The Competition between Hydrogen, Halogen, and Covalent Bonding in Atmospherically Relevant Ammonium Iodate Clusters

Nicoline C. Frederiks, Danika D. Heaney†, John J. Kreinbihl, and Christopher J. Johnson∗

Department of Chemistry, Stony Brook University, 100 Nicolls Rd., Stony Brook, NY 11794

E-mail: chris.johnson@stonybrook.edu

Abstract

Iodine containing clusters are expected to be central to new particle formation (NPF) events in polar and mid-latitude coastal regions. Iodine oxoacids and iodine oxides are observed in newly formed clusters, and in more polluted mid-latitude settings, theoretical studies suggest ammonia may increase growth rates. Structural information was obtained via infrared (IR) spectroscopy and quantum chemical calculations for a series of clusters containing ammonia, iodic acid, and iodine pentoxide. Structures for five of the smallest cationic clusters present in the mass spectrum were identified and four of the structures were found to preferentially form halogen and/or covalent bonds over hydrogen bonds. Ammonia is important in proton transfer from iodic acid components and also provides a scaffold to template the formation of a halogen and covalent bonded backbone. The calculations executed for the two largest clusters studied suggested the formation of a covalent I$_3$O$_8$ anion within the clusters.

†Present Address: Wellesley College, 106 Central St., Wellesley, MA 02481
Introduction

New particle formation (NPF) is responsible for the birth of approximately 50% of aerosol particles formed in the atmosphere, and results from the clustering of low volatility gaseous vapors. Acid-base chemistry and salt bridge formation play an important role in stabilizing early stage NPF clusters against evaporation, allowing these clusters to grow into atmospherically relevant sizes. Sulfuric acid – ammonia (– water) clusters have previously been studied in depth as these particles make up a majority of post-industrial revolution NPF contributors. However, in mid-latitude coastal and polar regional NPF events, H$_2$SO$_4$ – NH$_3$ (– H$_2$O) cluster formation rates alone could not account for observed NPF rates. Further investigation into these regional events led to the discovery that the presence of iodine in these regions helps fuel these NPF events. Coastal algae and other biota release I$_2$, HOI, and various organo-iodide species, such as CH$_2$I$_2$, at low tide, which can form various iodine oxoacids and iodine oxides through photolysis and photooxidation. Coastal nutrient enhancement, likely due to runoff, has greatly increased the algae population along with other anthropogenic emissions on and near the coast of China and has resulted in regionally high iodine concentrations. Since pre-industrial times, it’s believed that there has been a 70% increase in atmospheric iodine. I$^-$ in sea water in the presence of ample ozone concentrations, can also lead to the formation and emission of various organo-iodide compounds into the atmosphere. During the day, if concentrations of CH$_2$I$_2$ are in the 10s of ppt range, NPF can take place without any other contributing species. It has even been found that iodine oxoacid nucleation rates are higher than those of sulfuric acid – ammonia clusters at equal concentrations of acids. In the Arctic, over pack ice, the concentration of iodic acid is 6 - 10 times higher than that of sulfuric acid, and as a result NPF events are primarily centered around HIO$_3$, with minimal to no participation from sulfuric acid or any other species.

Since acid-base chemistry plays such an important role in these early stage NPF clusters, the role of ammonia has also been explored in iodine containing clusters as it is important in
stabilizing sulfuric acid and nitric acid containing clusters.\textsuperscript{49,50} It was found that ammonia can aid in the hydrolysis of \( \text{I}_2\text{O}_5 \) and it can also interact with \( \text{HIO}_3 \), increasing nucleation rates of these clusters through the lowering of transition state energies via increased hydrogen bond donors and acid-base interactions.\textsuperscript{49} Further quantum chemical calculations and atmospheric cluster dynamics code (ACDC) simulations probing the role of sulfuric acid and ammonia on iodic acid nucleation rates also found that ammonia can help stabilize these clusters and enhance growth rates.\textsuperscript{50}

There has been some debate on whether or not \( \text{I}_2\text{O}_5 \) and other iodine oxides are the driving force behind the formation of these clusters or whether \( \text{HIO}_3 \) and iodine oxoacids play a more substantial role. Iodic acid dimers can directly form \( \text{I}_2\text{O}_5 \) via a single dehydration reaction even though it has typically been believed to be a multiple step process.\textsuperscript{51} Nevertheless, exploration into the dehydration of iodic acid into iodine pentoxide has been found to be somewhat unfavorable based off of quantum chemical calculations, as it takes an energy input to proceed through the proposed transition states.\textsuperscript{52,53} Studies on the hydrolysis of iodine oxides and atomic iodine to form \( \text{HIO}_3 \) determined that water actually reacts quite slowly with these components, suggesting that clustering of iodine oxides is the primary channel of this type of cluster formation.\textsuperscript{36} Yet, specific relative humidity ranges of less than 65\% have been found to promote this hydrolysis reaction of \( \text{I}_2\text{O}_5 \) to \( \text{HIO}_3 \), which is an atmospherically plausible range.\textsuperscript{54} The importance of iodine oxides beyond cluster conception has been a source of controversy as well. \( \text{IO}_2 \), for example, has been found to play a more crucial role in the early growth stages of particle formation compared to initial cluster formation.\textsuperscript{55} However, in the Arctic Ocean, its been found that iodic acid almost exclusively propels NPF events.\textsuperscript{33} Other studies in Greenland; Maud Land, Antarctica; and Mace Head, Ireland, have also identified high concentrations of atmospheric iodic acid and concluded that clustering of \( \text{HIO}_3 \) is the dominant formation pathway, with the formation of \( \text{I}_2\text{O}_5 \) resulting from internal cluster rearrangement.\textsuperscript{34}

