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Self-Assembly of Iodine in Superfluid Helium Droplets: Halogen Bonds and Nanocrystals

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Abstract

We present evidence of halogen bond in iodine clusters formed in superfluid helium droplets based on results from electron diffraction. Iodine crystals are known to form layered structures with intralayer halogen bonds, with interatomic distances shorter than the sum of the van der Waals radii of the two neighboring atoms. The diffraction profile of dimer dominated clusters embedded in helium droplets reveals an interatomic distance of 3.65 Å, much closer to the value of 3.5 Å in iodine crystals than to the van der Waals distance of 4.3 Å. The profile from larger iodine clusters deviates from a single layer structure; instead, a bi-layer structure qualitatively fits the experimental data. This work highlights the possibility of small halogen bonded iodine clusters, albeit in a perhaps limited environment of superfluid helium droplets. The role of superfluid helium in guiding the trapped molecules into local potential minima awaits further investigation.

Graphical Abstract

Atom distances in iodine dimer revealed from electron diffraction: the distance between atoms 1 and 3 is 3.65 Å, much smaller than the van der Waals distance of 4.3 Å.

Intermolecular forces significantly affect the physical and chemical properties of molecular systems. Hydrogen bonding, dipole-dipole interactions, ion-dipole interactions, and van der Waals forces are thus the bases for chemical reactivity, catalysis, and biomolecular structures and functions. Recently, a relatively new type of intermolecular forces, the halogen bond (XB), has been observed in many different contexts.^[1] Halogen atoms are found to act as not

only electron density donors toward electron-deficient partners such as protons or metal cations, but also electron density acceptors in the vicinity of electron donors such as anions or other halogen atoms. In general, halogen bonds are depicted as $Y - X \cdots D$, where the three dots represent the bond, X is the electrophilic halogen atom (Lewis acid), D is an electron density donor (Lewis base), and Y is typically a carbon, nitrogen, or another halogen atom. The existence of XB is signified by a shorter intermolecular distance than the van der Waals distance. In recent years, XB has evolved from a scientific curiosity to practical applications in design and manipulation of aggregation processes.^[2]

Although in the biological field, XB is typically discussed when Y is a heteroatom, the definition from the International Union of Pure and Applied Chemistry has also included another category of XB where $Y = X$.^[3] This latter type is related to the crystalline structure of halogens. For example, the crystalline state of iodine is layered with both molecular and semiconducting characters.^[4] The intermolecular distance within the layer is 3.5 Å, much shorter than the van der Waals distance of 4.3 Å, while in between layers, the distance is 4.3 Å. Iodine crystals are thus a quintessential representation of homo-halogen bonds.

The halogen bond in crystalline iodine raises a question about the criterion of its formation: does XB exist in dimers or trimers, or does it only form in bulk crystals? Rich literature exists for iodine cluster anions and polyiodide anions,^[5] but there is paucity in studies of small neutral iodine clusters. Passchier and Gregory reported evidence of molecular dimers of iodine in the vapor phase, and the authors proposed a pair separation of 5.5 Å,^[6] even longer than twice the van der Waals radius. Raman spectroscopy offered evidence of small $(I_2)_n$ clusters in rare gas matrices and in liquid iodine, however, no geometric information was reported.^[7] Recently, Hulkko et al. reported a sheet-like planar structure for $(I_2)_n$ ($n = 2 - 7$) in a solid krypton matrix.^[8] Based on Raman spectroscopy, the authors assigned purely van der Waals bonding between iodine molecules in the cluster and suggested that all iodine molecules reside in the same plane. It is fair to say that so far the existence of halogen bonds in small neutral $(I_2)_n$ is still an open question.

