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Helium Droplets: An Apparatus to Study Ultra Cold Chemistry

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\begin{abstract}
A new pulsed helium nano droplets machine has been constructed. The droplets were generated by expansion of the pure helium through the cryogenic valve attached to a closed-cycle cryostat. The mean size of helium droplets can be controlled between $10^4$ and $10^5$ helium atoms by tuning the backing pressure (10–40 bar) and temperature (10–30 K). Compared with the continuous-flow beam source, the density of droplet is at least one order of magnitude higher, which offers the opportunity to combine the system with the commercial pulsed laser to study chemical reactions inside of the superfluid helium at ultra-low temperature.

The performance for the system has been checked by studying the photodissociation of CH\textsubscript{3}I doped droplets at 252 nm with the velocity map imaging technique. The photo-products, CH\textsubscript{3}, were detected by (2+1) resonance enhanced multiphoton ionization. The speed and angular distributions derived from resulting images show clear evidence of the relaxation effect by the surrounding helium atoms. The pulsed helium droplets depletion spectroscopy was also demonstrated. The depletion spectrum of benzene doped helium droplets indicates that less than 3% depletion can be observed with the newly constructed apparatus.

\textbf{Key words:} Helium droplet, Pulsed beam, Ion imaging, TOF mass spectrum
\end{abstract}

I. INTRODUCTION

Helium is a special substance that remains liquid at low temperature with normal gas pressure. There are two quite different properties phases of helium. One is the ordinary liquid ($^4$HeI) and the other is the superfluid ($^4$HeII) at different temperatures. When the temperature is below $T=2.18$ K ($\lambda$ point), the $^4$HeI turns into $^4$HeII. In 1938, the ultra-cold superfluid helium has been discovered by Kapitza [1] and Allen et al. [2] independently. Later Whittle et al. developed the technique of cryogenic matrix isolation for spectroscopic studies [3]. Although helium droplets were considered as the ideal spectroscopic matrix, the first application has been achieved by Toennies \textit{et al.} in 1990s [4–7]. Since then the ultra-cold superfluidity helium technique was widely used as a powerful tool for studying the spectra, structures, dynamics of atoms, molecules, radicals, and so on [8–25].

As the cryogenic, helium droplets technique has achieved great success in spectroscopic studies [4, 5, 8, 9, 26–33]. By studying the high resolution IR spectra of SF\textsubscript{6} doped in helium droplets, Toennies \textit{et al.} measured the temperature of droplets is $T=0.38$ K for pure $^4$He ($T=0.15$ K, $^3$He) [9, 10], which has been consistent with theoretical estimation. The experimental results indicate that helium droplets are the finite-sized superfluid system. Toennies \textit{et al.} studied the absorption spectra of the electronic $S_1-S_0$ transition of glyoxal molecules and observed the phonon wing which was not observed in gas phase [4]. The interaction between the substance and the confined superfluid helium was confirmed. Some odd materials were synthesized and characterized by spectroscopic method in helium droplets [34, 35]. Miller group produced the smallest ice, water hexamer in helium droplets which was not observed in nature [36]. The long chain HCN clusters which were not achieved with the moderate experimental conditions have been generated in the helium droplets by increasing the doping pressure of HCN [37].

Except spectroscopy studies, helium droplets have been developed as the nano reactors to study molecular reaction dynamics at the ultra cold environment. The first bimolecular reaction was studied by Lugovoj \textit{et al.} They studied Ba+N\textsubscript{2}O$\rightarrow$BaO$^+$+N\textsubscript{2} reaction in helium droplets in 2000 [38]. The chemiluminescent of BaO$^+$ was detected. The results implied that the reaction occurred only inside of the droplets. And the catalysis effect could be achieved with Xe atoms added in the helium droplets [38]. In 2005, Toennies \textit{et al.} carried out an ion-neutral reaction experiment in the helium droplets. By electron bombardment ionizing the helium atoms followed by the charge transfer to ion-
ize the reactants, they studied \( \text{N}_2^+ + \text{D}_2 \) and \( \text{CH}_4^+ + \text{D}_2 \) reactions which are more related to chemistry in interstellar medium and upper atmosphere [39]. More recently, the photodissociation dynamics in the helium droplets has been studied by Braun et al. They studied the photodissociation of CH\(_3\)I, CF\(_3\)I, and C\(_2\)H\(_5\)I in helium droplets where the signal were detected by the velocity mapping ion imaging (VMI) technique [15, 16]. The translational energy distributions and angular distributions show significant difference with the gas phase results. The results indicate that the speed and angular relaxations are mass dependent which is governed by the hard sphere collision model [40]. Furthermore, they observed the recombination and solvent effects in the photodissociation process, the special phenomena for chemical reactions in the helium droplets [40].

