Electron diffraction of CBr_4 in superfluid helium droplets: A step towards single molecule diffraction

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We demonstrate the practicality of electron diffraction of single molecules inside superfluid helium droplets using CBr_4 as a testing case. By reducing the background from pure undoped droplets via multiple doping, with small corrections for dimers and trimers, clearly resolved diffraction rings of CBr_4 similar to those of gas phase molecules can be observed. The experimental data from CBr_4 doped droplets are in agreement with both theoretical calculations and with experimental results of gaseous species. The abundance of monomers and clusters in the droplet beam also qualitatively agrees with the Poisson statistics. Possible extensions of this approach to macromolecular ions will also be discussed. This result marks the first step in building a molecular goniometer using superfluid helium droplet cooling and field induced orientation. The superior cooling effect of helium droplets is ideal for field induced orientation, but the diffraction background from helium is a concern. This work addresses this background issue and identifies a possible solution. Accumulation of diffraction images only becomes meaningful when all images are produced from molecules oriented in the same direction, and hence a molecular goniometer is a crucial technology for serial diffraction of single molecules. *Published by AIP Publishing.* [<http://dx.doi.org/10.1063/1.4958931>]

I. INTRODUCTION

Single molecule diffraction has been considered the ultimate promise of overcoming the difficulty of crystallization in protein crystallography.^{1,2} The much weaker diffraction signal from single molecules, as compared with single crystals (even nanocrystals), is to be compensated for by the newly available intense ultrashort x-ray pulses from free-electron lasers. However, the ultimate limit on single molecule diffraction is not imposed by the available facility, but rather by the molecules, i.e., the internal potential of the molecular system, since the probe has to be at the largest perturbation to the molecular Hamiltonian.³ Alternatively, electron diffraction of a stream of identically oriented single molecules allows accumulation of images for the desired signal-to-noise ratio; hence, this method has much milder requirements on the light source and the detector.⁴⁻⁶ Moreover, using DC or laser fields, several groups have demonstrated orientation of gas phase molecules.⁷⁻¹⁰ The thus obtained molecular goniometer relies on the interaction between the electric field and the permanent dipole (DC field orientation) or polarizability anisotropy (laser induced alignment) of the molecule, to overcome the rotational energy of the molecule. Unfortunately, adaptation of these gas phase methods for macromolecular protein ions is subject to the constraints of the sample's high fragility and low volatility. Supersonic molecular beams are inefficient in cooling the massive protein molecules from either a laser desorption ionization source¹¹ or an electrospray ionization

(ESI) source.^{12,13} Superfluid helium droplets with a terminal temperature of 0.38 K and a frictionless environment thus emerge as an ideal coolant.¹⁴ Moreover, efficient interface of a superfluid helium droplet source with an electrospray ionization source has already been demonstrated in more than one laboratory.¹⁵⁻¹⁷ A price for the extreme cooling of superfluid helium droplets, on the other hand, is the diffraction background from helium atoms of the droplet beam.¹⁸ The central issue is therefore the possible existence of an experimental condition where the droplet size is small enough or the sample concentration is high enough that molecular interference from the sample molecules is still observable above the atomic diffraction background of the helium atoms.

Here we demonstrate the feasibility of electron diffraction of molecules embedded in superfluid helium droplets. By varying the degree of doping and modeling the role of undoped droplets in the diffraction process, we conclude that the most important contributor of the diffraction background is the undoped droplets. For neutral dopants, this issue can be resolved by increasing the concentration of dopant molecules in the droplet beam, thereby producing droplets doped with multiple dopant molecules, as long as intermolecular diffraction from dimers and trimers can be accounted for. This approach has the added bonus of thinning the surrounding helium jacket to a negligible level for the doped molecules. Compared with our previous report on phthalocyanine gallium chloride (PcGaCl),¹⁸ this work identifies a crucial factor in extending the technology from gaseous species to macromolecular ions. The newly obtained quantitative information enables us to estimate the recording time for macromolecular ions based on a desired resolution.