Various field studies,\textsuperscript{18,29,31,33,34,41–43,56,57} quantum chemical simulations,\textsuperscript{44,49,50,52,53,55,58,59}
and laboratory experiments\textsuperscript{19,30,32,48,60–63} have been utilized to study these iodine containing atmospheric particles. Mass spectrometric\textsuperscript{32,36,54} and CLOUD studies\textsuperscript{48,60} have been conducted on anionic and cationic iodine oxide and iodine oxoacid clusters. However, no experiments have been performed on these clusters in order to glean structural information to help assist climate modelling for this subset of clusters\textsuperscript{54} even though ionic iodic acid nucleation has yet to be incorporated into these global climate models.\textsuperscript{60}

Methods
The clusters discussed in this work were formed by spraying a 5mM iodic acid/10mM ammonium hydroxide solution in a 50/50 water/methanol solution with 0.1% formic acid on an electrospray ionization (ESI) source. These clusters were generated on two different instruments: a Thermo Scientific LTQ XL linear trap mass spectrometer and a home-built guided ion beam/ion trap/tandem time-of-flight (TOF) photofragmentation mass spectrometer discussed in detail in previous work.\textsuperscript{64} The mass spectrum displayed in Figure 1 was recorded on the LTQ XL, which provided insight into the cluster compositions derived from this mixture. Further analysis took place through mass spectrometry coupled to infrared (IR) spectroscopy carried out on the home-built guided ion beam/ion trap/tandem time-of-flight (TOF) photofragmentation mass spectrometer.

Briefly, the ions are formed in an atmospherically-isolated ESI source, where they are then guided through a series of ion guides to a cryogenically cooled octopole ion trap. Inside the cryogenically cooled trap (cooled by Sumitomo RDK-408D2 cold head), the ions are collisionally cooled via introduction of pulsed helium gas. Most spectra of the clusters discussed herein were recorded via cryogenic ion vibrational predissociation (CIVP),\textsuperscript{65} where an inert tag species, in this case N\textsubscript{2} gas, is seeded into the cryogenic ion trap. The trap is cooled down to approximately 45 K in order for the tag to physisorb onto the cluster of interest. The tagged ion packet is then accelerated down a field free flight tube to the laser crossing, where a portion of the ion packet is intersected by tunable infrared laser light produced by a Nd:YAG-pumped OPO/OPA system (LaserVision). As the laser scans, the
tagged cluster will absorb a single photon when resonant with an IR transition, resulting in the tag desorbing from the cluster. A reflectron then separates the ions that lose a tag from those that did not, before they reach the microchannel plate detector. Spectra are computed from the ratio of untagged ions to tagged plus untagged ions multiplied by laser power, as a function of wavelength. CIVP allows for the collection of a linear spectrum and therefore direct comparisons of relative peak intensities can be made.

All of the calculations discussed in this work were performed using the Gaussian 16 suite of programs. The density functional CAM-B3LYP was used with a split basis set of aug-cc-pVDZ on light atoms and Def2SVPP on iodine. Spectra from harmonic frequency calculations are presented without scaling.

Results and Discussion

1. Observation of Stable Clusters by Mass Spectrometry

Figure 1 displays a mass spectrum featuring a series of singly protonated cationic clusters containing various numbers of ammonia, iodic acid and iodine pentoxide molecules. The clusters discussed in this paper will be referred to using the following nomenclature assignment: \((x, y, z) = (\text{NH}_3)_x(\text{HIO}_3)_y(\text{I}_2\text{O}_5)_z\text{H}^+\). There are several patterns that seem to appear as the clusters begin to grow larger in size. One of which involves the \((3, 2, z)\) clusters, where \(2 \leq z \leq 4\). Above 1000 m/z these are the most prominent peaks in the mass spectrum suggesting that these clusters form most readily and are relatively stable. This group of clusters grow via the addition of a single \(\text{I}_2\text{O}_5\), and have a consistent number of three ammonia and two iodic acid molecules. Their growth mechanism, by iodine pentoxide with an unchanging number of ammonia and iodic acid molecules, could suggest that once a cluster has sufficient ammonia and iodic acid molecules, the growth of these clusters is driven predominantly by the addition of iodine pentoxide to larger, more atmospherically relevant sizes. As mentioned above, iodine pentoxide can form from the dehydration of two iodic acid molecules. In this case, the nature of the cluster formation via ESI likely results in the dehydration process materializing prior to addition to the cluster since solvent evaporation
is one of the mechanisms at play in the production of these clusters with this type of ion source. However, in the atmosphere it is unclear whether this dehydration process would take place prior to addition to the cluster or succeeding its addition.

