operate at cryogenic temperatures.² A comparison of the performance of the pulsed source with conventional continuous supersonic expansion sources revealed a much higher helium droplet flux with the former. In addition, a pulsed source allows the use of smaller vacuum pumps, reduces the consumption of expensive high-purity helium, and is better suited to experiments in which the droplets are probed by pulsed lasers.

Unfortunately, in their initial study Vilesov and co-workers found it difficult to control the droplet size in any systematic and predictable fashion. Variation of the helium reservoir pressure and temperature yielded a very different response when compared with continuous droplet sources. Specifically, the average droplet size that could be produced was found to vary over a relatively narrow range ($2\text{--}7 \times 10^4$ helium atoms) and with a dependence on temperature

and pressure which bore no relationship to the conventional free jet scaling laws.^{3,4} Although $\langle N \rangle$ generally declined as the temperature was increased at fixed gas pressure, this was not universal, and unusual profiles were obtained at some reservoir gas pressures which in some cases showed maxima and minima. This erratic response to source conditions limits the utility of the pulsed helium droplet source since it makes it difficult to predict the likely size of helium droplets for a given set of source conditions. Furthermore, access to a greater range of droplet sizes would be highly beneficial in some experiments. For example, for laser depletion spectra of molecules embedded inside helium droplets the preferred droplet size consists of no more than a few thousand helium atoms.

In this article we will show that a simple modification of the nozzle geometry allows much greater control over helium droplet sizes. With this alteration, droplet sizes can be varied over a much wider range and can be controlled in a predictable way by adjusting the source temperature and/or pressure. This step forward puts pulsed helium droplet sources on a par with continuous sources and may open up a wide variety of applications.

EXPERIMENTAL DETAILS

The overall design of our helium nanodroplet instrument has been presented elsewhere^{5,6} and so the discussion here concentrates on the nozzle and the conditions under which it operates. We have found that the nozzle geometry is critical to achieve droplet size control in a smooth and reproducible fashion by variation of the source gas temperature and pressure. The pulsed source consists of a commercial solenoid pulsed valve (General Valve, series 99 model) attached to a homemade stainless-steel faceplate. The valve is cooled by contact with a closed-cycle cryostat which is capable of achieving temperatures as low as 4 K. The operating mechanism of the valve uses a retractable poppet to open and close the aperture. Following Slipchenko *et al.*,² we employ a poppet made from Kel-F, a material which is able to withstand

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FIG. 1. Scale drawing showing (a) the profile of the stainless steel faceplate of the pulsed valve and (b) an expanded view of the specific geometry of the nozzle. The entrance and exit channels machined into the faceplate are conical and are connected by a short, constrictive zone of diameter 0.6 mm and length ~ 0.1 mm.

repetitive use at low temperatures without fracture. A leak-tight seal between the walls of the valve body and the faceplate is achieved using an indium gasket.

We have experimented with a variety of nozzle shapes machined into the faceplate. With a straight channel of 0.5 mm diameter drilled through the faceplate the result was little ability to control the droplet size and a restriction to large droplets (average sizes $> 5 \times 10^4$ helium atoms). We next turned to the conical nozzle design reported by Slipchenko *et al.*,² where the converging and diverging cones meet at a simple knife-edge junction. In agreement with Slipchenko and co-workers, we again found that the ability to vary the droplet size in a systematic way was limited. However, a small alteration to the conical nozzle design was found to make a dramatic difference. This alteration adds a short constriction carefully machined between the two cones, as shown in Fig. 1. This constriction, or throat, was found to be critical for allowing the controlled and predictable growth of helium droplets as a function of helium gas pressure and nozzle temperature. This simple improvement was found empirically, but the explanation is probably that the short throat allows the onset of helium condensation prior to the rapid cooling that takes place in the exit cone. This intermediate zone confines the gas for short period of time, increasing the rate of collisions and providing the initial small nucleation centers upon which controlled growth can then subsequently take place in the diverging region of the nozzle. In addition to improved size control, the short throat was also found to substantially increase the droplet flux relative to a conical nozzle with a knife-edge throat.

The performance of the droplet source was monitored using mass spectrometry. Ions were produced using a 70 eV pulsed electron-beam source located approximately 1 m downstream of the nozzle. The firing of the electron beam was controlled by using a pulse delay generator and timed to coincide with the arrival of the gas pulse at the mass spectrometer source region. The resulting ions were then repelled by an electric field into a reflectron time-of-flight mass spectrometer for mass analysis.

FIG. 2. Temporal profile of He₂⁺ ion current for a nominal valve opening time of 140 μ s (as set by the valve controller, a General Valve IOTA ONE system). The delay shown on the abscissa is the time delay between the trigger pulses used for firing the pulsed valve and the electron-beam source.

