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Ion Mobility-Mass Spectrometry of Iodine Pentoxide-Iodic Acid Hybrid Cluster Anions in Dry and Humidified Atmosphere

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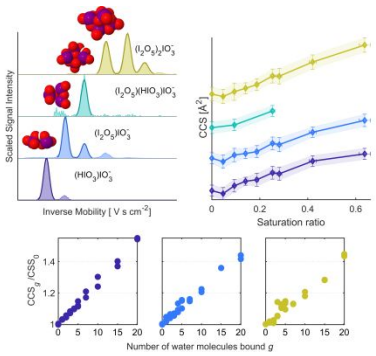
ABSTRACT

Nanometer scale clusters form from vapor phase precursors and can subsequently grow into nanoparticles during atmospheric nucleation events. A particularly interesting set of clusters relevant to nucleation is hybrid iodine pentoxide-iodic acid clusters of the form $(I_2O_5)_x(HIO_3)_y$, as these clusters have been observed in coastal region nucleation events in anomalously high concentrations. To better understand their properties, we have utilized ion mobility-mass spectrometry to probe the structures of cluster anions of the form $(I_2O_5)_x(HIO_3)_y(IO_\alpha)^-$ (x = 0 – 7, y = 0 – 1, α = 1 – 3), similar to those observed in coastal nucleation events. We show that $(I_2O_5)_x(HIO_3)_y(IO_\alpha)^-$ clusters are relatively stable against dissociation during mass spectrometric measurement, as compared to other clusters observed in nucleation events over continental sites, and that at atmospherically relevant relative humidity levels (65% and less), clusters can become sufficiently hydrated to facilitate complete conversion of iodine pentoxide to iodic acid, but that water sorption beyond this level is limited, indicating that the clusters do not persist as nanometer scale droplets in the ambient.

TOC GRAPHIC



Atmospheric nucleation events occur when vapor phase precursors bind to one another, forming stable, condensed phase molecular clusters.[1-3] Though considerable progress has been made in understanding atmospheric nucleation via a combination of field measurements, laboratory experiments, and computational models,[4-11] prediction of nucleation rates and construction of accurate cluster to nanoparticle growth models both remain difficult. This is in large part because the physicochemical properties of nucleation event formed clusters, which determine both their stability and their potential for subsequent growth, have not been fully characterized. Limitations in signal intensity and in cluster lifetime in the ambient typically prohibit in-situ characterization beyond chemical identification.

There is therefore interest in greater characterization of the stability, structure, and hydration (as clusters in the ambient are in frequent contact with water) of clusters identified as forming during atmospheric nucleation events. A particularly pertinent, yet relatively unstudied class of clusters are iodine pentoxide-iodic acid hybrid clusters of the form $(I_2O_5)_x(HIO_3)_y$. These clusters have been observed to form from biogenic iodine precursors during nucleation events in coastal regions,[12-16] wherein the cluster formation and growth rates are anomalously high[17] in comparison to continental nucleation events. In this study, we have utilized ion mobility-mass spectrometry (IM-MS,[18] with a high resolution differential mobility analyzer coupled to a mass spectrometer[19]) to measure the collision cross sections (CCSs) of cluster anions of the form $(I_2O_5)_x(HIO_3)_y(IO_\alpha)^-$ with $x = 0 – 7$, $y = 0 – 1$, and $\alpha = 1 – 3$. In using IM-MS as a cluster characterization technique, we follow the methods outlined by Oberreit *et al*[20] and Thomas *et al*,[21] with three specific objectives: (1) we assess relative cluster ion stability by monitoring dissociation between atmospheric pressure mobility measurements and low pressure mass spectrometry measurements; (2) we compare the CCSs, which were measured in CO_2, to

CCS predictions based on both specular and diffuse gas molecule scattering predictions with all-atom cluster models;[22-23] and (3) we examine CCS shifts in the presence of water vapor (near 295 K, at saturation ratios of up to 0.65).