Figure 1: Mass spectrum of 5mM iodic acid/10mM ammonium hydroxide solution in 50/50 water/methanol with 0.1% formic acid. The (2, 1, z) cluster series is shown in purple and the (3, 2, z) cluster series is shown in green. Other identified clusters are shown in grey. The clusters discussed in depth in this paper are listed in black, with red arrows.

A similar cluster trend can be observed with the (2, 1, z) clusters, where 1 ≤ z ≤ 4. These clusters follow the same growth pattern as the (3, 2, z) clusters discussed above, where the addition of an iodine pentoxide appears to be the main growth channel. Beyond the (2, 1, 1) cluster, the peak intensities of the (2, 1, z) cluster series are considerably lower than those of the (3, 2, z) cluster series, and also decrease in intensity at a much faster rate with each additional iodine pentoxide, suggesting lower stability of the (2, 1, z) clusters. The (3, 2, z) series clusters are able to accommodate more iodine pentoxide molecules with less
disruption to stability of the cluster as a whole, as these slightly larger clusters have more interaction sites where hydrogen and halogen bonding can take place and can more easily accommodate incoming iodine pentoxide molecules. These trends indicate the presence of ammonia in these clusters is important to supporting further growth via iodine pentoxide.

Another apparent trend in the cluster formation of this solution is the presence of the \((x, 1, z)\) clusters, where \(1 \leq x = z \leq 4\) (clusters labeled in light grey). This cluster series suggests that not only is iodine pentoxide addition a driving force in cluster growth to larger sizes, but also additional ammonia is crucial in the growth of ammonia/iodic acid/iodine pentoxide clusters. However, since these clusters overall possess significantly lower relative intensities compared to the \((3, 2, z)\) cluster series and even the \((2, 1, z)\) clusters, these clusters are presumably less stable. The lack of iodic acid constituents results in fewer interaction sites for proton transfer and salt bridge formation to occur with ammonia, likely resulting in the lower intensity peaks.

This paper is focused predominantly on the \((1, 0, 1)\), \((1, 2, 0)\), \((2, 2, 0)\), \((2, 1, 1)\), and \((2, 2, 1)\) clusters. These were the smallest clusters we were able to produce with sufficient signal to capture CIVP spectra of and they serve as a starting point for analysis of larger clusters. We will address smaller clusters first, in order to evaluate important structural configurations with increasing size.

2. The \((1, 0, 1)\) Cluster

The smallest cluster examined via IR spectroscopy was the \((1, 0, 1)\) cluster. This cluster contains only one ammonia and one iodine pentoxide molecule. Figure 2 displays the experimental spectrum (top) compared to the two calculated spectra for this cluster (bottom). The main features of the experimental spectrum include free \(\text{NH}_2\) symmetric and asymmetric stretching modes around 3300-3400 cm\(^{-1}\), \(\text{NH}_2\) twisting mode around 1650 cm\(^{-1}\), \(\text{NH}_2\) bending and wagging modes around 1400 cm\(^{-1}\), and the IO stretching modes below 1000 cm\(^{-1}\). There is also a large, broad hydrogen bonded \(\text{NH}\) stretching anharmonic feature spanning 2700-3250 cm\(^{-1}\), which is typically ignored since harmonic calculations cannot accurately
We performed calculations and then compared these computed spectra to the experimentally collected spectrum in order to identify key spectral features, that could then ideally be tracked in larger clusters. Both calculations are very close in energy to each other, essentially isoenergetic, and their energy difference is within the error of the calculation. From an energetic standpoint, it’s possible that both of these isomers exist in the experimental spectrum. Neither calculation appears to capture the experimental spectrum particularly well, most notably in the free NH$_2$ stretching region, as well as in the NH$_2$ bending/wagging region. In the experimental spectrum there is splitting in the free NH$_2$ symmetric stretching region that suggests the presence of isomers, whether they be structural isomers or tag isomers. In Figure S1, both untagged calculations along with all possible tag location calcu-
lations are compared to the experimental (1, 0, 1) spectrum. The tag calculations appear to drastically enhance the relative free NH stretching intensities, whereas in the experimental spectrum, there is not an evident intensity enhancement in this region. Although it is possible that tag effects could emphasize differences between the calculated and experimental spectra, it is likely not the only source of the spectral discrepancies in this case, as none of the NH$_2$ mode relative intensity patterns are captured any more closely in the tagged calculated spectra (Figure S1). However, if we observe Figure S2 in the supplemental information, with the overlay of the two (untagged) calculated spectra, it shows that it is highly likely that both isomers exist experimentally, as the overlayed spectra more closely captures the spectral features in the free NH$_2$ stretching region and the relative intensity pattern of the NH$_2$ bending/wagging modes in the fingerprint region are more appropriately reproduced.

Unfortunately, as we can see even at the smallest cluster size explored, iodine-local stretches and bends are not particularly diagnostic in identifying likely structure using IR spectroscopy. This is likely due to a couple of factors. One of which, is that the iodine containing modes take place at the lower end of the region of wavenumbers that we are able to scan. The power from the laser begins to drop off significantly below 1000 cm$^{-1}$, reducing signal to noise, making it difficult to clearly see all features in this region. Second, the binding energy of N$_2$ is around 800 cm$^{-1}$, so peaks below and around this cutoff will not necessarily be well represented within the experimental spectrum. Therefore, for the (1, 0, 1) cluster and the other clusters discussed in the upcoming sections, the ammonium and OH related modes are the most reliable for determining the structure of the clusters.

