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### Permalink

<https://escholarship.org/uc/item/0416s8c6>

### Journal

The Journal of Physical Chemistry A, 130(1)

### ISSN

1089-5639

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### Publication Date

2026-01-08

### DOI

10.1021/acs.jpca.5c07766

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# **X-ray Coherent Diffractive Imaging of Large Helium Nanodroplets Doped with Small Molecules**

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## Abstract

We report the first X-ray coherent diffractive imaging experiment on molecule-doped helium nanodroplets. It complements previous work, where we reported single-shot X-ray coherent diffractive imaging studies of Xe dopant clusters formed in  $^4\text{He}$  and  $^3\text{He}$  droplets. These noble gas clusters were used to visualize the impact of rotational excitation of the droplets on the spatial distribution of atomic dopants within the droplets, and to study the differences and connections between quantum and classical droplet rotational motion. Here, we expand our studies to the molecular dopants  $\text{CF}_4$ ,  $\text{CHF}_3$ ,  $\text{CH}_3\text{CN}$ , and  $\text{SF}_6$ , imaged with 1.5 keV photons. We find multiple Bragg spots in the diffraction patterns of molecule-doped droplets with radii of approximately 600 nm, which provide evidence that molecules form elongated clusters with preferential alignment along the angular momentum axis of the  $^4\text{He}$  droplets, in agreement with our previous results on the aggregation of Xe clusters on quantum vortices. Real-space reconstructions of molecular dopant cluster density profiles are obtained for droplets with smaller radii of approximately 300 nm. The diffuse images suggest the formation of low-density, potentially porous, molecular clusters upon aggregation at  $T=0.4$  K in  $^4\text{He}$  droplets. In the normal fluid  $^3\text{He}$  droplets, molecules aggregate into loose clusters on the droplets' equator, similar to previous observations for Xe atoms. Time-of-flight mass spectra reveal that the doped helium nanodroplet moieties fragment extensively into constituent atomic ions, producing only a small fraction of molecular fragment ions. The findings are discussed in the context of previously proposed schemes to use He droplets as potential tamper materials for ultrafast X-ray imaging experiments.

## Introduction

Quantum fluid nanodroplets made of  $^4\text{He}$  are exceptional hosts for cryogenic matrix isolation applications.<sup>1-6</sup> The droplets readily pick up atoms and molecules and facilitate the formation of clusters at very low temperatures.<sup>7</sup> Several recent reports highlight these efforts, which interrogate the structures of metallic clusters,<sup>8,9</sup> pyrene nanoclusters,<sup>10</sup> and hydrogenated gold clusters within helium nanodroplets.<sup>11</sup> We previously demonstrated that noble gas clusters assembled in helium nanodroplets can be studied by ultrafast X-ray coherent diffractive imaging (CDI).<sup>12,13</sup> Our experiments revealed that in superfluid  $^4\text{He}$  droplets, Xe atoms cluster along the cores of quantum vortices, which result from droplet rotation.<sup>12-14</sup> Related experiments with non-superfluid, rotating  $^3\text{He}$  nanodroplets produced diffuse Xe aggregates that formed ring structures along the droplets' equator, as would be expected for a classical liquid drop.<sup>15,16</sup>

Concomitant experiments with molecules, rather than atoms, of various molecular sizes, shapes, and polarities can deepen our understanding of atomic and molecular self-assembly at ultra-low temperatures. At ambient temperatures, self-assembly is a process that is often dictated by thermodynamics, where aggregation evolves toward a structure with the smallest free energy. In this work, we explore the regime close to absolute zero temperature, which may enable the aggregation of novel structures such as fractals,<sup>17</sup> metastable chains of polar molecules (e.g., HCN),<sup>18</sup> or a cyclic form of the water hexamer,<sup>19</sup> which was previously detected spectroscopically for small clusters containing less than ten water molecules. In this regime, interparticle interactions should be dominant, whereas entropic effects will be negligible. Thus, weak intermolecular forces such as dipole-dipole interactions and/or hydrodynamic attraction by quantum vortices are expected to play a significant role in the resulting structures.

Here, we expand our X-ray CDI studies of doped helium nanodroplets to a variety of small molecular dopants,  $\text{CF}_4$ ,  $\text{CHF}_3$ ,  $\text{CH}_3\text{CN}$ , and  $\text{SF}_6$ , to explore their aggregation in superfluid  $^4\text{He}$  droplets as well as normal fluid  $^3\text{He}$  at low temperatures. In addition to the structure of the molecular dopant clusters, the experiment also aims at a better understanding of the fragmentation patterns of molecular clusters immersed in liquid helium droplets upon ionization with intense soft X-rays. To this end, the X-ray scattering measurements are complemented by the simultaneous acquisition of single-pulse ion time-of-flight (TOF) spectra, which provide information about the relative abundance of different ionic products resulting from the X-ray – cluster interaction.<sup>20</sup>

## Experimental

The experimental setup has been described elsewhere.<sup>3, 12, 16, 21</sup> Briefly, large helium-4 ( $^4\text{He}$ ) and helium-3 ( $^3\text{He}$ ) nanodroplets are produced by expanding pressurized  $^4\text{He}$  (99.9999%) or  $^3\text{He}$  (99.9%) fluid through a cryogenic nozzle (diameter = 5  $\mu\text{m}$ ) into vacuum with a stagnation pressure of  $P_0 = 20$  bar and a nozzle temperature of  $T_0 = 2 - 5$  K.<sup>3, 12, 16, 21</sup> The droplets studied in this work have average radii of 350 nm and 160 nm for  $^4\text{He}$  and  $^3\text{He}$  droplets, respectively.<sup>16</sup> An exponential droplet size distribution<sup>15, 16</sup> leads to the detection of the droplets with radii of 100 - 600 nm containing about  $10^8$  -  $10^{10}$  helium atoms. In vacuum, the droplets evaporatively cool to 0.38 K for  $^4\text{He}$  and 0.15 K for  $^3\text{He}$ .<sup>7</sup> At these temperatures,  $^4\text{He}$  is a superfluid, whereas  $^3\text{He}$  remains a normal viscous liquid. The droplets pass through a skimmer and subsequently through a pickup chamber, which is filled with the dopant gas. The level of doping is controlled by the pickup chamber pressure and estimated by the attenuation of the total flux of the He atoms in the droplet beam due to dopant-induced He evaporation, as measured by the corresponding He

pressure drop in the terminal vacuum chamber. The magnitude of this attenuation is proportional to the number of captured dopants, which is in the range of  $10^5$  -  $10^6$  particles. The number of helium atoms evaporated upon capture of the dopants is mostly derived from the kinetic energy of the dopants, internal rotational and vibrational energy of the molecules, and the sublimation enthalpy of the dopant solid.