RESULTS

Figure 2 illustrates the temporal profile of the droplet pulse for a nominal valve opening time of 140 μ s. This profile was determined by detecting He₂⁺ ions ejected from the droplets by electron-impact ionization. These ions come exclusively from helium droplets and are therefore characteristic signatures of droplet formation. From the delay between the firing of the valve and the firing of the pulsed electron beam, we estimate that the flow velocity of the droplets is in the region of 400 m s⁻¹, which is comparable to the beam speeds seen in continuous helium droplet sources.¹ Short valve opening times (< 200 μ s) were found to give the strongest He₂⁺ signals, in agreement with the earlier findings of Slipchenko *et al.*² The full width at half maximum of the observed He₂⁺ profile is much narrower than the nominal opening time of the valve set by the control electronics but this merely reflects the mechanical response of the valve operating mechanism.

Two types of experiments have been performed to explore the effect of source conditions on the droplet sizes, the findings of which are described below.

Droplet size survey using residual water vapor

The simplest way to deduce the size of helium droplets is to exploit their ability to pick up foreign atoms or molecules. The probability (p_k) that a helium droplet will acquire k molecules is given by the familiar Poisson distribution

$$p_k(z) = z^k \exp(-z)/k! , \quad (1)$$

where $z = \sigma nl$, σ is the cross section of the helium droplet, n is the number density of the added gas, and l is the distance over which the droplet beam travels in contact with this gas.¹

Rather than add a particular gas, we surveyed the range of droplet sizes by exploiting traces of water vapor in our spectrometer. Normally a nuisance, the low levels of water vapor in our instrument persist for many weeks after the vacuum is broken and are difficult to remove without thorough baking of the vacuum apparatus. However, for this ex-

FIG. 3. Comparison of mass spectra for water pickup by helium droplets generated at different nozzle source pressures (P) and temperatures (T). Peaks marked by asterisks (*) correspond to $\text{H}_3\text{O}^+(\text{H}_2\text{O})_m$ clusters, where $m \geq 0$. The peak labeled ∇ is due to residual toluene from an earlier experiment.

periment the persistence of the water vapor at a low and virtually constant level provided a simple and rapid means of assessing the effect of stagnation pressure P and nozzle temperature T on droplet sizes.

Figure 3 shows mass spectra recorded under two very different sets of nozzle conditions. A series of peaks due to the formation of hydrated hydronium clusters, $\text{H}_3\text{O}^+(\text{H}_2\text{O})_m$, where $m \geq 0$, are highlighted by asterisks. In the lower panel we have employed a nozzle temperature and helium gas stagnation pressure that yields relatively large helium droplets, and this is reflected in the observation of hydrated hydronium clusters extending out to fairly large sizes. In contrast the lower pressure and higher temperature used to generate the mass spectrum in the upper panel in Fig. 3 shows that much smaller clusters predominate.

Clearly the differences in these two spectra contain information about the helium droplet sizes. To quantify the size information several approximations are commonly employed, two of which we specifically flag here. First, we ignore the contribution from any variation in helium droplet sizes and assume that all droplets have the average size $\langle N \rangle$. This is a widely used approximation and has been shown to yield an acceptable estimate of average helium droplet sizes.¹ Secondly, we have assumed that the relative intensities of $\text{H}_3\text{O}^+(\text{H}_2\text{O})_m$ peaks reflect the relative abundance of the neutral cluster $(\text{H}_2\text{O})_{m+2}$ in the helium droplets. In other words, we assume that electron-impact induces the process $(\text{H}_2\text{O})_{m+2}^+ \rightarrow \text{H}_3\text{O}^+(\text{H}_2\text{O})_m + \text{OH}$. Previous studies using electron-impact ionization have shown that this is the dominant process in the gas phase,^{7,8} but nevertheless the excess energy after ionization could induce some additional fragmentation such that the observed ion distribution becomes artificially skewed towards smaller clusters. In fact such fragmentation is known to occur to some extent even when water clusters are located in helium droplets, as shown in a spectroscopic and mass spectrometric study of water clusters by Fröchtenicht *et al.*⁹ The consequence of neglecting this

FIG. 4. Variation of z (see text) with helium stagnation pressure for a fixed nozzle temperature of 11 K.

ion fragmentation in calculating the helium droplet size is that the answer obtained will tend to underestimate the true average size. However, we expect this discrepancy to be relatively small and in any case we will persist with this approximation because our main aim in this section is to show the degree of *variation* in droplet sizes as a function of T and P , rather than determine reliable absolute sizes. Experiments with residual water vapor allowed us to carry out this survey of the $\{P, T\}$ dependence relatively quickly without any concerns over the precise and reproducible control of the added gas partial pressure.