3. The (1, 2, 0) Cluster

Moving on to the larger (1, 2, 0) cluster in Figure 3, we begin to see more vibrational modes appear, most notably above 3400 cm$^{-1}$. Since this cluster contains two iodic acid molecules and is singly protonated, we expect both iodic acid molecules to remain protonated resulting in the presence of OH modes in the experimental spectrum. We do see both free
OH stretching and NH$_2$ asymmetric and symmetric stretching modes implying that the experimentally present isomer contains at least one free iodic acid OH as well as two non-hydrogen bonded NHs. We also see what looks to be two peaks between 1000 and 1200 cm$^{-1}$, which are below the typical NH bending and wagging mode region and generally indicative of either a free or hydrogen bonded OH bending mode. The hydrogen bonded OH bend in the previously studied (NH$_3$)$_4$(HSO$_4$)$_3$H$^+$ dry and hydrated clusters was found to lie between 1300 and 1400 cm$^{-1}$, which would imply that the higher energy mode closer to 1200 cm$^{-1}$ is presumably a hydrogen bonded OH bending mode and the lower energy, lower intensity peak is possibly a free OH bend. These features allow us to eliminate the likelihood of the presence of either higher energy isomer, B or C, in the experimental spectrum. Isomer C, can also confidently be eliminated as a candidate, as this structure is significantly higher in energy than the lowest energy isomer, isomer A. The experimentally present structure is therefore likely isomer A, where there are both a free NH$_2$ and OH component, as well as a hydrogen bonded OH component. The relative intensity pattern within the fingerprint region of the experimental spectrum is also strikingly similar to that of isomer A, with the IO stretching modes around 800 cm$^{-1}$ most closely reproduced in the calculated spectrum of isomer A too.

None of the calculations were able to properly replicate the splitting of the higher energy peaks associated with the free NH and OH stretching modes above 3300 cm$^{-1}$ in the experimental spectrum. As mentioned in the (1, 0, 1) discussion, this splitting usually implies the existence of experimental isomers. However, since both higher energy calculations (isomers B and C) can be eliminated due to their lack of structural arrangements linked to several experimentally present vibrational modes, we turn to the calculations including N$_2$ tags performed on isomer A in Figure S3 to further interpret this splitting. There are three possible tag locations in this arrangement, and these include the free OH or one of the two free NHs. Upon comparison, these three tagged isomer spectra hint at the presence of isomers based on tag location, and not structural isomers. All three stretches (free symmetric NH$_2$, free
Figure 3: The experimental CIVP spectrum (top) is compared to the computed harmonic IR spectra (bottom) of the (1, 2, 0) cluster. The main features involve free OH stretching and bending modes (peaks in red), NH stretching and bending modes (peaks in blue) and IO stretching modes (peaks in purple). Isomer A is found to be the best match to the experimental spectrum as it contains both free OH and NH stretches and the fingerprint relative peak intensity pattern is well reproduced. Therefore isomer A is believed to be the experimentally present structure.

asymmetric NH$_2$, and free OH) exhibit splitting, and the presence of a very small red-shifted free OH stretching peak suggest that all three tag isomers exist in experiment.

Previous work on ammonium bisulfate clusters found that hydrogen bonding and salt bridge formation were crucial interaction forces at play in stabilizing these clusters against evaporation and for further growth into larger sizes.\textsuperscript{10–15} However, comparing isomers B and C to the experimentally present isomer A exemplifies that for this type of cluster, hydrogen bonding might not be the most important force at play. Structurally, in the higher energy isomers, B and C, there are four hydrogen bonds, whereas in the experimentally present
isomer A, there are only three hydrogen bonds. Looking closely at the structure of isomer A, we see that the iodine of the free OH iodic acid and the non-hydrogen bonded oxygen of the other iodic acid molecule appear to be oriented in a way where a halogen bonding interaction could optimally take place (shown as a green dashed line in Figure 3). Both halogen and hydrogen bonding have previously been found to be important in iodic acid – methanesulfonic clusters explored via ACDC.\textsuperscript{58} Yet, this finding for the (1, 2, 0) cluster suggests that halogen bonding may outcompete hydrogen bonding in terms of stabilizing this cluster experimentally.

4. The (2, 2, 0) Cluster

The next largest cluster explored was the (2, 2, 0) cluster. Figure 4 shows the experimental and calculated structures of the (2, 2, 0) cluster. In the experimental spectrum we see the presence of a free OH stretch and both free symmetric and asymmetric NH\textsubscript{2} stretches, suggesting at least one iodic acid molecule remains protonated. Again the fingerprint region is dominated by the NH\textsubscript{2} bending/wagging modes with the iodine related stretches showing up below 1000 cm\textsuperscript{-1}.