Most of previous experiments were performed with the continuous-flow (cw) droplets source. The highly purified \(^4\text{He}\), with the stagnation pressure of between 5 and 100 bar, was expanded through a nozzle with a diameter of 5 or 10 \( \mu\text{m} \) at the temperature between 4 and 30 K to form helium droplets [9, 27, 30, 41–43]. However, the traditional cw sources of He droplets have small droplet fluxes of about \( 10^{14} \) droplets/(sr-s). Combined with the pulse lasers, the cw beam obviously decreases the duty cycle of the experiment. The more intense droplets beam is desirable. In 2002, the pulsed helium droplets source was reported firstly by Slipchenko et al. [44]. The intensity of the pulsed droplets beam is \( 10^2 - 10^3 \) times higher than cw beam, which offers the opportunity to combine the helium droplets with other pulsed experimental techniques such as infrared depletion spectroscopy, laser induced fluorescence (LIF), laser ionization, and time of flight (TOF) mass spectroscopy [44]. Later Yang et al. modified the nozzle design and demonstrated that smooth control of the droplets sizes was possible by controlling the helium gas pressure and temperature [45]. In 2009, Pentlehner et al. developed a novel cryogenic valve which can be operated at low temperature down to 6 K and stagnation pressures of up to 100 bar [46]. The valve can be used as a reliable helium droplets source [46]. The test results show that the duration of the droplets pulse is 50 \( \mu\text{s} \) and the beam intensity is one order magnitude larger than the cw beam source.

In this work, we constructed a pulsed helium droplets machine combined with the ion imaging and time of flight mass spectroscopy as detections. The droplets are produced by expansion of helium from a pulse valve (Even-Lavie Valve, EL-C-C-2009) developed by Even et al. [46]. The temperature of the valve can be adjusted continuously between 10 and 30 K as well as the stagnation pressure can be varied from 10 bar to 40 bar. The average size of droplets can be controlled between \( 10^3 \) and \( 10^5 \) helium atoms. The droplets are applicable to study the photochemistry and photon induced chemical reactions at the cryogenic environment. By ionization of the reaction products, we may overcome the difficulty of the neutral probe inside of the superfluid helium. The translational energy distributions and angular distributions will be derived from the resulting images directly and simultaneously. The chemical reaction dynamics at ultra low temperature and the interaction between material and superfluid helium will be studied in details on the newly constructed machine.

II. APPARATUS DETAILS

A schematic overview of the experimental setup is shown in Fig.1. The apparatus consists of three differentially pumped vacuum chambers named source, doping, and detection chambers, respectively. The source chamber is equipped with a large turbo molecular pump 2200 L/s (STP-A2203C, Edwards) to keep the pressure at 0.01 nbar without the droplets beam and 0.1–1 nbar with the beam. The doping chamber and detection chamber are equipped with nominal helium pumping speeds of 260 L/s (TC600, Pfeiffer vacuum) and 1000 L/s (STP-1003C, Edwards), respectively. The vacuums of doping and detection chambers are 0.1 and 0.01 nbar without the beam, respectively. The droplets source consists of an assembly holding a cryogenic Even-Lavie valve (EL-C-C-2009), which is thermally connected to the cold head of a closed-cycle refrigerator system (RDK-415E, Sumitomo Heavy Industries). The temperature of the nozzle can be adjusted with an accuracy of 0.5 K by heating the assembly by a 25 W cartridge heater which is powered by a temperature controller (TC202, East Changing). The high purity helium gas (99.9999%, Da te special gas) with a stagnation pressure of 10–40 bar was precooled at temperature in the range of 10–30 K and expanded through the nozzle.

![Schematic illustration of the experimental setup.](image)

FIG. 1 Schematic illustration of the experimental setup.
The expanding gas accelerates and cools adiabatically. Then the helium clusters beam is formed and collimated by a conical skimmer (Beam Dynamics) with a diameter of 2 mm which is placed at a distance of 15 cm from the source. Passing through the skimmer, the droplets beam enters the doping chamber and picks up impurities via collision. The doping sample is introduced into the chamber through a leak valve (LV940, VG Scienta) which is continuously controllable between $10^{-6}$ and $10^{-14}$ bar/s. The length of the doping chamber is 8 cm. By adjusting the leak rate, the constant scattering gas pressure is obtained. The doped droplets enter the detection chamber by passing through the other 2 mm skimmer (Beam Dynamics). There are two detection methods, named ion imaging and electron impact time of flight mass spectrometer (EI-TOF) installed in the detection chamber. The imaging detector is a 75 mm diameter Chevron type dual MCPs coupled to a P-47 phosphor screen. The gate of the MCPs for mass selection is pulsed by a fast high voltage switch (PVM-4210, DEI). The resulting images from the phosphor screen are recorded by a digital camera (scA780-54gm) with a camera lens (C3514-M). The digital camera is connected with a computer by a network interface port. The images are accumulated and analyzed by the homemade Labview programs. The homemade EI-TOF probe is used to check the composition of the droplets and depletion spectroscopy study. After electron bombardment ionization, the ions were accelerated by the focusing electric field and struck a 40 mm diameter dual microchannel plates (MCPs) coupled to an electronic receiver. The electric signal is collected by the data acquisition board which is installed on the computer. The timing of the pulse valve, the lasers, and the gate pulse applied on the MCPs was controlled by a multichannel digital delay pulse generator (BNC Model 555).