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II. EXPERIMENTAL SETUP

Details of the experimental setup are described in the supplementary material.¹⁹ The droplet source is pulsed and the pulsed valve is kept at 18 K with a stagnation pressure of 50 atm. The droplet beam passes through a doping region filled with CBr₄ and picks up one or more dopant molecules.²⁰ In the diffraction region, a synchronized pulsed collimated electron beam spatially and temporally overlaps with the doped droplets, and the resulting diffracted electrons are detected by a phosphor screen and a camera. A background image is measured between two consecutive droplet pulses, and the images from the droplet pulse and from the background are accumulated separately in a computer. The difference between the two accumulated images is the net diffraction from the droplets, with and without dopant. Hence the effective repetition rate of the overall experiment is 5 Hz, while the data acquisition rate of the camera is 10 Hz.

To characterize the droplet beam and its doping conditions, two time-of-flight mass spectrometers are used, one in-line with the droplet beam located at the exit of the diffraction chamber and the other perpendicular to the droplet beam located below the diffraction region.²¹ Relying on electron impact ionization (EI) and non-resonant multiphoton ionization (MPI), we have determined that the most probable size of our droplet beam is ~2000 helium atoms/droplet, in agreement with the general result by Gomez *et al.*²² We have also determined that doping of one CBr₄ molecule requires evaporation of ~600 helium atoms.²³ An important feature of the pulsed droplet beam is velocity slip among different sized droplets: the overall droplet beam spans over 200 μ s in the diffraction region, but depending on the timing of the ionization laser, different sized droplets are sampled in the MPI experiment.

III. RESULTS

Gas phase electron diffraction of randomly distributed molecules is typically plotted on the scale of momentum transfer s defined as²⁴

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

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 the structure-sensitive component is typically expressed in terms of a modified molecular scattering intensity $sM(s)$,

$$sM(s) = \frac{sI_{mol}(s)}{I_{at}(s)} = s \frac{I_{tl}(s) - I_{at}(s)}{I_{at}(s)} = s \frac{I_{mol}(s)}{I_{at}(s)} - s, \quad (2)$$

where contributions of all the atoms of the diffractive species are collectively represented by $I_{at}(s)$, the coherent sum of diffractions from each correlated pair is represented by $I_{mol}(s)$, and the total diffraction intensity $I_{tl}(s)$ includes both atomic and molecular diffractions.

Compared with typical gas phase electron diffraction experiments,²⁴ our diffraction pattern contains contributions not only from the sample molecule but also from the surrounding helium atoms and small molecular clusters due to multiple doping of one droplet. The relative contributions of these effects depend on the experimental conditions, including the pressure and path length of the doping region and the droplet size, and hence the pressure and temperature of the pulsed valve. We compare the theoretical modified molecular scattering intensity $sM(s)$ of CBr₄ and the experimental data using the equation

$$sM(s) = \frac{A_s \cdot I_{total}(s) - A_d \cdot I_{droplet}(s) - A_b \cdot I_{background}(s) - C_c \cdot I_{T,c}(s)}{I_{T,at}(s)} \cdot s - s + C, \quad (3)$$

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,¹⁸ and C is for baseline correction. Parameters C_c and $I_{T,c}(s)$ are related to multiply doped CBr₄. Among contributions of intermolecular atomic pairs from clusters, the most intense should come from Br...Br pairs, and the most prominent in the diffraction image should be from the shortest Br...Br intermolecular pairs. This is because the most intense contributions from other longer distance pairs are distributed closer to the Faraday cup and are hence blocked out by the cup and its halo. In Eq. (3), $I_{T,c}(s)$ is the theoretical diffraction profile of the shortest Br...Br pair with a separation of 4 Å,^{25–27} and C_c is the

weight of the theoretical contribution of the cluster in the overall diffraction. The quantities I_{total} , $I_{droplet}$, and $I_{background}$ are experimental values directly from the diffraction image, and both I_{total} and $I_{droplet}$ should contain some degrees of $I_{background}$. In particular, I_{total} and $I_{droplet}$ are obtained under the same exposure conditions, thus independent variations of A_s and A_d in Eq. (3) allow adequate account for the difference in flux between the doped droplet beam and the undoped droplet beam, and loss of helium atoms due to doping. The quantity of $I_{T,c}$, on the other hand, is a theoretical value from calculation.¹⁸ Thus while C_c represents the contribution of clusters relative to that of monomers, the contribution of undoped (pure) droplets to the overall signal should be A_d/A_s .

