

Communication: Electron diffraction of ferrocene in superfluid helium droplets

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We report electron diffraction of ferrocene doped in superfluid helium droplets. By taking advantage of the velocity slip in our pulsed droplet beam using a pulsed electron gun, and by doping with a high concentration of ferrocene delivered via a pulsed valve, we can obtain high quality diffraction images from singly doped droplets. Under the optimal doping conditions, 80% of the droplets sampled in the electron beam are doped with just one ferrocene molecule. Extension of this size selection method to dopant clusters has also been demonstrated. However, incomplete separation of dopant clusters might require deconvolution and modeling of the doping process. This method can be used for studies of nucleation processes in superfluid helium droplets. *Published by AIP Publishing*. [http://dx.doi.org/10.1063/1.4953250]

INTRODUCTION

Gas phase electron diffraction (GED) has long been a high precision structural tool, with resolutions on the order of hundredths of Angstroms, thanks to the much shorter wavelengths and the much larger diffraction cross sections of high energy electrons than those of x-ray photons.¹ In recent years, GED has been adapted for time-domain investigations of structural evolutions of photochemical reactions.^{2,3} The large scattering cross sections of electrons, however, have also limited the penetration depth of an electron beam; hence, for condensed phase studies in the transmission mode, electron diffraction is only applicable for ultrathin samples. Incidentally, the nucleation or condensation process of vapor phase molecules produces nanoscale naturally thin samples, and hence electron diffraction is ideally suited for studies of structural evolutions of nanomaterials.

Superfluid helium droplets have recently been recognized as an interesting medium for nucleation events,^{4,5} and a flurry of activities in growing esoteric species in superfluid helium droplets have been reported.^{6,7} Although one of the initial motivations was to use the dopant atoms as probes for vortices in droplets,^{8,9} the field has recently expanded to potential means of producing core-shell structures of nanomaterials.¹⁰ Characterization of the resulting solid structure has so far relied on depositing doped droplets on a substrate and then analysis using transmission electron microscopes. The post deposition analysis procedure reveals the final product of doping, after evaporation of helium and after equilibration with the substrate, without information of the nucleation process.

Here we report a possible approach to perform electron diffraction of size selected doped droplets, with the potential of obtaining structures of doped droplets prior to deposition. Unlike spectroscopic studies where the excitation and detection methods are intrinsically sensitive to only doped droplets, electron diffraction is sensitive to all particles in an electron beam, including undoped droplets. Thus incorporation of superfluid helium droplets for diffraction also comes with a price: the helium jacket has to be thin enough not to generate a substantial background.¹¹ In addition, undoped droplets, a byproduct of incomplete doping, are also problematic.¹² In our previous work, we have demonstrated that by increasing the number of doped molecules per droplet, we can overcome the background issue, and that our diffraction pattern contains definitive contributions of dopant monomers, dimers, and trimers.¹² We have also performed a thorough investigation of the size distribution and doping statistics of our droplet beam.¹³ This observation has led us to a proposal of achieving diffraction of singly doped droplets without the interference of dopant clusters. Here we demonstrate this idea using electron diffraction of ferrocene. Different from other experiments of neutral dopants, we have used a pulsed valve to deliver gas phase ferrocene. Our diffraction image shows only contributions from ferrocene monomers, and our analysis reveals that more than 80% of the droplets in the diffraction region contain exactly one dopant molecule. The agreements between experimental and calculated diffraction patterns and pair correlation profiles are exceptional.

EXPERIMENTAL SETUP

We have used two pulsed valves for droplet formation and for sample doping, and the overall setup is shown in Figure 1. Details of the helium droplet source and the gas phase electron diffraction system have been described in our previous publications.^{11,12,14} Superfluid helium droplets were formed by supersonic expansion of precooled ultrapure helium (99.9995%) from an Even-Lavie pulsed valve (referred to as the droplet PV in the following). The droplet beam was further collimated by a skimmer with an orifice of 2 mm in diameter about 11 cm downstream from the droplet PV. In the doping chamber, another pulsed valve (Parker, series 9, referred to as the sample PV) with a homemade nozzle housed the ferrocene

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FIG. 1. Experimental setup showing the two pulsed valves, one for generation of superfluid helium droplets, and the other for release of gaseous ferrocene.