Differential mobility analysis-mass spectrometer measurements were performed on electrospray generated cluster anions (using 1 mM iodic acid in HPLC water), with additional details on measurements provided in the *Supporting Information*. In using electrospray ionization to generate clusters, we assume that the clusters formed, for a given chemical composition, adopt similar structures to those generated during atmospheric nucleation, i.e. clusters "equilibrate" to conformations which are not dependent on their formation process. Measurements result in detected ion signal as a function of mass-to-charge ratio and the applied differential mobility analyzer voltage, which is convertible to inverse mobility after instrumentation calibration.[24-25] Contour plots of raw data for cluster ions with mobility measurements made in dry CO_2 at 295 K (with immeasurably low water content, below 1% relative humidity) are shown in Figure 1a. Signal corresponding to ions of a specific composition and specific structure take the form of "line segments", and line segments are grouped by charge-state. We focus solely on the singly charged cluster ions in this study, as multiply charged clusters are generally unique to electrospray ionization and are unlikely to be observed in atmospheric nucleation events. For selected singly charged cluster ions where the excess charge is carried by the IO_3^- ion, post-calibration inverse mobility spectra are provided in Figure 1b. Evident in the figure, for all ions, there are multiple peaks detected. In many instances, peaks of "neighboring" cluster ions, i.e. cluster ions with compositions differing by a single iodine pentoxide (I_2O_5) or iodic acid (HIO_3), or with I_2O_5 displaced by HIO_3, coincide exactly with one another in location. In IM-MS measurements this is known to arise because of either

dissociation reactions (*i.e.* $(I_2O_5)_x(HIO_3)_y(IO_3)^- \rightarrow (I_2O_5)_{x-1}(HIO_3)_y(IO_3)^- + I_2O_5$ and $(I_2O_5)_x(HIO_3)(IO_3)^- \rightarrow (I_2O_5)_x(IO_3)^- + HIO_3$) or displacement reactions (the reaction $(I_2O_5)_x(IO_3)^- + H_2O \rightarrow (I_2O_5)_{x-1}(HIO_3)(IO_3)^- + HIO_3$ in this instance) after mobility measurement but prior to mass measurement.[26] Signal appears in such instances at the inverse mobility of the parent ion, but the mass-to-charge ratio of the product ion. For all detected clusters ions, the peaks of the smallest inverse mobilities can be identified as arising from unreacted parent ions. However, for all cluster ions smaller than $(I_2O_5)_4IO_3^-$, the secondary and tertiary peaks at higher inverse mobilities clearly align with peaks in the inverse mobility spectra of higher mass ions; this suggests that they arise from dissociation or displacement reactions. For $(I_2O_5)_xIO_3^-$ with x = 4 – 7 (with the spectrum for x = 7 not shown), secondary inverse mobility peaks are apparent, yet these peaks do not coincide with peaks in the spectra of larger ions. They are likely indicative of a second, unique structure type adopted by larger cluster ions which does not interconvert with the lower inverse mobility structure type during measurement.

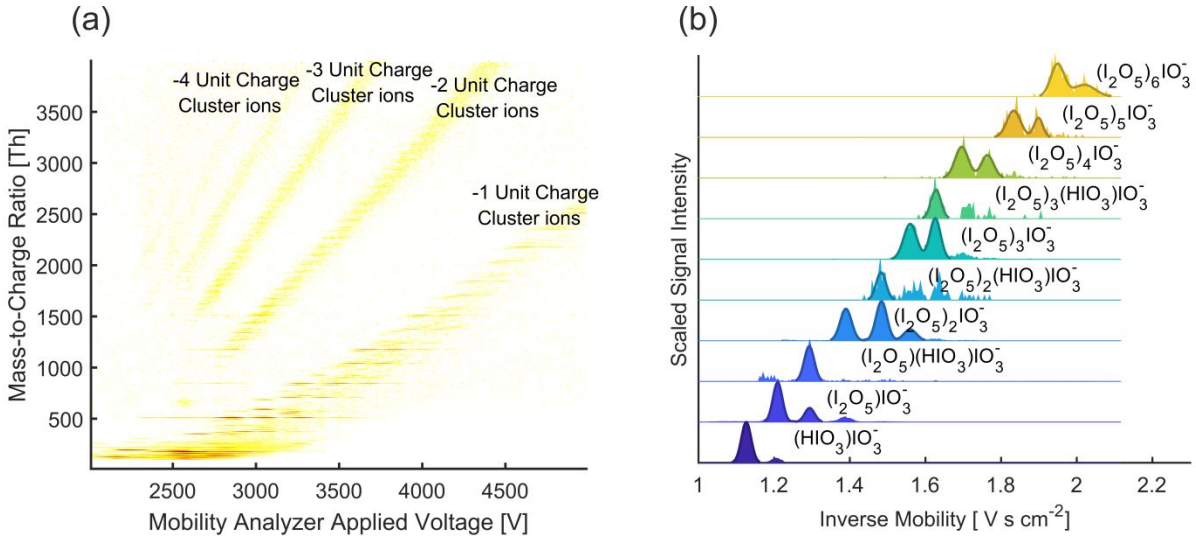


Figure 1. (a) A contour plot of measured signal intensity as a function of mass-to-charge ratio and mobility analyzer applied voltage for electrospray generated cluster anions. **(b)** Post-calibration inverse mobility spectra for specific mass identified cluster anions. The chemical compositions of the selected ions are noted.