The experiments are performed using the LAMP end station at the Atomic, Molecular, and Optical (AMO) instrument of the Linac Coherent Light Source (LCLS). Doped droplets are irradiated by a focused X-ray Free-Electron Laser (XFEL) beam operated at a wavelength  $\lambda = 0.826$  nm ( $h\nu = 1.5$  keV ).<sup>12</sup> The XFEL beam consists of ultrashort pulses ( $\sim 100$  fs FWHM), containing up to  $\sim 10^{12}$  photons/pulse, with a repetition rate of 120 Hz, and a pulse energy of  $\sim 1.5$  mJ, focused to a beam waist diameter of  $2\omega \approx 5$   $\mu\text{m}$ . The small pulse duration and large photon flux enable the instantaneous capture of diffraction images from individual, isolated doped droplets. Diffraction patterns are recorded with a *pn*-charge-coupled device (*pn*CCD) detector containing  $1024 \times 1024$  pixels, each  $75 \times 75$   $\mu\text{m}^2$  in size, which is centered along the XFEL beam axis  $\sim 735$  mm downstream from the interaction point. The detector consists of two separate panels ( $1024 \times 512$  pixels each) located closely above and below the X-ray beam. Both panels have a rectangular cutout at the center of the edge facing the other panel to accommodate the primary X-ray beam by the resulting rectangular hole. Droplet sizes and dopant density distributions are reconstructed from the diffraction patterns using an iterative phase retrieval algorithm, termed Droplet Coherent Diffractive Imaging (DCDI).<sup>13</sup> The minimum radius (*R*) of the droplets that can be imaged is approximately 50 nm, which is limited by the weak scattering signals from smaller droplets. Diffraction images containing more than  $2 \times 10^5$  detected

photons are selected for real-space reconstructions. The acquisition rate for these high intensity images is approximately one in 5 minutes of run time. Absorption of X-ray photons induces ionization of the droplets. Light ionic fragments are analyzed with the help of a single-field Wiley-McLaren ion time-of-flight (TOF) spectrometer,<sup>22</sup> which is aligned perpendicular to both the X-ray and the droplet beams.

## Results And Discussion

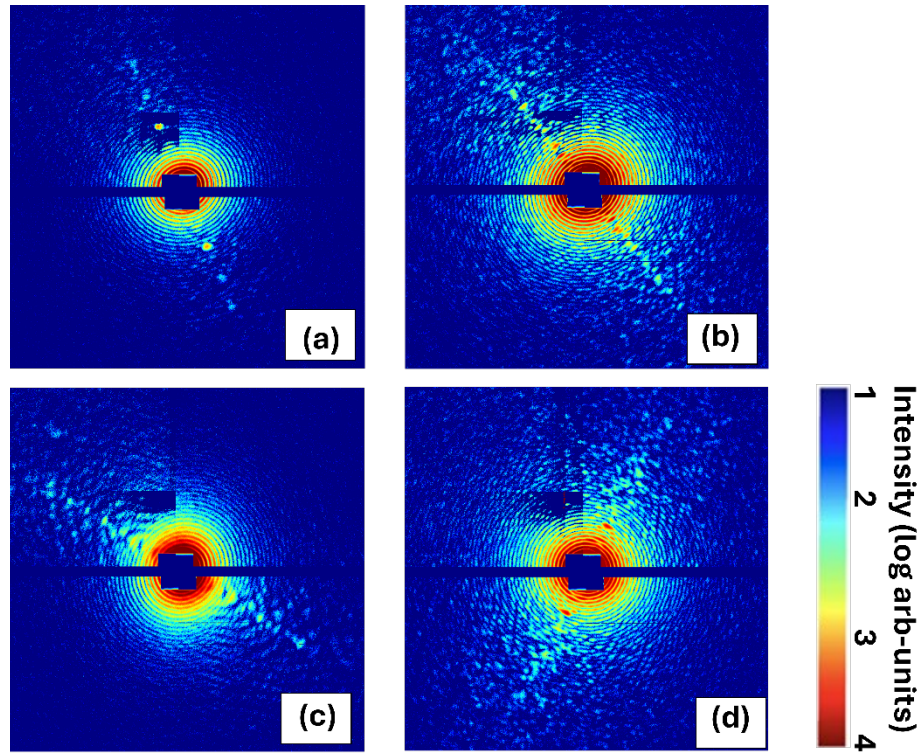


Figure 1. Diffraction patterns from large superfluid  $^4\text{He}$  droplets doped with (a,b)  $\text{CHF}_3$ , (c)  $\text{CF}_4$ , and (d)  $\text{SF}_6$ . The dark horizontal stripes in the patterns stem from the physical gap between the upper and lower detector plates.