sample and was heated to 73 °C. The sample PV was located 10 cm downstream from the opening side of the skimmer and 5 mm away from the center of the traversing droplet beam. Without any carrier gas, the sample PV produced diffusive sample molecules permeating the pickup chamber. Doping of ferrocene was confirmed from the observation of $\text{Fe} \cdot \text{He}_n$ clusters, following the procedure detailed in Ref. 14. The sample PV and the electron gun were operated at 14 Hz, while the droplet PV ran at half the frequency, and the difference image obtained when the droplet PV was on and off was the net image from the droplets, with or without dopant. This "toggle" mode of operation effectively removes the contribution from diffused bare sample into the diffraction region, thus any molecular diffraction should be related to the sample in the droplet beam.

To obtain diffraction from only singly doped droplets, we relied on our knowledge of the characteristics of the droplet beam and the doping statistics.¹³ Since the opening time of the droplet PV is much shorter than the traveling time to the detection region, we can consider that all droplets are formed at the same time. Smaller droplets travel faster and arrive at the diffraction region earlier, and limited by their capacity to absorb the heat and momentum of a dopant molecule, they are also only capable of carrying just one dopant molecule into the diffraction region. On the other hand, if the doping process is sufficient, all droplets can be doped with at least one dopant molecule. Thus by timing the pulsed electron gun at the leading edge of the doped droplets, we can sample only singly doped small droplets.

To implement the above idea, several experimental conditions have to be fulfilled. Efficient doping requires sufficient doping pressure and path length. The extensive doping condition also causes diffusion of gaseous dopant molecules into the diffraction region, which requires background subtraction. To minimize diffusion and to limit the gas load in the doping chamber, pulsed delivery of dopant is therefore highly preferred. Consequently, the relative timing between the two pulsed valves becomes an important factor. A shorter delay results in a lower doping pressure when the droplet beam traverses the doping chamber, hence a limited percentage of droplets should be doped. Too long a delay also results in a missed time window for effective doping, since most dopant molecules should have been pumped out.

RESULTS AND ANALYSIS

The diffraction pattern from ferrocene doped droplets is a combination of diffractions from ferrocene molecules, the helium jacket outside the dopant molecule, undoped helium droplets, and background from the residual gas in the diffraction chamber. Typical gas phase experiments are expressed in terms of modified molecular scattering intensity sM(s), where s is the momentum transfer defined as¹

$$s = \frac{4\pi}{\lambda}\sin(\frac{\theta_d}{2}),\tag{1}$$

where λ is the de Broglie wavelength (0.06 Å at 40 keV) and θ_d is the diffraction angle. Each unique pair of atoms (correlated pair) generates a set of rings for randomly oriented samples, and only the interference of correlated pairs contains the structure information of the sample. To magnify the structural information, in typical GED, the sM(s) profile removes all contributions from atoms and background, and the remaining molecular interference is further magnified by the momentum transfer *s*,

$$sM(s) = \frac{A_s \cdot I_{total}(s) - A_d \cdot I_{droplet(s) - A_b \cdot I_{background}(s)}}{I_{T,at}(s)} \cdot s - s,$$
(2)

where $I_{total}(s)$, $I_{droplet}(s)$, and $I_{background}(s)$ are intensities from the experiment of doped droplets, pure droplets, and background, A_s , A_d , and A_b are the corresponding fitting parameters, $I_{T,at}(s)$ is the theoretical diffraction intensity from the atoms of the dopant molecule. The values of $I_{total}(s)$, $I_{droplet}(s)$, and $I_{background}(s)$ are from the experiment directly obtained from the diffraction image, and $I_{total}(s)$ and $I_{droplet}(s)$ are obtained under the same experimental conditions with the sample PV on and off respectively. Since the quantity sM(s) should contain only molecular interference from atoms of ferrocene, all contributions from helium atoms should be removed in Eq. (2), and the ratio A_d/A_s should reflect the ratio of the number of helium atoms after doping to that without doping. The calculation method for $I_{T,at}(s)$ and for the theoretical values of the modified molecular scattering intensity sM(s) has been explained in the supplementary material of our previous publication.11 Different from our previous work on CBr₄, the above equation does not include any contribution from dopant clusters.