III. PERFORMANCE TEST

Helium droplets were produced by an expansion of the high pure (99.9999%) $^4$He from the Even-Lavie valve. After expansion, the beam was electron impact ionized at 57 cm downstream. The typical mass spectrum is shown in Fig.2, which represents the droplets generated at the stagnation pressure of $P=30$ bar and the temperature of $T=10.6$ K. The mass spectrum shows the strongest $\text{He}_2^+$ ions and other larger helium clusters. The helium is usually impossible to form clusters in the gas phase. These helium clusters are solid evidence for droplets generation and come from the droplets decomposition. Hence the temporal profile of helium droplets can be represented by the temporal profile of helium clusters ions. Figure 3 shows the temporal profile of helium droplets which is determined by detecting $\text{He}_2^+$ ions from the droplets by the electron impact ionization. The full wave at the half maximum (FWHM) of the droplets beam was determined about 50 µs.

By passing through the doping chamber, the droplets will be doped with species. The CH$_3$I molecules were introduced into the doping chamber through the leak valve. The doped helium droplets were electron impact ionized. Both the CH$_3$I$^+$ and He$^2_+$ ions from the electron impact ionization were detected by TOF mass spectrometer, as shown in Fig.4. The temporal profile of CH$_3$I$^+$ ions matches well with that of He$^2_+$ ions. It indicates that both the CH$_3$I$^+$ ion and He$^2_+$ ions came from the doped helium droplets. The probability ($P_k$) for helium droplets to pick up $k$ foreign atoms or molecules is described by the following formula:

$$P_k(z) = \frac{z^k e^{-z}}{k!}$$

where

$$z = n l \sigma$$

\(n\) is the number of droplets, \(l\) is the length of the doping chamber, and \(\sigma\) is the cross-section area of the droplet.
up the CH through the doping chamber the helium droplets picked been performed. As mentioned before, by passing through the doping chamber at the CH₃I partial pressure of 5.24 nbar.

The average size of helium droplets was estimated by \( \langle N \rangle \times \alpha^{3/2} \) [47].

Figure 5 shows the pickup probability vs. doping pressure. It should be pointed out that the ion gauge sensitivity was not corrected in the present study due to lack of the sensitivity coefficient data for CH₃I. The helium droplets were produced at the stagnation pressure of \( P=30 \text{ bar} \) and the temperature of \( T=12.6 \text{ K} \). The cross section was determined as \( \sigma=(16016\pm281) \text{ A}^2 \) which implied that the average size of helium droplets was about \( 34211\pm900 \text{ helium atoms per droplet} \). By varying the stagnation pressure from 21 bar to 37 bar and the valve temperature from 11 K to 26 K, the average size \( \langle N \rangle \) of droplets was well controlled from \( 3\times10^3 \) atoms to \( 8\times10^4 \) atoms. Previous works offered a simpler scaling law, \( \langle N \rangle \times P^{\alpha}T^3 \) [48, 49] to estimate the average size of helium droplets. It was usually used as \( P^2T^{-5} \). Yang et al. constructed a pulsed droplets beam and determined the parameters of \( \alpha=0.956\pm0.15 \) and \( \beta=-6.04\pm0.33 \) from their work [45]. However, in this work the parameters were determined as \( \alpha=1.445\pm0.22 \) and \( \beta=-2.687\pm1.12 \), respectively.

As an ultra-low temperature nano reactor, helium droplets were widely used to study the spectroscopy and molecular reaction dynamics. However, most of previous studies have been carried out with the cw lasers. To demonstrate the ability to combine our droplets machine with the pulsed lasers, a typical pump-probe experiment has been carried on the newly constructed pulsed helium droplets ion imaging machine. The photodissociation of the CH₃I doped helium droplets has been performed. As mentioned before, by passing through the doping chamber at the CH₃I partial pressure of 5.24 nbar.