The inset of Figure 1 shows the diffraction image and radial profile after quadrant averaging, Wiener filtering,²⁸ and

FIG. 1. Radial profiles relevant to diffraction from CBr_4 doped superfluid helium droplets. The inset shows the image after treatment using the Wiener filter and after removing contributions from molecular clusters assuming a $\text{Br} \cdots \text{Br}$ pair with a separation of 4 Å. The profile “Exp w/o $\text{Br} \cdots \text{Br}$ ” was obtained by subtracting the theoretical contribution from clusters (“ $\text{Br} \cdots \text{Br}$ Calculation”) from the overall experimental profile (“Total Exp”), which should be compared with the theoretical profile from CBr_4 including both atomic and molecular contributions (“ CBr_4 Calculation”).

removal of intermolecular diffraction from CBr_4 clusters. The corresponding raw images are shown in the supplementary material.¹⁹ The radial profiles of different components are shown in the main part of Fig. 1. There the total experimental radial distribution (“Total Exp”) is compared with the scaled theoretical contribution of clusters in the form of $\text{Br} \cdots \text{Br}$ interference denoted “ $\text{Br} \cdots \text{Br}$ Calculation,” and the difference between the experimental data and this theoretical component is labeled as “Exp w/o $\text{Br} \cdots \text{Br}$.” The latter profile should be compared with the theoretical diffraction profile labeled as “ CBr_4 Calculation.” The halo of the Faraday cup is not included in the profiles. The experimental corrected radial profile contains one clearly observable ring, corresponding to the feature at $s = 2.5 \text{ Å}^{-1}$ and a weaker feature at about 4.3 Å^{-1} .

We have also recorded gas phase electron diffraction images of CBr_4 by injecting the gaseous sample through a needle positioned directly in place of the droplet beam. The radial profiles and the corresponding pair correlation functions are shown in Fig. 2, and they are both similar to those from a previous report²⁹ (not shown in Fig. 2). It is important to note that the “doped” trace in Fig. 2 is the net difference recorded with and without the droplet beam, while the doping chamber was maintained at a constant pressure. Contributions from the diffused gas in the trace of the “doped” sample are therefore removed. Nevertheless, the doped sample shows a similar diffraction profile as the gaseous sample, and both experimental results are similar to the theoretical calculation.¹⁸ Although the gaseous sample was at room temperature while the doped sample was at 0.38 K, the predominant factor that determines the width of each interference ring is the wave physics, not the vibrational movement of the atoms in a molecule.²⁴ Evidently the superfluid helium environment

FIG. 2. Comparisons of results from gaseous and doped CBr_4 with theoretical calculations: (a) molecular diffraction profiles $sM(s)$, and (b) pair correlation functions.

exerts negligible perturbation to the enclosed molecular structure. The weak features near the major features centered at 4.5 and 6.5 Å^{-1} in the $sM(s)$ profile from the doped sample could be due to residual contributions from clusters of CBr_4 . The same argument is applicable to the pair correlation profiles, where the profile from the doped sample also contains an extra shoulder near 4 Å.

Different from a diffused sample, however, a droplet can pick up a number of molecules k with a probability P_k ,^{21,23} thus diffraction of the droplet beam contains contributions from dopant clusters as well as undoped pure droplets. The contribution of pure droplets from the fitting of Eq. (3), A_d/A_s , should be proportional to P_0 , the probability of not picking up any dopant. The contribution of dopant molecular clusters C_c should be proportional to the ratio between the number of intermolecular $\text{Br} \cdots \text{Br}$ pairs with a separation of 4 Å and the average number of dopant molecules in a droplet $\langle k \rangle$,

$$\langle k \rangle = \sum_k k \cdot P_k. \quad (4)$$

If we assume that the electron gun samples the most probable size of the droplet beam of 2000, then there should be at maximum 3 dopant molecules in a droplet. Since there are 3 equivalent $\text{Br} \cdots \text{Br}$ pairs with a separation of 4 Å in a dimer and 4 such pairs in a trimer,²⁷ the value of C_c should be proportional to $(3P_2 + 4P_3)/\langle k \rangle$.