Superfluid helium droplets have recently been recognized as an interesting medium for nucleation events.^[9] The low temperature (0.37 K) and the rapid cooling rate of a droplet can lead to formation of unusual clusters.^[10] For example, alkali metal atoms are known to reside on the surface of helium droplets, and alkali dimers are observed to exist only in triplet states on the surface.^[10a, 11] Only sufficiently large alkali clusters can switch from a surface location to an interior location.^[12] Magnesium foams have been observed to form within helium droplets, and these metastable foams appear to collapse into compact clusters after a weak excitation.^[10d] For molecular clusters, Nauta and Miller first experimented with $(HCN)_n$ ($n = 2 - 7$) clusters and confirmed the long chain structure of the clusters using vibrational spectroscopy.^[10b] Although thermodynamically, a more compact structure is more stable for a finite cluster, long chains are the structural motif of crystalline HCN. Subsequently, Slipchenko et al. have investigated $(NH_3)_n$ ($n = 2 - 10^4$), and the authors have also concluded that the ammonia clusters form a crystalline structure in helium droplets.^[10c] This common phenomenon of small clusters forgoing their own global minimum and adopting the global minimum of crystalline bulk has been attributed to the rapid cooling rate

in superfluid helium droplets and the long-range dipole–dipole force between the dopant molecules.

Size-dependent evolution of cluster structures has been the subject of basic and applied research, and structure determination is one of the critical challenges of cluster science. Spectroscopy has long been hailed as a powerful tool, but interpretation of spectroscopic signatures relies on the precision of theoretical calculations. Alternatively, gas phase electron diffraction (GED) has enjoyed a long history of success for more than half a century.^[13] Recently, the technique has been adapted for time domain studies of reaction intermediates and transient processes.^[14] Maier-Borst et al. has coupled a Paul ion trap with an electron diffraction apparatus for studies of ionic clusters.^[15] Data from GED is the Fourier transform of the charge distribution of a molecule, and reverse Fourier transform reveals interatomic distances corresponding to all unique pairings of atoms in a molecule. By comparing features between experimental and simulated profiles, and by iterative refinement of the simulation model, cluster structures can be determined with confidence.

Our group has constructed an electron diffraction apparatus for structure determination of molecules and clusters doped in superfluid helium droplets.^[16] Here we report results of size-selected I₂ clusters in helium droplets, achieved by taking advantage of the velocity slip in our pulsed droplet beam.^[17] We demonstrate the existence of halogen bonds in two different groups of iodine clusters. The diffraction image from the smaller sized clusters alludes to a predominantly dimeric cluster with an intermolecular distance of 3.65 Å, much shorter than the van der Waals distance. The diffraction profile of the larger clusters deviates from that of a single sheet, implying a multilayer structure. Although the agreement between experiment and simulation is still imperfect, the basic conclusion on the formation of a multilayer iodine nanocrystal inside superfluid helium droplets is indisputable.

The overall setup has been described in our previous publications.^[16b, 16c] 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 I₂ solid at room temperature. It was sufficient to produce a stable doping pressure without heating the sample PV. The sample PV and the electron gun were operated at 10 Hz, while the droplet PV ran at half the frequency, and the difference image obtained when the droplet PV was on and off is the net image from doped and pure droplets.

Typical gas phase electron diffraction data are expressed in terms of modified molecular scattering intensity $sM(s)$, where s is the momentum transfer defined as^[13]:

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

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 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 :

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

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 and without the sample. The calculation method for $I_{T,at}(s)$ and for the theoretical values of the modified molecular scattering intensity $sM(s)$ have been explained in the supplementary material of our previous publication.^[16a]

Fig. 1 shows the $sM(s)$ profiles recorded under two different experimental conditions: the top panel was obtained under a lower effective doping pressure and by sampling the leading edge of the droplet beam, while the bottom panel was obtained under opposite conditions. Details of the experimental parameters are provided in the supplementary material. The experimental radial profiles (red dots) in the two panels are quite different, indicating very different structures sampled under the two different experimental conditions.