Figure 1 (a-d) shows typical diffraction patterns for larger  $^4\text{He}$  droplets with radii of approximately 600 nm, doped with  $\text{CHF}_3$ ,  $\text{CF}_4$ , and  $\text{SF}_6$  molecules as indicated. The pattern in Fig. 1 (a) exhibits a circular ring structure close to the center, with the signal intensity decaying rapidly towards larger scattering angles. Six Bragg spots arranged along a diagonal line are clearly visible in the image (a), indicating a periodic structure inside the droplet. The spot intensity decreases with increasing distance from the image center. These findings are consistent with the formation of clusters along the cores of quantum vortices, which form lattices inside the rotating helium droplets, as observed in our previous work with Xe dopants.<sup>13-15</sup> Figure 1 (b) also exhibits a circular ring structure close to the center but differs from the pattern in Fig. 1 (a) in several other aspects. A diagonal streak through the image containing Bragg spots is observed, similar to Fig. 1 (a). However, the spots in Fig. 1 (b) are not as well defined as those in Fig. 1 (a). Figure 1 (c) shows a diffraction pattern of a  $\text{CF}_4$ -doped  $^4\text{He}$  droplet. The pattern exhibits a diagonal streak similar to those observed for  $\text{CHF}_3$  dopants, but with a lower contrast, and the Bragg spots are less pronounced. Figure 1 (d) shows the diffraction pattern of an  $\text{SF}_6$ -doped  $^4\text{He}$  droplet that shows similar features as the patterns in Fig. 1 (a-c). It also exhibits significant azimuthal intensity modulations, reminiscent of the pattern in Fig. 1 (b) for a  $\text{CHF}_3$ -doped droplet. Rings further away from the image center exhibit pronounced speckles, i.e., azimuthal intensity modulations, which are due to interferences between X-ray scattering contributions from the droplet and the dopants ( $\text{CHF}_3$  and  $\text{SF}_6$ ) clusters in Figs. 1 (b) and 1 (d).

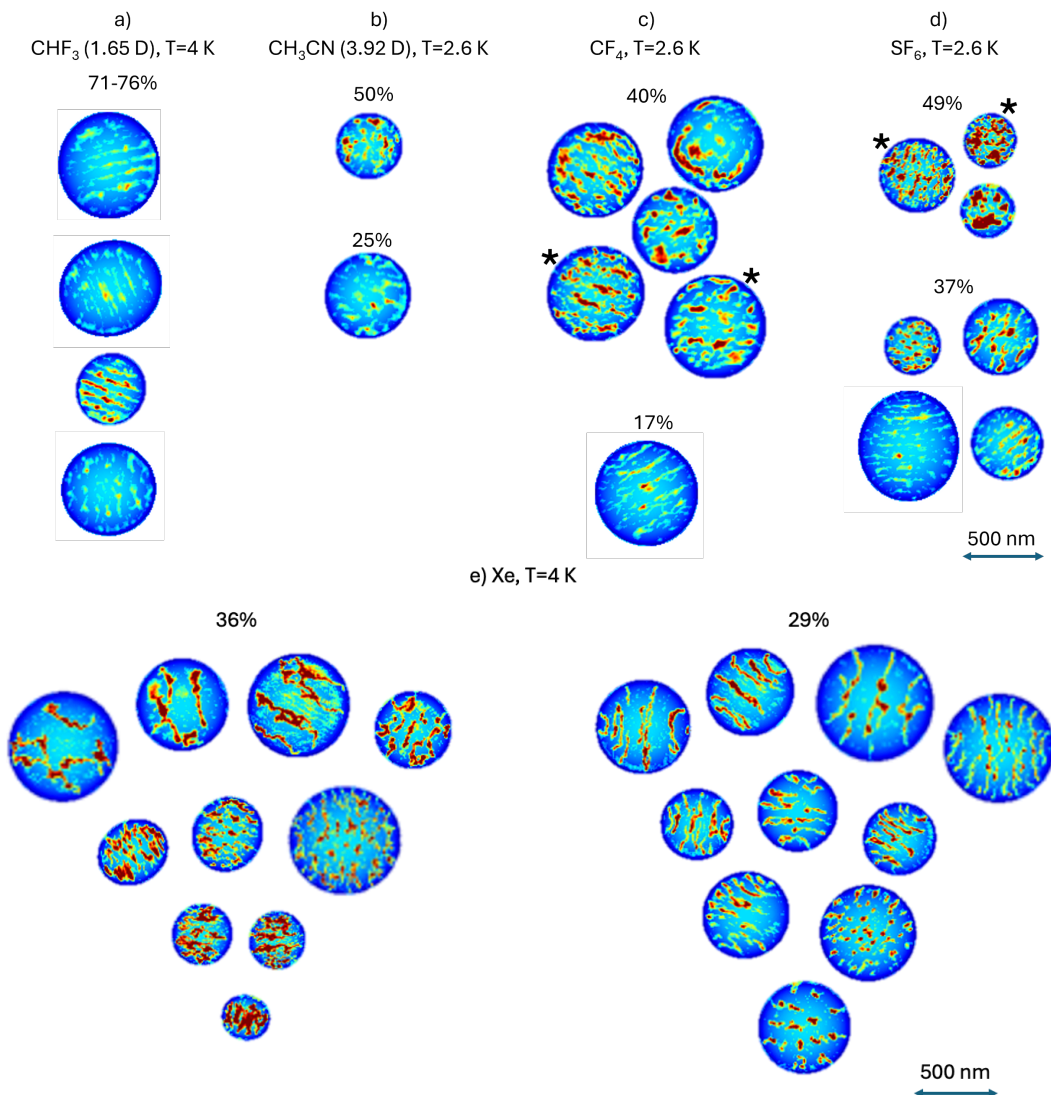
From the diffraction ring spacing at various azimuthal angles, the projections of the droplet contours onto the detector plane were found to be elliptical.<sup>12, 13, 23, 24</sup> This is consistent with spheroidal shapes of rotating droplets resulting from centrifugal deformation.<sup>12, 13, 23, 24</sup> The shape of a spheroid is characterized by the distance between its center and its surface in three mutually