To model the doping statistics, we have to take into consideration the polydispersity of the droplet beam. Fortunately, the velocity slip among different sized droplets and the limited duration of the electron beam (16 μs) determines that the electron beam only samples droplets in a limited size range, and for simplicity, we only need to consider one group of fixed sized droplets, similar to our previous work on EI and MPI of doped droplets.²¹ Depending on the relative timing of the electron beam to the droplet beam, different sized droplets are sampled. We do not have the direct information on the size of the sampled droplets of this experiment; however, based on the MPI experiment,²¹ we are certain that the droplet

size sampled in the diffraction experiment should be smaller than the average size of the droplet beam. Thus we choose the most probable size in modeling the doping statistics. In addition, we have also discovered that the actual size does not affect the qualitative conclusion of the calculation within a range of 1800–3000 atoms/droplet, given the uncertainty of the experimental data.

Figure 3 compares the experimental fitting results with the Poisson statistics. Fig. 3(a) shows the contribution of pure undoped droplets relative to that of doped droplets, and the ratio (vertical axis) is expected to be proportional to the probability of undoped droplets. At a doping pressure of 1×10^{-5} Torr, less than 15% of the droplets are undoped, and this value is reproduced from the experimental fitting value of A_d/A_s . With increasing doping pressure, more and more droplets are doped, and the portion of undoped pure droplets decreases accordingly. At the lowest doping pressure, the error bar is considerably large and a disagreement exists. We attribute this point to the residual gas in the doping chamber since the base pressure in the doping chamber without any doping gas was 1×10^{-6} Torr.

A coincidence in the diffraction cross section plays a role in the agreement of Fig. 3(a) at higher doping pressures, even though the doped droplets are smaller than the undoped droplets under the same droplet source conditions. The adsorption of one CBr_4 molecule removes 600 helium atoms from the surface of the droplet,²³ and incidentally, at the electron wavelength of 0.06 Å, the total atomic diffraction cross section of one CBr_4 molecule is roughly the same

as those of 600 helium atoms.³⁰ Hence the experimental diffraction intensities of doped droplets and pure droplets are not substantially modified by the change in size due to sample pickup.

Fig. 3(b) compares the contribution of clusters calculated using $(3P_2 + 4P_3)/\langle k \rangle$ (designated as “Cluster” in the figure) based on the Poisson statistics^{20,21} with the experimental fitting value for clusters C_c . At a doping pressure of 1×10^{-5} Torr, contributions of clusters relative to those of monomers is slightly more than 1:1, and this ratio increases to 1.3:1 at higher doping pressures. This upper limit is attributed to the maximum number of molecules that an average sized cluster can pick up before it is destroyed completely. The coefficients of P_2 and P_3 in the expression $(3P_2 + 4P_3)/\langle k \rangle$ do not play a critical role when varied between 3 and 6: they only affect the scaling of the profile, not the general trend.

IV. DISCUSSION

The above comparison highlights the crucial issue in using superfluid helium droplets as an ultra-cold gentle matrix for electron diffraction from field aligned and/or oriented molecules, i.e., the helium background. In our previous work on phthalocyanine gallium chloride,¹⁸ we were limited by the experimental condition to only explore the regime of low doping pressures. However, based on the Poisson model, if the doping pressure in an oven of 2.5 cm (from our experiment of PcGaCl , different from the current doping cell) is 1×10^{-5} Torr, more than 82% of the droplets will not pick up any number of molecules and will only contribute to the monotonic background in the diffraction pattern. This large unwanted diffraction intensity can potentially overwhelm the detector. This issue should be much more severe for an ion doped droplet beam since the equivalent vapor pressure of ions at the space charge limit is only 10^{-9} Torr;¹⁵ hence, more than 99% of the droplets contain no protein ions at all even in the unrealistically favorable assumption of Poisson statistics.³¹ Under low doping conditions, it is therefore the presence of undoped droplets that will dominate the background, and hence elimination of undoped droplets is essential for reducing the background of helium.

To overcome this issue, neutral molecules can be heavily doped by increasing the doping pressure or path length as shown in Fig. 3(b), but this approach is complicated by the formation of clusters. Fortunately, contributions from clusters tend to be in the low s region close to the Faraday cup because of the longer distances between intermolecular pairs,³² and data in this region are fortunately either blocked by the Faraday cup or can be discarded during data processing. Moreover, by multiple doping, the size of a helium droplet is reduced, resulting in further reduction in the helium background.