The observed relative abundances of $\text{H}_3\text{O}^+(\text{H}_2\text{O})_m$ in each mass spectrum were fitted to the Poisson distribution in Eq. (1) for a wide range of temperatures and pressures. These data were used to extract z , which is related to N , the number of helium atoms in the droplet, through the relationship $N \propto \sigma^{3/2}$.¹ Since we do not know the partial pressure of the water vapor in our instrument, the absolute droplet sizes cannot be determined from these measurements alone. However, there are sufficient data to ascertain how $\langle N \rangle$ scales with P and T .

Figures 4 and 5 illustrate how z varies as P and T are varied. A rapid growth in droplet size is found as the temperature is lowered for a fixed helium stagnation pressure. Similarly, at fixed temperature the droplet grows systemati-

FIG. 5. Dependence of z (see text for details) on the nozzle temperature for two fixed helium stagnation pressures.

FIG. 6. Dependence of the toluene monomer cation signal on the toluene partial pressure in the pickup chamber for two different nozzle conditions. The solid lines are fits to the experimental data based on Poisson pickup statistics. The fitted data reveal droplets consisting of $29\,100 \pm 200$ ($P = 10$ bars, $T = 10.5$ K) and $10\,880 \pm 40$ ($P = 14$ bars, $T = 13$ K) helium atoms.

cally as the pressure is increased. This smooth and predictable response to changes in source conditions contrasts sharply with the earlier work on pulsed droplet sources by Slipchenko *et al.*,² but is very much in line with the response seen from continuous helium droplet sources.¹⁰

Absolute droplet sizes

To provide an estimate of the absolute helium droplet sizes, we added a specific gas into the pickup chamber at known partial pressures and monitored the mass spectrum as a function of the pressure. Toluene was chosen for this purpose and two example data sets, focusing on the toluene monomer cation, are shown in Fig. 6. These plots were fitted to a Poisson distribution and yielded droplet sizes of $10\,880 \pm 40$ ($P = 14$ bars, $T = 13.0$ K) and $29\,100 \pm 200$ ($P = 10$ bars, $T = 10.5$ K) helium atoms. Having extracted these absolute droplet sizes, the toluene data can be used to calibrate the droplet sizes for the water vapor experiments and this in turn makes it possible to determine helium droplet sizes across the full range of explored source conditions. However, we emphasize that, as for water clusters, any contributions from toluene cluster ion fragmentation have not been accounted for in the data analysis. While we do not expect this effect to be large, as demonstrated in comparable measurements using benzene in a continuous helium droplet beam,¹¹ we nevertheless caution that our droplet sizes are likely to be lower limits to the true mean droplet size.

DISCUSSION

The size of helium droplets emanating from continuous sources is commonly estimated using known scaling laws, which provide an explicit relationship between the average droplet size, $\langle N \rangle$, and the source conditions P and T . The use of scaling laws to estimate helium droplet sizes is clearly far more convenient than making time-consuming measurements of droplet sizes each time the nozzle source conditions are altered. There has been much discussion about scaling laws in the literature and different formulas of the type $\langle N \rangle$

$\propto P^\alpha T^\beta$ have been proposed.^{3,4,10} However perhaps the most widely used expression among the helium nanodroplet user-community shows $\langle N \rangle$ scaling as approximately $P^2 T^{-5}$.¹⁰

A scaling law can be extracted from the data recorded in this work yielding $\alpha = 0.956 \pm 0.15$ and $\beta = -6.04 \pm 0.33$. The strong dependence of droplet size on the nozzle temperature is similar to that found for continuous sources, but the pressure dependence is weaker for the pulsed source. Our current measurements have been made over the ranges $P = 8\text{--}20$ bars and $T = 10\text{--}16$ K, and are therefore strictly valid only within this region of $\{P, T\}$ space. However, even over this range we find that it is possible to vary the droplet size smoothly over almost two orders of magnitude. Based on the size calibration using toluene, the helium droplets at the highest nozzle temperature and lowest stagnation pressure are estimated to consist of ~ 2000 helium atoms. This is likely to be a lower limit of the true cluster size for reasons rehearsed earlier, but it nevertheless suggests that the pulsed nozzle described in this work can produce droplets of a size small enough to suit, for example, laser depletion spectroscopy experiments. At the other extreme, the highest pressure (20 bars) and lowest temperature (10 K) employed, we produce droplets with a size $\langle N \rangle \geq 80\,000$ helium atoms. Such large helium droplets may find utility in studying large molecules and extended clusters within superfluid liquid helium.

In this work we have shown that smooth and predictable control of helium droplet sizes is possible with a pulsed nozzle by variation of gas pressure and temperature in a manner that is entirely comparable with existing continuous helium droplet sizes. Pulsed helium droplet sources are therefore now viable alternatives to continuous sources and may soon see a wide range of applications.

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