perpendicular directions:  $a = b \geq c$ , whereby the  $c$  axis is aligned parallel to the droplet's angular momentum vector. Due to the unknown orientation of the droplets' angular momentum with respect to the X-ray beam propagation direction, each diffraction pattern only provides two semi-axes of the projection of a droplet onto the detector plane: the major half axis,  $a$ , which is the axis perpendicular to the direction of the angular momentum, and  $c^*$ , an upper bound for the minor half axis,  $c$ , which is the droplet's symmetry axis.<sup>12, 25</sup> The image is characterized by the aspect ratio  $AR = a/c^*$ . The accuracy of the determination of the  $a$  and  $c^*$  values is on the order of a few nanometers. The uncertainty of the AR values is typically less than  $\pm 0.01$ .<sup>23</sup> The AR provides a measure of a droplet's degree of distortion compared to a sphere, which in turn contains information about its angular momentum.<sup>23, 25</sup> Approximately 99% of the studied droplets have aspect ratios  $AR < 1.1$ , which we assign to rotating droplets that acquire spheroidal shapes due to centrifugal deformation.<sup>23, 25</sup> However, a small number of droplets are observed with  $AR > 1.2$ , corresponding to strongly distorted shapes with high angular momenta.<sup>14</sup> The major half axes,  $a$ , and projection aspect ratios, AR, of the droplets that caused the diffraction in Fig. 1 were found to be (a)  $a = 614$  nm,  $AR = 1.09$ ; (b)  $a = 640$  nm,  $AR = 1.08$ ; (c)  $a = 594$  nm,  $AR = 1.08$ , and (d)  $a = 646$  nm,  $AR = 1.04$ . The obtained aspect ratios are comparable to the results of our previous studies of neat and Xe doped He droplets, where average ARs in the range of 1.05 - 1.10 were observed.

<sup>12, 14, 16, 26</sup>

The application of the DCDI phase retrieval algorithm to the diffraction images in Fig. 1 yields partly unreliable real-space density distributions of the molecular clusters inside the droplets, which are shown in Fig. S1 (e-h) of the Supporting Information (SI). We previously experienced the same issue for large droplets ( $R > 500$  nm) doped with Xe atoms with strong Bragg spots, similar to those in Fig. 1, which yielded a larger number of scattered photons, but reliable

reconstructions were also challenging. This is likely related to the phase in reconstructing large droplets for which the distance between the diffraction rings becomes comparable with the pixel size of the CCD. Therefore, based on our previous experience with Xe-doped droplets,<sup>13-15</sup> we focus on DCDI reconstructions of smaller droplets with  $R < 400$  nm to analyze the morphologies of the dopant clusters.



*Figure 2. Density reconstructions of  $^4\text{He}$  droplets with 200-400 nm radii, doped with molecules (in panels (a-d)) and Xe atoms (in panel (e)) as indicated. The reconstructions are derived from bright diffraction images with more than  $2 \times 10^5$  detected photons. Note the different nozzle temperatures and He droplet beam depletion levels as stated. For  $\text{CHF}_3$  and  $\text{CH}_3\text{CN}$ , the static electric dipole moments of the molecules are indicated. In droplets marked with asterisks, high dopant concentrations and large numbers of vortices may have led to partial decoupling of dopant motion and vortex core locations. See text for details.*

Figure 2 (a-d) shows reconstructed densities for a variety of molecular dopants in smaller droplets with 200-400 nm radii, for which reliable reconstructions are achieved. For comparison,

reconstructions for Xe-doped droplets, which were obtained during the same experimental run, are shown in panel (e). Based on our previous experience with Xe dopants, bright diffraction images containing  $\geq 2 \times 10^5$  photons are used for all reconstructions shown in Fig. 2. These bright images correspond to scattering events where droplets reside in the center of the XFEL focus, whereas the weaker images emerge from droplets displaced from the center. Due to weaker scattering off the molecules, the probability of obtaining a bright diffraction pattern with molecular dopants is lower than for Xe-doped droplets. Most of the Xe dopant images in Fig. 2 (e) exhibit patterns of well-defined spots or well-resolved filaments aligned along a common direction. The filaments exhibit kinks and intensity modulations and often consist of an assembly of fused sub-clusters. The Xe images usually feature groups of distinct clusters with very little or no residual density between them, except for the He background. In comparison, most of the images with molecular dopants in Fig. 2 (a-d) do not exhibit such well-defined filaments aligned along a common direction. Some images contain significant contributions of diffuse, red/yellow/green patches in between the sharper features, such as in images marked by asterisks in Fig. 2.

The diffraction signal from the dopants scales approximately as the square of the number of electrons they contain. The addition of each dopant to the droplet leads to the evaporation of several hundred helium atoms. Therefore, the maximum number of dopant particles – and the number of electrons they contain – is limited by the evaporation of the entire droplet. We estimate that adding one electron causes evaporation of about 6 He atoms in the case of Xe dopants. For the heaviest molecular dopants used in this work ( $\text{SF}_6$ ), the estimated number of evaporated He atoms is a factor of two larger than in the Xe atom case, and it is even larger for the other molecules. Therefore, Xe atoms are by far the most favorable dopant for tracing vortices in He droplets by CDI. Note that the relative concentration of dopant atoms is largest for the smallest droplets. The

trend is most prominent in Figs. 2(d) and 2(e), and is consistent with a quantitative estimate of doping concentrations according to equation (4) of reference <sup>27</sup>.

The scarcity of filaments in the reconstructions of droplets doped with molecules in Fig. 2 deserves more consideration. Because of the lower scattering cross section of molecular dopants compared to Xe atoms, some experiments with molecules were performed at a higher level of droplet beam attenuation (i.e., a higher doping level) of up to 70% in comparison to 30-35% for Xe atoms. In our previous experiments, we found that at high Xe doping levels corresponding to >50% droplet beam attenuation, the Xe filaments collapse into spaghetti-like structures. The precise mechanism of this effect remains to be investigated. Here, we limit the discussion to some qualitative considerations. In a neat, rotating, oblate droplet, the entire angular momentum is endowed by a collection of quantum vortices that form a lattice structure that is stationary in the rotating frame. <sup>12, 14</sup> The lattice structure is a result of the hydrodynamic repulsion of the vortices. Upon loading the vortices with a small number of particles, the vortex structure remains intact, but a fraction of the angular momentum is bestowed upon the dopants, which rotate together with the vortices in the laboratory frame. If a droplet contains only a small number of vortices and these vortices are subject to excessive doping, the lattice expands and, eventually, some or all of the doped vortices will abruptly move to the surface, leaving the dominant fraction of the angular momentum contained in the rotational motion of the dopants. <sup>28, 29</sup> However, if many vortices are present, excessive doping may lead to the decoupling of the dopant filaments from the quantum vortices and recombination of the freely floating dopant filaments, which would give rise to more convoluted structures, such as the ones marked with asterisks in Fig. 2.