We believe that the upper panel should correspond to diffraction from smaller sized iodine clusters. Upon comparison with the theoretical $sM(s)$ of I_2 monomer, shown in the supplementary material, we can confidently eliminate the possibility of only monomers and consider diffraction from iodine clusters or mixtures of monomers and clusters. Based on the timing of the electron gun and the size distribution of the droplet beam, we are confident that the general size of the sampled droplets should be smaller than 1500 atoms/droplet.^[16c, 17b] In general, pickup of one iodine molecule requires removal of 400 – 600 helium atoms for cooling, and to ensure that the doped droplets continue to travel into the diffraction region, at least 500 helium atoms need to remain with the droplet after doping.^[17b, 18] Taking these numbers into consideration, the sampled iodine cluster in the top panel of Fig. 1 should contain no more than three iodine molecules. We calculated the theoretical $sM(s)$ of iodine dimers by fixing the intramolecular bond length at 2.67 Å. Visual inspections of the diffraction profiles of a few possible structures of the dimer, including the “T” shape, the “L” shape, and the parallel configurations, lead to the conclusion of a possible “L” shape structure. We then manually varied the relative distance and angle between the two iodine molecules, compared the resulting diffraction profiles with the experiment, and relied on the fitting result of multi-linear regressions of the diffraction profiles from Eq. 2. The continuous black trace is the best fit, with an adjusted intermolecular distance of 3.65 Å between the two nearest iodine atoms. Due to the shadow of the Faraday cup, we paid limited attention to the region below 3 Å⁻¹ to avoid possible contamination. The calculation is not a perfect reproduction of the experimental result, but it has sufficient merit in

reproducing the general trend. We have also calculated the $sM(s)$ profiles of trimers based on several possible structures, a one-layer structure from several different cuts of crystalline iodine, and a bi-layer structure with a dimer and a 3rd molecule in a different plane. As provided in the supplementary material, none of the profiles can be considered qualitatively acceptable. We therefore conclude that the diffraction profile is predominantly due to iodine dimers.

The lower panel in Fig. 1 should correspond to diffraction from larger sized iodine clusters, such as tetramers, pentamers or even hexamers. To identify the structures of these clusters, we first consider the situation of pentamers. We tried to place all five iodine molecules in one layer according to the crystalline structure^[4] (light-blue dashed line), and the result is qualitatively unacceptable. Realizing that the most salient feature in the diffraction profile centered at $3.5 \text{ \AA}^{-1}$, corresponding to a distance of $\sim 4.3 \text{ \AA}$, we then considered pseudo-double layer structures with two iodine molecules in each plane and the fifth adjustable out of either plane. We cut fragments from an iodine single crystal, calculated the diffraction profiles, and compared with the experimental result. The best result from this adjustment is shown by the black line. We can confidently state that the larger iodine clusters sampled in the bottom panel does NOT belong to any single layer structure. Instead, a bi-layer structure must have been formed.

Unlike the case of the smaller clusters, the calculated $sM(s)$ profiles for tetramers, pentamers, and hexamers are all similar (see supplementary material), as long as the iodine molecules form bi-layer structures. The pairings from atoms on the outer edges of each cluster do not have repeats, hence their contribution in the overall diffraction profile is overshadowed by those that have many repeats, such as the interlayer distances between corresponding atoms. The diffraction technique is hence insensitive to the actual size of the iodine cluster under the current conditions. In the following discussion, we choose pentamer as a representation of this cluster group, partly because we have the best success in reproducing the experimental diffraction profile with one particular pentamer structure. We do acknowledge that the experimental data could well be a mixture of clusters with sizes from tetramer to hexamer but with similar structural motifs.

Reverse Fourier transform of the $sM(s)$ profile reveals all the unique pairings of the sample. Fig. 2 shows the pair correlation functions of the two diffraction profiles obtained from Fig. 1. The limited range of s values from our image detector requires a large damping factor in the calculation, which not only broadens the profile but also introduces extraneous oscillations in large distances. The estimated uncertainty in the resulting distance is on the order of $0.1 \text{ \AA}$. The inset of each panel shows our proposed structures and the numbering schemes. To avoid clumsiness in labeling, all intramolecular distances between the two covalently bonded iodine atoms are labeled “Intra”, while only a few intermolecular distances are labeled. The shaded region represents intermolecular pairs such as 3...8, 4...9 and 5...10.

For the case of dimer dominated diffraction, each unique interatomic distance can be more or less resolved under the current conditions, although the fitting is still imperfect. The proposed structure has a distance of $3.65 \text{ \AA}$ between atoms 1 and 3, and this value is

substantially shorter than the sum of the van der Waals distances of two iodine atoms (4.3 Å), but are similar to the in-plane intermolecular distance of 3.5 Å in crystalline iodine.^[4] Moreover, all four iodine atoms are in the same plane in the proposed dimer structure. This result unambiguously confirms the halogen bond between the two iodine molecules.