The bottom panel of Figure 2 shows the radial distributions directly obtained from an image accumulated from 200 000 shots. The electron gun had a current of 1 mA and a duration of 10 μ s, and its timing was set to sample droplets with about 2000 atoms/droplet.¹³ We divided the raw image into four nearly equal quadrants, using the support of the Faraday cup—a strip on the image—as one of the dividing lines. The average of the four quadrants was used to generate



FIG. 2. Electron diffraction of ferrocene doped droplets. The left half of the image is the averaged experimental data after removing the contribution of helium, and right half is the simulation result based on the known molecule structure of ferrocene. The bottom panel is the radial profile from an accumulated image of 200 000 shots, with and without dopant, and the difference between the two profiles.

the radial profile. The difference between the profiles from the doped sample and the pure droplet background shows a large modulation in the bottom panel of Fig. 2. Using these profiles as the intensities of Eq. (2) and based on comparisons with the theoretical sM(s),¹⁵ we performed multilinear regression to obtain the coefficients of each component A_s , A_d , and A_b . The left half of the image shown in Fig. 2 is the difference image after removing the contribution of pure droplets based on the obtained coefficients. The right side of the image is the theoretical calculation. The agreement between theory and experiment is quantitative, and the fitting has a coefficient of determination (R²) of 0.92.

To analyze the doping condition, we performed the experiment under different delay times between the two pulsed valves. Table I shows the fitting results from images obtained under different time delays. For each delay, 70 000 to 100 000

TABLE I. Fitting results at different delay times between the two pulsed valves.

Delay (µs)	500	1000	1200	4000
$\overline{A_d/A_s}$	0.16	0.04	0.04	0.10
I_F/I_{He}	0.11	0.26	0.49	0.20
n_{He}/n_F	2400	1015	539	1320
Pressure (Torr)	$6.6 imes 10^{-5}$	1.1×10^{-4}	1.1×10^{-4}	$8.1 imes 10^{-5}$
$P_1/(P_0 + P_1)$	0.72	0.81	0.81	0.76

images were accumulated, and the sample PV was kept at a duration of 280 μ s. In all cases, the fitting parameter of the background A_b only accounts to less than 1% of the total diffraction signal A_s . At delay times between 1000 and 1200 μ s, the number of helium atoms in the doped droplet beam is reduced to only 4% of their number in a pure droplet beam (A_d/A_s). The intensity ratio between ferrocene and helium in the overall diffraction signal of the doped droplets I_F/I_{He} can then be derived from

$$\frac{I_F}{I_{He}} = \frac{A_s \cdot I_{total}(s)}{A_d \cdot I_{droplet}(s)} - 1,$$
(3)

since the contribution of the background is negligible. Although the values of the experimental diffraction intensities I_{total} and $I_{droplet}$ are dependent on the momentum transfer, their ratios only vary slowly in the range of 1.2 and 6 Å⁻¹, and an average value is listed in Table I. We notice that the helium content is the same for the two central columns, but the intensity ratio is quite different. These two sets of data were recorded in two different days, with perhaps slight variations in the experimental conditions. It is therefore likely that a slightly different size or size distribution contributes to the marked difference, since the sampling method is critically dependent on small sized droplets.

To further obtain the number ratio of helium atoms vs. ferrocene molecules $n_{\rm He}/n_{\rm F}$, a ratio of the diffraction cross sections is required, which depends greatly on the *s* number. If we only take into consideration the atomic component of the diffraction cross section and ignore the modulation of molecular diffraction, the ratio of the total cross section is 264.¹⁶ The numbers listed in Table I are therefore only qualitative. In theory, this number ratio should have a lower limit determined by the number of the remaining helium atoms after picking up one ferrocene molecule. From Table I, at a shorter delay between the two PVs, there are more than 2000 helium atoms for every ferrocene molecule, but as the delay increases, a higher pressure build-up is achieved, and the number of helium atoms decreases, mostly due to the increase in the number of doped droplets. At a much longer delay, the number of helium atoms increases again.