It is also possible that, due to more directional intermolecular interactions compared to atomic dopants, molecules may form more porous clusters than Xe atoms, which have a propensity to condense into compact clusters. The formation of some porous molecular aggregates is in agreement with the observation of the diffuse patches of density in the images from the molecular clusters in Figs. 2 (a-d). Porous clusters would also be attracted to the vortex cores, but the vortices will have more freedom to accommodate different cluster orientations by passing through the pores, and the molecular aggregates may be larger in size compared to Xe dopant clusters for the same number of particles.

Diffraction patterns from molecule-doped  $^3\text{He}$  droplets were also studied. Figure 3 shows diffraction images and DCDI reconstructions obtained from  $^3\text{He}$  droplets doped with (a,e)  $\text{CHF}_3$ , (b,f)  $\text{CF}_3\text{Cl}$ , (c,g)  $\text{CF}_4$ , and (d,h)  $\text{SF}_6$ . The most striking difference between the  $^3\text{He}$  diffraction patterns in Fig. 3(a-d) compared to those of  $^4\text{He}$  droplets shown in Fig. 1 (a-d) is the complete absence of any Bragg spots. Furthermore, the outer rings in the diffraction patterns in Fig. 3 (a-d) consist of speckles that are more pronounced than those in Fig. 1 (a-d). The lack of Bragg spots in Fig. 3 (a-d) is consistent with the absence of quantum vortices in the normal fluid  $^3\text{He}$  droplets. Instead, molecular dopants in  $^3\text{He}$  droplets aggregate in ring structures along the droplets' periphery, as recently observed for Xe dopants<sup>15</sup>. The rings are the result of classical  $^3\text{He}$  droplet rotation, with centrifugal forces pushing dopants toward the equator, where they aggregate.

The X-ray beam forms an arbitrary angle with each droplet's rotational axis, and each reconstruction corresponds to the droplet's column density projection onto the detector plane. The molecular cluster formations appear either as stripes (Fig. 3 g), ellipses (Fig. 3, e, h), or both stripes and elliptical structures (Fig. 3 f). These density images obtained with molecular dopants in  $^3\text{He}$

droplets closely resemble those previously obtained with Xe atoms.<sup>15</sup> It is conceivable that molecular aggregates in  $^3\text{He}$  droplets have porous microscopic structures that are determined by intermolecular interactions. However, such structures cannot be resolved here, as the effective CDI resolution in this work is  $\sim 20$  nm, and a resolution of  $<10$  nm or better would likely be required to resolve features within a porous molecular aggregate. In the future, it would be interesting to extend the experiments to the hard X-ray regime to improve the spatial resolution. Additionally, it would be desirable to minimize the droplets' rotation to study aggregation at ultralow temperatures in an isotropic environment.<sup>30</sup>

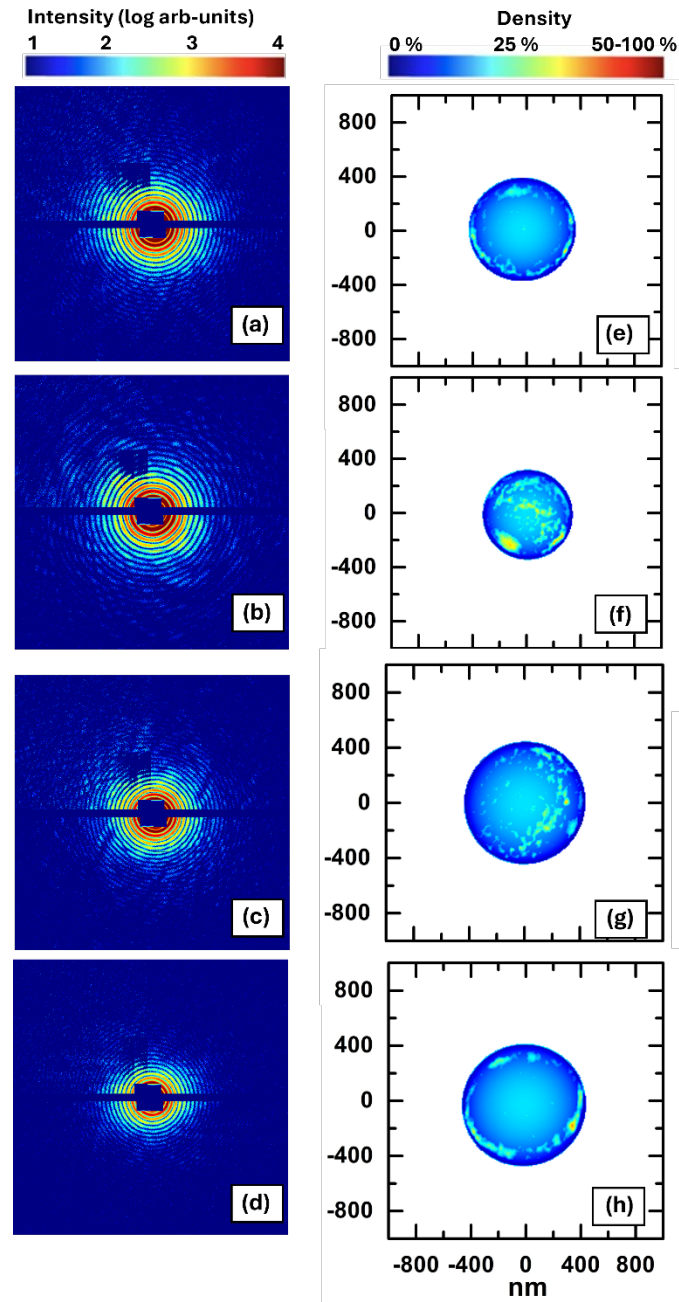


Figure 3. Diffraction patterns from normal fluid  $^3\text{He}$  droplets doped with (a)  $\text{CHF}_3$ , (b)  $\text{CF}_3\text{Cl}$ , (c)  $\text{CF}_4$ , and (d)  $\text{SF}_6$ . The dark horizontal stripes in the patterns stem from the physical gap between the upper and lower detector plates. (e-h): Density reconstructions obtained with the DCDI algorithm applied to the patterns in (a-d).