For charged species, elimination of neutral undoped droplets from the charged doped droplets is straightforward using electric fields (magnetic fields are generally avoided because of the difficulty in field containment for electron diffraction). An ion doped droplet beam can be bent from the initial path via an electric field generated by a stack of electrodes in, for example, a reflectron type of design,

FIG. 3. Comparisons between Poisson statistics and experimental results. (a) Calculated probabilities of undoped droplets P_0 in a droplet beam and fitting results A_d/A_s from experiment. (b) Contributions of CBr_4 clusters C_c from experiment and calculated ratios of cluster and monomer contributions (designated as “Cluster”).

which also has the benefit of compressing the droplet pulse spatially and temporally. Alternatively, charged droplets can be accelerated or decelerated relative to the neutral undoped droplets, while the pulsed orientation laser and electron gun can be synchronized to interact only with the doped beam. Electrostatic steering has the additional benefit of size selection, which could be used to eliminate excessively large droplets due to their high helium content, hence the large background contribution. Moreover, collisional size reduction of neutral doped molecules has been demonstrated in the literature,³³ and its application to charged droplets has been successfully demonstrated in our own laboratory.

The quality of the diffraction signal in this experiment represents a major step forward compared with our previous work on PcGaCl .¹⁸ However, further improvements are needed to expand to diffractions of macromolecular ions. One such improvement is to expand the central region of the diffraction image since the diffraction intensity scales with s^{-4} . Experimentally this involves lowering the phosphor screen so to minimize the footprint of the Faraday cup. Based on Bragg's law, to determine a minimum distance (resolution) of 1.5 Å using a light source of 0.06 Å, the minimum diffraction angle should be 1.1°. The scale of Fig. 1 extends to a diffraction angle of 2.2° ($s = 8 \text{ Å}^{-1}$); hence, there is at least a factor of 10 to be gained in the diffraction intensity, if we were to reduce the data range to the minimum angle determined by the desired resolution. This measure also benefits detections of larger spatial dimensions, for example, macromolecules such as proteins, since a longer distance translates into a smaller diffraction angle and a smaller s number. Another improvement is in hardware, i.e., more gains are possible with improved electron detectors, and faster data acquisition at higher repetition rates can also speed up the experiment. For the latter, bigger vacuum pumps for the gas load and faster cameras for data transfer are both viable options. Altogether, Fig. 1 is the result of 460 000 shots, and to reach a resolution of 1.5 Å without any improvement in hardware, ~50 000 shots or 5000 s at 10 Hz are needed for each projection, and to reconstruct a 3-dimensional structure, several projections (hence hours) are necessary. To extend to macromolecular ions that suffer from the space charge limit in concentration, significant improvements in hardware, particularly repetition rates and electron detection efficiencies, are still needed. An advantage of macromolecular ions, on the other hand, is that they can be trapped in the diffraction region for a much longer time than the traveling neutral droplet beam, which could to some degree compensate for its low particle density.

The need of superfluid helium droplet cooling in single molecule electron diffraction is justified by the achievable spatial resolution via orientational control. At 0.38 K, a green fluorescing protein with a polarizability volume of 28 000 Å³ can be confined in a cone of 1° in a laser field of 10⁹ W/cm².⁶ This moderate requirement for such a high degree of alignment is only possible because of the superior cooling effect of superfluid helium droplets. Although background diffraction from helium poses a bigger threat in image contrast when only carbon, nitrogen, and oxygen atoms are present in proteins, the net charges on protein doped helium droplets

allow size selection and reduction using electrostatic fields thereby minimizing the unwanted helium content.

In conclusion, we have demonstrated the practicality of performing electron diffraction of molecules doped in superfluid helium droplets. We have learned that when the droplet size is controlled to a few thousand atoms, the major diffraction background is from helium atoms of undoped droplets. This problem can be solved by increasing the dopant concentration in the droplet beam for neutral molecules since the contribution of molecular clusters is largely limited to the central region of the diffraction image, in the shadow of the Faraday cup. This work confirms the practicality of using superfluid helium droplets for rotational cooling therefore the potential for field induced orientation in single molecule diffraction. The superior cooling capability of superfluid helium can significantly reduce the necessary field strength for effective orientation, particularly for macromolecules such as proteins. The thus obtained molecular goniometer should be applicable in serial crystallography, using either x-ray photons or electrons.

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¹⁹See supplementary material at <http://dx.doi.org/10.1063/1.4958931> for detailed experimental setup and raw images.

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