the detection chamber by passing through a 2 mm skimmer. The pump and probe lasers were introduced into the detection chamber counter propagation and crossed with the doped beam vertically. The pump beam was a 252 nm laser which was produced from the doubling of a tunable dye laser (Continuum Surelite II plus Radiant) pumped by a neodymium-doped yttrium aluminum garnet (Nd:YAG). The typical energy was \( \sim 1.3 \text{ mJ/pulse} \) and focused by an \( f=300 \text{ mm} \) lens. After photodissociation, the CH₃ products were ionized by the probe laser. The probe laser beam was provided by a Nd:YAG (Continuum PL DLS 8000) pumped dye laser (Sirah CBST-G-24) operating on the dye DCM:LDS698=1.5:1 with the subsequent doubling of the dye laser output in a BBO crystal, which gave about 4–5 mJ/pulse around 333.5 nm. After ionization, the CH₃⁺ ions were accelerated to an imaging microchannelplate (MCP) detector, gated to respond only to this mass. The timing of the pulsed molecular beam nozzles, the firing of photolysis, probe lasers, and detector gate pulse was controlled by using a delay generator (BNC 555). The resulting image was recorded using a charge coupled device (CCD) camera (scA780-54gm). The accumulation of the image took about 0.5–2 h to reach a satisfactory signal to noise ratio.

Figure 6 shows typical velocity map images of the CH₃ products resulting from the CH₃I photodissociation at 252 nm for selected droplets sizes. The photofragments, CH₃ radicals were state selectively ionized by the well-characterized (2+1) REMPI around 333.5 nm. The ground states of CH₃ images reveal that the surrounding helium atoms affect both the speed and angular distributions of the photofragments. Comparing with the well studied gas phase results, the speed distributions derived from accumulated images indicate that most of the mean kinetic energy releases (>95%) was relaxed by the helium atoms. With the increasing of the droplets sizes, the fraction of the...
relaxed mean kinetic energy increased, as shown in Fig. 7(a). Figure 7(b) shows that the anisotropy parameters vary with the photofragment speeds. In contrast to the mean kinetic energy releases, the angular distributions show no significant difference in the medium size droplets even though the anisotropic parameters from the doped helium droplets photodissociation are significantly lower than that from the averaged gas phase value. Previous studies indicate that the speed and angular relaxations are strongly mass dependent, which are simulated by classical Monte Carlo calculations based on a binary hard-sphere scattering model [15]. Qualitatively the present experimental results agree well with the previous results.

As an idea cryogenic matrix, helium droplets were widely used on the spectroscopy studies. Most of conventional continuous-flow helium droplets instruments used the quadruple mass spectrometer as the probe. After picking up one or more molecules the doped droplets are exposed to the laser beam. The energy deposited in the droplets following resonant absorption of a laser photon leads to the evaporation of He atoms. The decrease in the overall size of the droplet reduces the electron-impact ionization cross section. The mass spectrum shows a distinct dip at resonance, which is called a “depletion” spectroscopy. The modified version of the helium droplets depletion spectrometer used a liquid helium cooled bolometer instead of a mass spectrometer to monitor the laser induced depletion of the beam intensity. Despite the importance, there is no depletion spectroscopy study carried on the pulsed helium droplets apparatus, even though the first pulsed droplets beam has been constructed in 2002. The stability of the pulsed droplets beam and probe technique could be the bottleneck. Here we demonstrated the ability of the new constructed pulsed helium droplets machine to perform the depletion spectroscopy study. Combined the time of flight mass spectrometer with commercial pulsed lasers, we studied the depletion spectroscopy of benzene doped in helium droplets, as shown in Fig.8. The absorption spectrum of benzene doped in droplets is recorded by the photofragment C₄H₃ which is produced by dissociation of benzene followed by the resonance absorption of benzene. The depletion spectrum of benzene doped droplets is shown by recording the benzene parent ion mass spectrum with the scanning of laser wavelengths. It is clear to see that more than 20% depletion was achieved in the benzene doped droplets system. Moreover, the experimental results show that less than 3% depletion could be observed by the new constructed machine. The detailed interaction of benzene with finite-sized superfluid helium system will be described elsewhere.

In the present work, we constructed a pulsed helium droplets machine. The distribution of helium droplets is uniform under certain experimental conditions. The measured beam intensity is at least one order of magnitude higher than the continuous-flow helium droplets beam at the same experimental conditions. The average size of helium droplets between 10³ and 10⁵ atoms could be controlled by continuously changing the valve temperature from 10 K to 30 K and stagnation pressure.
between 10 and 40 bar. By combining the pulsed helium droplets with the ion imaging technique, we studied the photodissociation dynamics of the CH$_3$I doped helium droplets. The results show the clear evidence of the speed and angular relaxations inside of the helium droplets. The first pulsed helium droplets depletion spectroscopy was also demonstrated. The performance check implies that the application of the technique could be widely extended by combining with the pulsed laser to study the molecular spectroscopy inside the superfluid environment. As an idea cryogenic nano reactor, the helium droplets may be used to study the photochemistry and photon induced chemical reactions inside of the finite sized superfluid helium which are more related to the chemistry in the atmosphere and interstellar medium. It looks promising that the technique has fascinating prospects on the ultra cold chemistry, novel material, and nano catalysis studies.

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