As we can see from the highest energy structure, isomer C (Figure 4), the calculated free NH\textsubscript{2} and free OH stretching region shows significant complexity in the NH\textsubscript{2} stretching region that is not found in the experimental spectrum and the fingerprint region of isomer C also does not properly capture the relative peak intensity pattern or number of modes in the NH\textsubscript{2} bending/wagging region. These spectral differences along with the considerably higher energy of this structure in comparison to the other calculated structures is sufficient evidence to eliminate the possibility of this isomer’s occurrence in the experiment. Isomer B is much closer in energy to the the lowest energy isomer A, but isomer B does not have a free OH. Although it was mentioned previously that the iodine related vibrational modes pose challenges in being diagnostic of structure, they can still help dismiss unlikely structures. For this cluster, in the experimental spectrum we see a sharp well defined IO related stretching mode just above 800 cm\textsuperscript{-1}, and the presence of two very faint peaks, one just below 800 cm\textsuperscript{-1}.
Figure 4: The experimental CIVP spectrum (top) is compared to the computed harmonic IR spectra (bottom) of the (2, 2, 0) cluster. Isomer A is lowest in energy, followed by isomer B, and isomer C is significantly higher in energy. The main features involve OH stretching and bending modes (peaks in red), NH stretching and bending modes (peaks in blue), and IO stretching modes (peaks in purple). Again, the lowest energy isomer, A, is found to be the likely experimentally present isomer as it has a free OH stretching mode and two free NH stretching modes. The fingerprint relative peak intensity pattern composed of NH bending and wagging modes, an OH bend, and IO stretching modes is also very well replicated.

and one just above 600 cm$^{-1}$ (both denoted by purple lines in the experimental spectrum in Figure 4). The low intensity of these peaks is likely due to the N$_2$ binding energy of about 800 cm$^{-1}$ as mentioned earlier. These iodine-related peaks are best reproduced in the lowest energy calculated spectrum of isomer A, along with the NH$_2$ bending/wagging modes and free NH$_2$ and OH stretching modes. The similarities between the calculated spectrum of isomer A and the experimental spectrum and the determination of isomer A as the lowest energy isomer, suggest that isomer A is the experimentally present structure at the (2, 2, 0) cluster size.
As with the (1, 2, 0) cluster, we find that in the (2, 2, 0) cluster our experimentally present structure has the fewest hydrogen bonds of all the structures explored. Isomer C has six hydrogen bonds and isomer B has five hydrogen bonds, whereas isomer A only has four. Again we find a minimum energy structure featuring halogen bonds. The non-hydrogen bonded oxygen on the iodate molecule appears to form a halogen bonding interaction with the iodine of the iodic acid molecule, resulting in what could be called a halogen bonded backbone of the cluster (shown as a dotted green line in Figure 4). In both cases where we have seen halogen bonding there have only been ammonia and iodic acid molecules, will this trend persist if an iodine pentoxide molecule is added to the cluster?

5. The (2, 1, 1) Cluster

Figure 5 displays the CIVP spectrum of the smallest cluster studied that is comprised of at least one ammonia, one iodic acid, and one iodine pentoxide, the (2, 1, 1) cluster. Figure 5 also shows the computed spectra for the three calculations found to be lowest in energy. Looking at the experimental spectrum, we can immediately see that there are no free OH stretches and likely no OH bends, suggesting a full proton transfer has taken place from the iodic acid to an ammonia. The vibrational modes that dominate this spectrum are free NH\textsubscript{2} symmetric and asymmetric stretching modes around 3400 cm\textsuperscript{-1}, NH\textsubscript{2} and NH\textsubscript{3} bending and wagging modes around 1400 cm\textsuperscript{-1} and 1600 cm\textsuperscript{-1}, and the IO stretching modes around 600 cm\textsuperscript{-1} and 800 cm\textsuperscript{-1}. The fact that the NH\textsubscript{2} symmetric and asymmetric stretching modes are intact at this cluster size suggests that the experimentally present structure is highly symmetric.

The lowest energy calculations displayed in Figure 5, isomers A, B, and C, exhibit similar binding arrangements to each other with slight modifications. Isomer C, which is 17.38 kcal/mol higher in energy than isomer A, explores the likely spectrum of a structure where the iodic acid does not donate its proton to an ammonia. This structure is still quite high in energy compared to the lowest energy calculation and is therefore energetically improbable to be experimentally present. Comparing the experimental spectral features to those of
isomer C also results in an unlikely match. The experimental relative intensity pattern of the NH$_2$ bending/wagging modes is not well reproduced in isomer C’s spectrum. There are two peaks around 1200 cm$^{-1}$ (one of which is an OH bend), that do not exist within the experimental spectrum. The iodine-related vibrational mode relative intensity pattern in

Figure 5: The experimental CIVP spectrum (top) is compared to the computed harmonic IR spectra (bottom) of the (2, 1, 1) cluster. Isomer A is lowest in energy, followed by isomer B, and isomer C is again significantly higher in energy. The main features involve NH stretching and bending modes (peaks in blue) and IO stretching modes (peaks in purple). Isomer A is found to be the experimentally present isomer as it reproduces the relative peak intensity pattern of the NH modes particularly well in both the fingerprint region and higher energy stretching region. Isomer A is also the lowest energy isomer.

isomer C’s spectrum is also quite different from that of the experiment. Between 800 and 900 cm$^{-1}$ several equal intensity transitions are predicted in isomer C’s spectrum whereas in
the experimental spectrum there are three transitions in this region, of ascending intensity with ascending wavenumber. There are significantly more transitions in the free NH/ NH$_2$ stretching region in the calculated spectrum of isomer C than in the experimental spectrum. The experimental spectrum exhibits approximately two transitions in this region, whereas isomer C has about four, which also have a very different relative intensity pattern.