Due to the transient nature of the doping process, we could not measure the actual pressure in the doping region. However, based on the Poisson pickup statistics¹⁷ and the fitting results A_d/A_s , we can determine the average number of effective collisions between ferrocene and droplets, assuming that trapping of one ferrocene molecule results in a droplet size change from 2000 to 800 (the average of the two middle columns in Table I). For an ideal gas at 346 K over an

estimated path length of 5 cm, we can then calculate the equivalent pressure for doping, and then the probability of picking zero (P_0) and one (P_1) ferrocene molecules. Further assuming that there are no droplets containing two or more ferrocene molecules in the diffraction region, we can then calculate the fraction of singly doped droplets.

Table I shows that at delays of 1000 and 1200 μ s, more than 80% of the droplets are singly doped. It is worth noting that under these doping conditions, for a droplet of size 2000, only 7% are doped with one ferrocene molecule and 2% are undoped, while the remaining 91% are destroyed because of further collisions with dopant molecules.

The above results also imply that regardless of the doping pressure, as long as the contribution of helium atoms can be effectively removed according to Eq. (2), there is no essential difference between the resulting sM(s) profile. Hence the images obtained from the last three columns were added to improve the signal-to-noise ratio of the final result shown in Fig. 2. The data from the first column were not used because of its low ferrocene content. The excellent quality of the fitting procedure also confirms the hypothesis on the sampling condition: in all delay conditions, only singly doped droplets are sampled in the experiment, with no detectable contributions from ferrocene dimers.

Inverse Fourier transform of the modified molecular scattering intensity results in the pair correlation function, which peaks at the unique atomic pairs in the molecule. Figure 3 shows the experimental and theoretical sM(s) profiles and the pair correlation functions obtained from Figure 2 and from known molecular structures.¹⁸ Contributions from hydrogen pairs are neglected because of their low intensity. The strongest contribution in the pair correlation profile is from the Fe···C pair, followed by intra-ring carbon pairs. The longer distance carbon pairs between different rings constitute the minor ring. It is worth noting that the contribution from C—H pairs constitute a shoulder in the profile, certainly not negligible at our level of signal-to-noise ratio.

Gas phase ferrocene is known to be in the eclipse conformation for the two pentacene rings.¹⁵ Unfortunately, to resolve the relative conformation between the two rings, a larger range of momentum transfer is required. This is because the difference between the staggered and the eclipsed conformations is in the inter-ring C···C pairs, which has distances of 3.32, 3.62, 4.06 Å in the eclipsed form and 3.40, 3.87, 4.13 Å in the staggered form.¹⁸ To resolve such a difference from the diffraction pattern, the range of *s* values needs to exceed 12 Å⁻¹.

This work demonstrates the feasibility of sampling only singly doped droplets. To extend the methodology to clusters of dopant molecules, a delay in the electron gun relative to the droplet PV is necessary so to sample larger droplets capable of picking up more dopant molecules. To further increase the flux for larger sized droplets, a concurrent decrease in the source temperature of the droplet beam should be beneficial. Unfortunately limited by the cooling capacity of our cryostat and the large heat capacity and linear momentum of ferrocene, experimental demonstrations of this idea using ferrocene are still challenging. However, in our previous work on CBr₄,¹² even under the same conditions as those of the



FIG. 3. Modified molecular scattering intensities (a) and pair correlation profiles (b) of doped ferrocene. Contributions from relevant unique atomic pairs are indicated as sticks, and the numbering scheme is shown in the inset. The residual between experiment and theory is also shown in the bottom of the profile.

current experiment, we have observed significant contributions from dimers and trimers of CBr₄.

Several factors determine the degree of size selection via velocity slip,^{13,19} including the physical and chemical properties of the dopant and the dimension and performance of the experimental apparatus. The current approach hence is not "one-size-fits-all", and in many cases, statistical analysis and deconvolution procedures will be necessary.

In summary, we have achieved electron diffraction of singly doped superfluid helium droplets. The background issue from undoped droplets and excessively large droplets was resolved by sufficient doping of the droplet beam, and size selection was achieved by taking advantage of the velocity slip among different sized droplets. Exact timing of the electron beam and effective background subtraction were two of the key factors for the success of this experiment. This method can be extended to studies of dopant clusters, as demonstrated in our previous work on CBr₄ dimers and trimers, but the size resolution could be limited in some cases.

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