The differential mobility analyzer-mass spectrometer system employed has been utilized under identical measurement conditions (including inlet voltage settings) to analyze a variety of other cluster ions. The extent of dissociation reactions observed here can be compared to these prior results, and hence used to qualitatively assess the stability of hybrid iodine pentoxide-iodic acid cluster ions. Ouyang *et al.*[27] examined positively charged alkali metal-iodide cluster ions of the form $(XI)_nX^+$ (X = Na, K, Rb, Cs and n = 1–13), and Thomas *et al.*[21] examined positively and negatively charged hybrid dimethylammonium bisulfate-sulfuric acid cluster ions with up to 8 dimethylammonium bisulfate ion-pairs and 3 sulfuric acid molecules (which are similar in composition to those detected in atmospheric nucleation events in a number of continental sites).[5-7, 28-29] In both of these prior studies, multiple successive dissociation reactions were observed to take place subsequent to mobility analysis and prior to mass analysis; for positively charged dimethylammonium bisulfate-sulfuric acid cluster ions dissociation was often severe enough to leave parent ions undetectable. The extent of dissociation and displacement reaction observed in this study is much less for iodine pentoxide-iodic acid hybrid clusters than observed in prior studies of other cluster ion types. They can thus be regarded as a particularly stable class of cluster anions compared to those studied previous via atmospheric pressure IM-MS. We postulate that their high levels of stability may contribute to the high nucleation rates observed when such clusters form, as when dissociation is minimal, the nucleation rate can approach a collision-controlled limit.[30-31]

More direct than stability, IM-MS measurements yield the CCSs of the identified cluster ions via application of the Mason-Schamp equation (the equation linking mobility/diffusivity to collision cross section).[32] By comparing measurement results to predictions of CCSs based on computationally derived structures, we can assess to what extent computationally modelled

structures capture the global structural features of clusters. In the experiment-model comparison we considered only the CCSs of ions based upon the primary peak (lowest inverse mobility) in each inverse mobility spectrum, as we are confident these peaks do not arise from post-mobility analyzer dissociation or displacement reactions. Experimentally inferred CCSs for these ions are noted in Table 1. Candidate cluster structures for CCS calculations were generated as described in the *Supporting Information*. Briefly, for the clusters $(HIO_3)IO_3^-$, $(I_2O_5)IO_3^-$ and $(I_2O_5)(HIO_3)IO_3^-$, structures were optimized using Density Functional Theory (DFT) at the ωB97xD//aug-cc-pVTZ-PP level. For larger clusters, cluster structures were identified by first determining the partial atomic charges extracted for each of the iodine-containing monomer acids, oxides, and anions (i.e. HIO_3, I_2O_5, and IO_3^-) in cluster ions by running a single-point population analysis calculation, and then using partial charges in configurational sampling via the Artificial Bee Colony (ABC) algorithm[33] with rigid molecules to construct clusters, which were again reoptimized with a low DFT level of theory. To compute CCSs, we utilized IMoS,[22-23] considering the ion-induced dipole potential between impinging CO_2 molecules and clusters,[34-35] but treating atoms as hard spheres, considering both elastic hard sphere scattering (EHSS) and diffuse hard sphere scattering (DHSS) models. In the EHSS model, gas molecule collisions are modeled as elastic and specular (translational kinetic energy is conserved), while in the DHSS model, gas molecules are reemitted from the ion surface at a diffuse angle (randomly selected) upon impingement on the ion surface, and the gas molecule's velocity is resampled from a modified Maxwell-Boltzmann distribution.[22] Discussed previously,[27, 36] for nanometer scale ions these two scattering models lead to appreciable differences in CCS predictions (as much as 30% in many instances), and for polyatomic gas molecules such as CO_2, we expect that the DHSS

model should more accurately describe gas molecule scattering process on an ion modeled as frozen (fixed) during calculation.[27, 35-37]