In our experiment, cations resulting from the ionization of the droplets by X-rays are analyzed by single-pulse TOF mass spectrometry. During the measurements, some droplets are exposed to the strong X-ray flux within the beam waist, giving rise to strong hits as opposed to the weak hits for droplets located on the edges of the X-ray beam. The TOF spectra of the strong hits, such as those resulting in the diffraction images in Fig. 1-3, are heavily saturated. Therefore, we select representative TOF spectra from relatively weak hits for pure and doped  $^3\text{He}$  and  $^4\text{He}$  droplets, which are exposed to a photon flux on the order of approximately  $10^{20}$  -  $10^{21}$  photons/m $^2$ . In comparison, the images in Fig. 1-3 are obtained with  $\sim 10^{22}$  -  $10^{23}$  photons/m $^2$ .

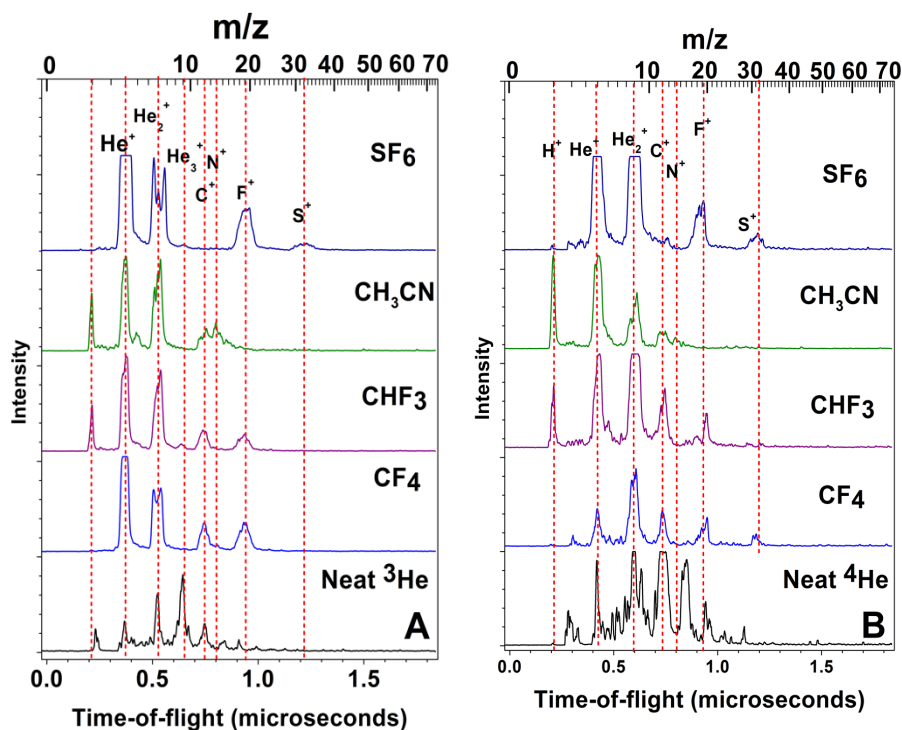


Figure 4. TOF spectra obtained upon X-ray irradiation of neat and doped  $^3\text{He}$  (A) and  $^4\text{He}$  (B) as indicated. The corresponding  $m/z$  scale is shown on top of each panel. Traces from bottom to top in each panel are for neat droplets and for droplets doped with  $\text{CF}_4$ ,  $\text{CHF}_3$ ,  $\text{CH}_3\text{CN}$ , and  $\text{SF}_6$ , as indicated. Vertical dashed lines mark the positions of  $\text{H}^+$ ,  $^3\text{He}^+$ ,  $^3\text{He}_2^+$ ,  $^3\text{He}_3^+$ ,  $\text{C}^+/\text{}^3\text{He}_4^+$ ,  $\text{N}^+$ ,  $\text{F}^+$ , and  $\text{S}^+$  ions for  $^3\text{He}$  droplets, and of  $\text{H}^+$ ,  $^4\text{He}^+$ ,  $^4\text{He}_2^+$ ,  $\text{C}^+/\text{}^4\text{He}_3^+$ ,  $\text{N}^+$ ,  $\text{F}^+$ , and  $\text{S}^+$  ions for  $^4\text{He}$  droplets, from left to right.

Figures 4A and 4B show representative single-pulse TOF spectra obtained for  $^3\text{He}$  and  $^4\text{He}$  droplets, respectively, which result from single X-ray pulses. In each panel, the bottom trace corresponds to neat droplets and the other traces to droplets doped with  $\text{CF}_4$ ,  $\text{CHF}_3$ ,  $\text{CH}_3\text{CN}$ , and  $\text{SF}_6$ , as indicated. The mass spectra for neat droplets show peaks due to  $\text{He}^+$  ions and a progression of  $\text{He}_n^+$  cluster ion peaks, whose intensities are maximal for  $n \approx 3$  and decrease rapidly with further increasing  $n$ . In neat droplets, the lowest TOF peaks correspond to  $\text{He}^{2+}$  doubly charged ions. The same spectra are translated to a linear  $m/z$  scale using a Jacobian transformation, and are shown in Fig. S2 of the SI.