Isomer B is substantially lower in energy than isomer C, and exhibits full proton transfer from the iodic acid to ammonia, such that the cluster is comprised of two ammoniums, one iodate, and an iodine pentoxide molecule. Isomer A contains the same proton transfer components as isomer B and structurally they both only differ by the orientation and subsequent hydrogen bonds of a terminal IO$_3$. Although visually isomer A and B do not appear to differ significantly, their predicted spectra show considerable differences in both fingerprint and NH/ NH$_2$ stretching regions. Comparing them both directly to the experimental spectrum, we see that isomer A is an excellent match to the experimental spectrum. Isomer A has two transitions in the free NH/ NH$_2$ stretching region, as does the experiment, whereas isomer B has three transitions there. Moving down to the fingerprint region, we find the relative intensity pattern of isomer A to be more representative to that of the experiment. In this region in isomer B, the relative intensity pattern is not well reproduced as there are a couple transitions (somewhat overlapped) just above 1300 cm$^{-1}$ that do not exist in the experimental spectrum. Although the transitions in the IO stretching region just above 800 cm$^{-1}$ in the isomer A spectrum are not as well resolved as they are in the experiment, the ascending relative intensity pattern is present with ascending wavenumber unlike in the predicted spectrum of isomer B. Taken together, isomer A is assigned as the experimentally present structure for the (2, 1, 1) cluster.

The three lowest energy calculations (in Figure 5) exhibit the same number of hydrogen bonds between the cluster constituents, unlike the higher energy calculations of the smaller halogen bonded clusters previously discussed. Another dissimilarity between the (2, 1, 1) cluster and the smaller clusters of this class emerges, where we see what appears to be equal
bond lengths between the central iodine and two neighboring oxygens, as well as identical bond lengths of the central oxygens to the outer iodine molecules in isomer A. These bond lengths are shorter than the previously explored halogen bond lengths and therefore suggest that a stronger interaction than a halogen bond might be forming. However, we will discuss this interaction in more detail in the upcoming sections. Irrespective of the classification of this interaction, it results in the continuation of the O–I–O backbone, and emphasizes the importance of the ammonium hydrogen-bonded scaffold in facilitating an optimal orientation of I$_2$O$_5$ and IO$_3^-$ for an interaction to take place.

5. The (2, 2, 1) Cluster

The final and largest cluster to be discussed is the (2, 2, 1) cluster. Figure 6 displays the three lowest energy calculated spectra compared to the experimental spectrum. Figure S10 in the supplementary information contains all of the structures and calculated spectra explored at this cluster size. The experimental spectrum contains a single free OH stretch, and now only contains a single free NH stretch unlike the smaller clusters of this class. The single, somewhat broad NH stretch suggests that both ammoniums are likely triply hydrogen bonded and mostly symmetric. There is a broad tail on the lower wavenumber side of this peak, which is presumably due to tag effects, as that bump does not appear in the infrared multiphoton dissociation (IRMPD) spectrum in the SI (Figure S9). There is also a very small free OH stretch peak (highlighted in red) in the experimental spectrum red-shifted from the more prominent, labeled free OH stretch that is also likely the result of tag isomers (tag on OH versus tag on NH). The IRMPD spectrum of this cluster does not contain this peak, further supporting this claim.

Unlike in the (2, 1, 1) cluster case, all three lowest energy isomers (A, B, and C) are quite similar in energy. However, the experimental spectrum has several key features that allow the assignment of the experimentally present isomer to be relatively straightforward. One feature is the presence of the free OH stretch in the experimental spectrum. Another feature is the two sets of doublets between 1400 and 1500 cm$^{-1}$ in the NH$_2$/NH$_3$ bending/wagging mode.
The final feature is the presence of a free OH bend. Using these three vibrational mode regions, both isomers B and C can be eliminated almost immediately. Only isomer A has a free OH and can therefore be the only structure to have both free OH stretch and bend present in the predicted spectrum. Isomer A is also the only structure whose predicted spectrum has two sets of doublets in the NH$_2$/NH$_3$ bending/wagging mode region. The spectrum of isomer A appropriately reproduces the free NH stretch, NH$_2$ twist mode, and the majority of the relative intensity pattern of the IO stretching modes above 700 cm$^{-1}$.