For the larger clusters, our experiment is incapable of resolving several unique intermolecular distances, but a few features are still identifiable. The intramolecular distance at 2.67 Å, which has five repeats, is clearly resolved. The next longer distances are the halogen bonds between atoms 2 ... 3 and 2 ... 5 at ~3.5 Å and the van der Waals bonds between atoms 3 ... 6 and 7 ... 10 at 3.85 Å. These distances have only two repeats each, and hence they contribute to the leading edge of the peak labeled “Inter”. Three major contributions constitute the major feature of the pair correlation profile: the interlayer distance between 2 ... 9, 3 ... 9, and 4 ... 10 at ~4.1 Å has three repeats, the interlayer distance between 3 ... 7 and 4 ... 7 at 4.3 Å has in total seven repeats, and the intralayer distance between 3 ... 5 at 4.5 Å has four repeats. The resulting center of the convoluted peak is therefore at 4.3 Å. Other interlayer and intralayer distances involving atoms across the longer diagonals of the parallelepipeds are in the range longer than 5.6 Å and have fewer repeats, hence they are clustered together in the shaded region.

The current pentamer structure contains two halogen bonds between atoms 2...3 and 2...5 at ~3.5 Å, while other distances of the parallelepiped of atoms 3...5 and 3...7 are van der Waals in nature. Attempts to rearrange the 1 – 2 atoms into a more symmetric position stapling the two layers failed to match the current fitting result. The distances of 1...3, 1...5 and 1...9 range from 5.0 to 6.0 Å: these values are less than one Angstrom longer than the intralayer van der Waals distance of 3...5 at 4.5 Å. Perhaps the availability of two halogen bonds in the current structure prevails over the more symmetric structure, which offers fewer possibilities of halogen bonds.

Our results demonstrate clear evidence of halogen bonds in iodine dimers formed in superfluid helium droplets. In a near “L” shaped structure, overlapping between the *p* orbitals of the two non-covalently bonded iodine atoms is optimized.^[19] In light of the reports on hydrogen bonded molecular clusters in superfluid helium droplets,^[10b, 10c] this result is not too surprising. Theoretical efforts in understanding the driving force between the two iodine molecules are daunting, while further calculations on the interaction between molecular iodine and superfluid helium are even more difficult. We currently are in the process of developing a comprehensive fitting procedure to systematically optimize the atomic structure from a diffraction image. Together with more detailed theoretical calculations, we hope to further elucidate the role of halogen bonds in iodine clusters.

An interesting result is the structure of the larger clusters where instead of a single layer, a bi-layer structure seems to dominate when more than three iodine molecules are present. It is possible that different from bulk crystals, small clusters are more stable in a bi-layer structure, particularly in a superfluid helium environment. Alternatively, the missing one-layer structure might be related to the limited size range sampled by the electron beam. Formation of halogen bonds should be associated with large energy releases, and the formation of a single layer pentamer requires evaporation of many more helium atoms than

the formation of a bi-layer cluster. It is possible that within the size range of the droplet beam sampled by the electron gun, only bi-layer structures can survive the evaporative cooling process and maintain the traveling momentum to the diffraction region.^[17b] Unfortunately, given the insensitivity of the diffraction technique, further experimental confirmation of this speculation is difficult if possible at all.

The present results demonstrate the formation of iodine clusters in superfluid helium droplets. The near-covalent nature is demonstrated in the short intermolecular distance between the two I₂ molecules. For larger clusters, interlayer bonding is van der Waals in nature, while evidence of some intralayer halogen bonding is also present. Electron diffraction of molecules and clusters doped in superfluid helium droplets is proven a direct structure tool, and in combination with velocity slip, size selective electron diffraction is experimentally feasible.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Figure 1. Modified molecular scattering intensities of smaller iodine clusters (a) and larger iodine clusters (b). The solid black lines are calculated profiles based on proposed structures.

Figure 2. Pair correlation profiles of doped iodine clusters and their proposed structures. The insets show the structures of the clusters and the numbering of the atoms.