We note that the X-ray intensities used in this study lead to substantial ionization, up to the formation of nanoplasmas, and correspondingly high kinetic energies of the ejected ions. Our collaboration studied these processes in great detail for pristine  $^4\text{He}$  droplets at a photon energy of 838 eV and fluences in the range of  $\sim 10^{21}$ - $10^{23}$  photons/m $^2$ .<sup>20</sup>  $\text{He}^+$  ions were found to have kinetic energies between a few and  $\sim 300$  eV, depending on the degree of droplet ionization. The TOF spectra of pristine droplets in the current work qualitatively agree with those obtained previously at comparable X-ray fluences.<sup>20</sup> However, the TOF mass spectrometer used in this work has a significantly lower resolution than that used during the previous measurements.<sup>20</sup> Therefore, ion kinetic energies cannot be reliably determined, and individual mass peaks can only be resolved up to  $m/z=20$ . Thus, we restrict our analysis of the TOF spectra to the primary focus of identifying small ions produced upon irradiation of the doped droplets.

In the TOF spectra of the droplets doped with  $\text{CF}_4$ , the two leftmost peaks correspond to  $\text{He}^+$  and  $\text{He}_2^+$  ions, with a small contribution of  $\text{He}^{2+}$  in the case of  $^4\text{He}$ . Around  $m/z = 12$  (TOF =

0.73  $\mu$ s), a peak corresponding to carbon ions is observed, followed by  $F^+$  ions thereafter at  $m/z = 19$  (TOF = 0.92  $\mu$ s). The peak at  $m/z=12$  may also contain contributions from  $^3\text{He}_4^+$  or  $^4\text{He}_3^+$  ions. However, these contributions are likely insignificant, considering the lack of any  $^3\text{He}_3^+$  or  $^4\text{He}_4^+$  signals in the  $m/z=12$  peak vicinity. The mass spectrum in  $^4\text{He}$  droplets also shows a weak peak at  $m/z=31$  due to  $\text{CF}^+$  ions, but no peaks due to larger  $\text{CF}_{n>1}^+$  ions.

The next traces in Fig. 4 show the TOF spectra obtained from  $\text{CHF}_3$ -doped  $^3\text{He}$  and  $^4\text{He}$  droplets. The leftmost peak for both kinds of droplets ( $^3\text{He}$  and  $^4\text{He}$ ) corresponds to  $H^+$ . In both cases, two prominent peaks can be seen directly adjacent to the  $H^+$  peak, corresponding to  $\text{He}^+$  and  $\text{He}_2^+$ , followed by intense peaks from  $C^+$  and  $F^+$  ions. Due to relatively low resolution of the mass spectra, a contribution from  $\text{CH}^+$  and  $\text{FH}^+$  ions cannot be excluded. In the TOF spectra for  $\text{CH}_3\text{CN}$ -doped droplets, a sequence of peaks can be seen, corresponding to  $H^+$ ,  $\text{He}^+$ ,  $\text{He}_2^+$ ,  $C^+$ , and  $N^+$ , however, the  $C^+$  and  $N^+$  peaks overlap. Finally, in the TOF spectra of  $\text{SF}_6$ -doped droplets, two prominent peaks can be seen for both kinds of droplets, corresponding to  $\text{He}^+$ , and  $\text{He}_2^+$  followed by a fluorine peak at  $m/z = 19$  and a weaker sulfur peak at  $m/z = 32$ .

The results show that molecular clusters in both  $^4\text{He}$  and  $^3\text{He}$  droplets, irradiated by soft X-rays, fragment very effectively into constituent atomic ions. This is in contrast with the outcome of the ionization of molecules encapsulated in helium droplets with electron impact or VUV photoionization, which is known to yield different molecular fragment ions such as  $\text{SF}_n^+$  and  $(\text{SF}_6)_m\text{SF}_n^+$  upon ionization of  $\text{SF}_6$  molecules and clusters in helium droplets.<sup>31, 32</sup>

The fragment ion distributions observed in this work resemble those obtained from free molecules upon irradiation with soft X-ray radiation. In particular, the fragmentation products from  $\text{CF}_4$  molecules exposed to 1.5 keV photons have been studied in great detail.<sup>33</sup> At this photon

energy, well above the K-edges of the carbon ( $\sim 280$  eV) and fluorine ( $\sim 700$  eV) atoms, the removal of core electrons is followed by Auger-Meitner decay, leading to doubly or triply charged ions that primarily fragment into  $C^+$  (16.6%),  $F^+$  (60.6%) and  $CF^+$  (14.3%), and only a very small fraction producing larger molecular ions and doubly charged ions. The observation of strong  $C^+$  and  $F^+$  signals and a weaker  $CF^+$  signal for  $CF_4$  dopant clusters, as seen in Fig. 4, is qualitatively consistent with the results for isolated  $CF_4$  molecules ionized with 1.5 keV photons. However, in comparison to the gas phase measurements, the relative intensity of the  $C^+$  peak is higher in He droplets. The  $CF^+$  peak is smaller in the doped  $^4He$  droplet measurement compared to the free molecule measurement, and it is entirely missing for  $CF_4$ -doped  $^3He$  droplets.

A doped droplet with a radius of 300 nm consists of approximately  $10^9$  He atoms and  $10^6$  embedded molecules, which form clusters in the droplet's interior. Both dopants and He atoms are ionized upon the absorption of X-ray photons. The probability for absorption of the 1.5 keV X-rays per H, He, C, N, F, and S atom at a photon fluence of  $10^{21}$  photons/m<sup>2</sup> can be calculated from the corresponding  $f_2$  atomic scattering factors to be  $2.9 \times 10^{-7}$ ,  $1.0 \times 10^{-5}$ ,  $1.4 \times 10^{-3}$ ,  $2.5 \times 10^{-3}$ ,  $6.2 \times 10^{-3}$ , and  $4.5 \times 10^{-3}$ , respectively. Thus, in a  $CF_4$ -doped droplet, for example,  $\sim 10^4$  photons will be absorbed by He atoms and  $\sim 2.6 \times 10^4$  by  $CF_4$  molecules. The ensuing creation of a large amount of charge leads to the disintegration of the droplets, as was previously studied in greater detail for pristine droplets.<sup>20</sup>