Figure 6: The experimental CIVP spectrum (top) is compared to the computed harmonic IR spectra (bottom) of the (2, 2, 1) cluster. Isomer A, B, and C are all relatively close in energy, with isomer A marginally lowest in energy. The main features involve OH stretching and bending modes (peaks in red), NH stretching and NH$_2$/NH$_3$ bending modes (peaks in blue), and IO stretching modes (peaks in purple). Isomer A appears to be the experimentally present isomer as it has a free OH stretching mode, a singular NH stretching mode, as well as a relative peak intensity pattern that is well replicated in the fingerprint region.
As a result isomer A once again was found to be the experimentally present structure. Halogen bonding once again plays a crucial role in this cluster, however, only isomer A contains a halogen bond along with an additional interaction. All of the higher energy isomers contain only one non-hydrogen bonding interaction. Similar to the (2, 1, 1) cluster, the (2, 2, 1) cluster exhibits almost equal bond lengths between what started as the iodine pentoxide and iodate constituents and the internal bond of what was the iodine pentoxide (bonds highlighted in green). These bond lengths are also slightly shorter than halogen bonds, but slightly longer than a typical I–O covalent bond, complicating the identification of the interaction taking place within the cluster. Once again isomer A has the fewest hydrogen bonds (six), whereas isomers B and C each have seven hydrogen bonds, and isomers D and E (SI Figure S10) have eight. This further reinforces the preferential importance of halogen bonding/non-hydrogen bonding interactions in stabilizing these clusters over that provided by hydrogen bonding. The (2, 2, 1) cluster shows the extension of the O–I–O backbone through both halogen bond formation and an additional stronger interaction, further emphasizing the role of these intermolecular forces in the growth of this type of cluster into larger, more atmospherically relevant sizes.

6. Halogen Bonding vs. Covalent Bonding

Taking a closer look at the clusters that contain halogen bonds, we can see emerging themes for this type of cluster. Figure 7 depicts the structures of theses clusters excluding the (1, 0, 1) cluster as it does not involve halogen bonding and/or covalent-like bond formation. The (1, 2, 0) and (2, 2, 0) clusters differ by one ammonia, with the addition of ammonia resulting in deprotonation of one iodic acid. We see that difference reflected in the halogen bond interaction distance: in the (1, 2, 0) cluster, the hydrogen bond formed between the OH of one iodic acid and an oxygen of the other results in a more strained geometry that leads to a weaker halogen bond than in the (2, 2, 0) cluster. The addition of the second ammonium allows for a more optimal halogen bonding orientation to form, leading to a shorter halogen bond interaction and therefore a stronger halogen bond, as can be referenced in Table S1
Figure 7: Experimentally identified structures of the (1, 2, 0), (2, 2, 0), (2, 1, 1) and (2, 2, 1) clusters that all contain halogen bonding and/or a new covalent-like bond. The (2, 1, 1) and (2, 2, 1) clusters both appear to exhibit covalent-like bond formation resulting in the presence of an intra-cluster I$_3$O$_8^-$ complex. The O–I–O backbone bond lengths are displayed in black, with the respective Wiberg indices listed in red just below. All of the O–I–O backbone bonds are numbered as well, to aid in discussion.
(bond 2 versus bond 6). As discussed above, halogen bonding appears to be an important stabilizing interaction in these clusters. The experimentally determined structures of both the (1, 2, 0) and (2, 2, 0) clusters are capable of supporting one more hydrogen bond to an iodic acid OH group, but instead the formation of the halogen bond is favored.

In the larger clusters, we find hydrogen and halogen bonding in competition with covalent bond formation. At first glance, both larger clusters appear to contain an I$_3$O$_8^-$ molecule rather than distinct I$_2$O$_5$ and IO$_3^-$ moieties. Examining the O–I–O backbone of the putative I$_3$O$_8^-$ in the (2, 1, 1) cluster structure, we see essentially identical bond lengths of 2.13 Å between bonds 10 and 11 (Figure 7 and Table S1), where we initially might have expected to find a halogen bond (bond highlighted in green, for example). These bonds are slightly longer than neighboring IO bonds 9 and 12, which also exhibit equal bond lengths of about 1.92 Å. Is this genuinely a covalent bond that forms within the cluster to make an I$_3$O$_8^-$ complex? Several observations of I$_3$O$_8^-$, for a range of applications, have been reported previously. Metallic iodates have been explored in nonlinear optics, such as NaI$_3$O$_8$, where the formation of the I$_3$O$_8^-$ ion was found to originate from the condensation of three iodate anions.$^{74}$ Studies on hydration mechanisms surrounding HIO$_3$ found that HI$_3$O$_8$ can form in a multi-step dehydration process from iodic acid.$^{51,75}$ A quantum chemical study examining likely atmospheric interactions between I$_2$O$_4$, I$_2$O$_5$, HIO$_2$, and HIO$_3$ with water have identified the prospect of the generation of an I$_3$O$_8^-$ complex as well.$^{53}$ Since the (2, 1, 1) cluster contains an iodate along with I$_2$O$_5$, which forms from the dehydration of two HIO$_3$ molecules, there is ample potential that an intra-cluster covalent I$_3$O$_8^-$ is forming.