We conclude the discussion with some considerations regarding a previously proposed concept of improving intense X-ray imaging of large molecules and molecular clusters by encapsulating them in atomic or molecular tamper layers.<sup>34-36</sup> These sacrificial layers are meant to be ionized alongside the sample of interest, thereby providing (quasi-)free electrons that can

neutralize the sample throughout the interaction with the X-ray pulse, thus minimizing and/or delaying electronic damage and sample distortion by Coulomb repulsion. It was predicted that liquid He is not a good tamper material, since it does not provide many electrons per atom and has a low mass density.<sup>34</sup>

Sample damage occurs on multiple timescales, from the attosecond to few-femtosecond initial photo- and Auger-Meitner ionization processes, through few- to few-tens of femtosecond motion of atoms with various masses in the refined electronic potentials of excited and/or ionized molecules, to disintegration of the entire helium droplet and the formation of the free ions, which takes place on  $\sim$ picosecond timescales.<sup>37</sup> All these timescales are much shorter than the times of flight of ions, which are on the order of microseconds and reflect the asymptotic distribution of ion yields and kinetic energies after target disintegration, integrated over all timescales of ion formation. Thus, establishing a direct link between the observed ion fragmentation patterns and the tamper behavior on ultrafast timescales is challenging. However, the results of our experiments, showing that molecules fragment to atomic ions when irradiated with comparably weak ( $10^{20}$ - $10^{21}$  photons/m<sup>2</sup>) XFEL pulses, are consistent with a picture where target ionization and disintegration are not substantially mediated by a surrounding tamper material on a persistent basis.

Yet, previous time-resolved X-ray scattering experiments on much more highly ionized, similarly sized He droplets indicate that the droplets remain largely intact within the first few hundred femtoseconds and only undergo relatively modest surface expansion at characteristic surface density profile broadening rates of  $\lesssim 70$  nm/ps.<sup>37</sup> It is therefore conceivable that, at least during the  $\sim 100$  fs X-ray/sample interaction time, the droplet environment may have some

beneficial effect with respect to controlling ultrafast sample damage. Additional studies with better temporal and spatial resolution would be required to quantify any such effects, though.

Similar TOF patterns were derived for  $^4\text{He}$  and  $^3\text{He}$  host droplets. This is likely because typical kinetic energies of the produced ions are much larger than the interaction energy between neutral helium atoms, so that the effects of nuclear spin statistics or the superfluid state of the  $^4\text{He}$  droplets play no significant role.

## Conclusions

The aggregation of  $\text{CF}_4$ ,  $\text{CHF}_3$ ,  $\text{CH}_3\text{CN}$ , and  $\text{SF}_6$  molecules in  $^3\text{He}$  and  $^4\text{He}$  nanodroplets is investigated by soft X-ray CDI and TOF mass spectroscopy. We show that ionization of molecular clusters in both superfluid  $^4\text{He}$  and non-superfluid  $^3\text{He}$  droplets results in extensive fragmentation, yielding primarily atomic ions, regardless of the superfluid nature of the liquid. The diffraction patterns of molecule-doped  $^4\text{He}$  droplets with radii of approximately 600 nm have strong Bragg spots, which indicate that the molecules form regularly spaced, straight structures that are preferentially oriented parallel to the short axis, i.e., the rotational axis of the droplets. These findings are consistent with the formation of clusters along the cores of quantum vortices, as observed in our previous work with Xe dopants, and significant droplet shape deformations due to rotational excitation. Real-space reconstructions of molecular dopant cluster density profiles are obtained for droplets with smaller radii of approximately 300 nm. Due to the weaker scattering signals from molecules compared to Xe atoms, much fewer images can be reconstructed with the same degree of confidence. The diffuse images suggest the formation of low-density molecular clusters. One of the main motivations for this work was to study the effect of directional

intermolecular forces on molecular aggregation at ultralow temperatures. Achieving this goal turns out to be challenging. In addition to weaker scattering signals from molecular dopants, quantum vortices in  $^4\text{He}$  droplets attract dopants and may influence the structure of molecular aggregates. From this perspective, studying aggregation in non-superfluid  $^3\text{He}$  droplets devoid of vortices seems more promising. Any future studies, however, will require stronger scattering signals from the dopants. One way to achieve this goal may be to use molecular dopants containing a heavy atom, such as  $\text{CH}_3\text{I}$ . Due to the smaller latent heat of evaporation of  $^3\text{He}$  compared to  $^4\text{He}$ , an about a factor of three larger number of atoms are evaporated upon capture of a dopant by a  $^3\text{He}$  droplet. Therefore, larger  $^3\text{He}$  droplets with radii of approximately  $1\text{ }\mu\text{m}$  are required for such experiments to accommodate the excessive evaporation. In the future, it would be interesting to extend the experiments to the hard X-ray regime and improve the spatial resolution to a level that would allow resolving a possible porous morphology of the molecular dopant clusters.

### **Supporting Information**

S1: Attempted reconstructions of the density of molecular clusters in large helium droplets with radii  $>500\text{ nm}$ .

S2: Time-of-flight mass spectra of doped droplets after ionization by an intense soft X-ray pulse.

### **Acknowledgements**

This material is based upon work supported by the National Science Foundation under Grant No. DMR-1701077, DMR-2205081, CHE-2102318, and CHE-2404883 (A.F.V.). C.A.S., B.W.T., M.B. and O.G. were supported by the Atomic, Molecular, and Optical Sciences program of the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Chemical Sciences, Geosciences and Biosciences Division, through Contract No. DE-AC02-05CH11231.

M.B. acknowledges support by the Alexander von Humboldt foundation. C.B. acknowledges support from the Swiss National Science Foundation. Portions of this research were carried out at the Linac Coherent Light Source (LCLS) at the SLAC National Accelerator Laboratory. SLAC National Accelerator Laboratory, is supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Contract No. DE-AC02-76SF00515. Additionally, we acknowledge the Natural Sciences and Engineering Research Council of Canada. We acknowledge the great support of the LCLS operators as well as the scientific and technical staff.

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## Table of Content