We performed DFT calculations on both I$_2$O$_5$ and I$_3$O$_8^-$ molecules at the same level of theory as all of the clusters discussed above in order to compare bond lengths of the individual molecules to those of the clusters. Natural bond orbital calculations (NBO) were also performed on the four clusters displayed in Figure 7, as well as I$_2$O$_5$ and I$_3$O$_8^-$. The optimized I$_3$O$_8^-$ complex is found to have marginally longer bonds overall compared to I$_2$O$_5$. The central O in I$_2$O$_5$ is equally distanced from either I (2.01 Å), whereas the symmetric
central bond lengths in I$_3$O$_8^-$ are 2.11 Å ($I_{central}$–$O_{central}$) and 1.95 Å ($O_{central}$–$I_{terminal}$). Terminal IO bond distances in both I$_2$O$_5$ and I$_3$O$_8^-$ are essentially equivalent to each other (1.80 and 1.81 Å, respectively). Since I$_2$O$_5$ is an iodine oxide proven to exist, the similarity of the bond distance and Wiberg indices indicate the existence of I$_3$O$_8^-$. The optimized I$_3$O$_8^-$ structure exhibited comparable bond lengths to those of the suspected I$_3$O$_8^-$ complex within the (2, 1, 1) cluster, further supporting the hypothesis of intra-cluster covalent complex formation. The NBO calculations for the (2, 1, 1) cluster suggest that the interaction taking place at bond 11 is stronger than a halogen bond but slightly weaker interaction than a typical covalent IO bond. However, upon comparison to the NBO calculations of the I$_3$O$_8^-$ complex, we find very similar bond indices between the suspected (2, 1, 1) I$_3$O$_8^-$ and the optimized I$_3$O$_8^-$, suggesting that the I$_3$O$_8^-$ present in these clusters is consistent with a free I$_3$O$_8^-$. For the (2, 2, 1) cluster, we find both a halogen bond (bond 20 in Figure 7) and an apparent I$_3$O$_8^-$. The halogen bond, at about 2.53 Å, is significantly longer than the newly formed, presumable covalent bond (17, highlighted in green in Figure 7), which is approximately 2.18 Å. The I$_3$O$_8^-$ in this cluster features slightly asymmetric O–I–O backbone bonds, with bond 17 (green highlighted bond) slightly longer (2.18 Å) than bond 16 (2.13 Å). The neighboring IO bonds 15 and 18 in (2, 2, 1) are also found to be nonequivalent, unlike their counterparts in both the (2, 1, 1) cluster and I$_3$O$_8^-$. These slight differences in interaction distances are likely a result of a perturbation by the halogen bond (bond 20). The Wiberg indices of this cluster generated from the NBO calculations confirm that the shorter bond (17) is slightly weaker than bond 16 as well as to the equivalent bonds in the I$_3$O$_8^-$ molecule (Figure S12). However, these interatomic distances are still consistent enough that the assignment of an intra-cluster covalently bound I$_3$O$_8^-$ complex is highly probable. At the very least a covalent–like interaction is taking place at bond 17. In order to determine with more confidence whether this interaction is halogen bonding at play between an iodine pentoxide molecule and iodate molecule or if in fact an I$_3$O$_8^-$ covalent complex is forming, more
sophisticated theoretical analysis will be required.

Summary

In this study we investigated the compositions and structures of clusters involving ammonia, iodic acid, and iodine pentoxide via mass spectrometry, IR spectroscopy, and quantum chemistry. These techniques allowed the lowest energy structures of some of the smallest clusters of this class to be determined with high confidence. This revealed the formation and expansion of the O–I–O backbone via both halogen bonding and likely also covalent bonding, resulting in the formation of $\text{I}_3\text{O}_8^-$ in the largest clusters investigated. Of the five clusters explored, this halogen/covalently bonded backbone appeared in the largest four clusters, suggesting this binding arrangement is likely important to the growth of these clusters into atmospherically relevant sizes. Halogen bonding appeared to outcompete hydrogen bonding in stabilizing these clusters, as all of the newly determined structures for the four largest clusters exhibited the fewest number of hydrogen bonds compared to all structures explored at that size and at least one halogen bond and/or new covalent-like bond. This further emphasizes the importance of these intermolecular forces in stabilizing and potentially accelerating the growth of these clusters. Ammonia also likely helps reduce the evaporation of these clusters through ionic interactions with iodic acid, allowing these clusters to grow to larger sizes and may even catalyze the dehydration reaction between two iodic acid molecules to form $\text{I}_2\text{O}_5$. These results also suggest ammonia might improve growth of these clusters through hydrogen bonding interactions, by aligning incoming $\text{HIO}_3$ and $\text{I}_2\text{O}_5$ molecules into optimal positions such that halogen bonding and/or covalent bond formation can adequately take place, and may even facilitate the formation of the intra-cluster covalently bound $\text{I}_3\text{O}_8^-$ complex.
Acknowledgement

This material is based upon work supported by the National Science Foundation under Grant No. CHE-1905172. DDH acknowledges support from the National Science Foundation Research Experiences for Undergraduates program under Grant No. CHE-2050541. Any opinions, findings, and conclusions or recommendations expressed in this material are those of the author(s) and do not necessarily reflect the views of the National Science Foundation.

Supporting Information Available

The supplementary material contains additional experimental and calculated spectra comparisons, along with coordinates for all of the computed clusters.

References


(11) Waller, S. E.; Yang, Y.; Castracane, E.; Racow, E. E.; Kreinbihl, J. J.; Nickson, K. A.; Johnson, C. J. The interplay between hydrogen bonding and coulombic forces in deter-