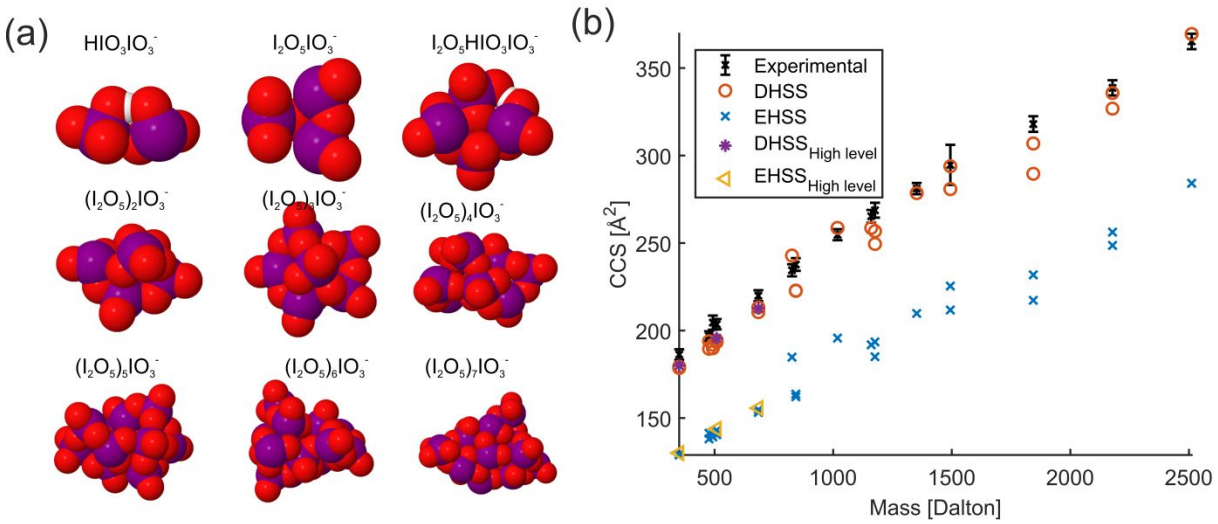


Figure 2. **(a)** Depictions of selected cluster ion candidate structures. Purple: Iodine atoms. Red: Oxygen Atoms. **(b)** Experimentally inferred and calculated CCSs as a function of cluster ion mass. The subscript "High Level" refers to structures obtained from density function theory (ωB97xD//aug-cc-pVTZ-PP level) using a sufficiently large basis set. Error bars are based upon the uncertainty in the mobility analyzer voltage corresponding to the peak signal intensity.

Table 1. A summary of the cluster formulae, masses, measured CCSs, and predicted CCSs using the EHSS and DHSS calculation approaches. N is the number of candidate cluster structures, with the predicted CCSs shown for each candidate.

Molecular formula	mass [Da]	CCS [Å^2]	N	EHSS [Å^2]		DHSS [Å^2]	
$(HIO_3)_1IO_2^-$	334	187 ± 4	0				
$(HIO_3)_1IO_3^-$	350	186 ± 3	2	129	129	179	179
$(I_2O_5)_1IO^-$	476	197 ± 3	2	138	141	190	194
$(I_2O_5)_1IO_2^-$	492	205 ± 4	2	139	141	190	192
$(I_2O_5)_1IO_3^-$	508	204 ± 3	2	140	143	193	194
$(HIO_3)_2IO_2^-$	510	203 ± 3	0				
$(I_2O_5)_1(HIO_3)IO_3^-$	684	220 ± 3	2	153	155	211	213
$(I_2O_5)_2IO_2^-$	826	234 ± 3	1	185		243	
$(I_2O_5)_2IO_3^-$	842	238 ± 4	1	164	162	223	223
$(I_2O_5)_2(HIO_3)IO_3^-$	1018	255 ± 3	1	196		259	

$(I_2O_5)_3IO_2^-$	1160	265 ± 4	1	192		259	
$(I_2O_5)_3IO_3^-$	1176	269 ± 4	2	185	194	249	257
$(I_2O_5)_3(HIO_3)IO_3^-$	1352	281 ± 3	1	210		279	
$(I_2O_5)_4IO_2^-$	1494	295 ± 11	0				
$(I_2O_5)_4IO_3^-$	1510	293 ± 4	2	225	212	294	281
$(I_2O_5)_3(HIO_3)_3IO_3^-$	1703	314 ± 6	0				
$(I_2O_5)_5IO_3^-$	1843	318 ± 4	2	232	217	307	290
$(I_2O_5)_6IO_3^-$	2177	339 ± 4	2	249	256	327	336
$(I_2O_5)_7IO_3^-$	2511	365 ± 4	1	284		369	

Predicted CCSs based on the two models are shown in Table 1 for direct comparison to experimentally inferred values. Depictions of the cluster ion structures employed in calculations (for selected clusters) are shown in Figure 2a, and a plot of measurement inferred and calculated CCSs as a function of cluster ion mass is shown in Figure 2b. Calculation results are shown for multiple potential cluster ion structures. Consistent with prior studies on the influence of cluster structure on the CCS,[38] differences in the predicted CCSs for different structures are significantly smaller than the influence of scattering model. Results show clearly that DHSS model predictions are in good agreement with measurements. Noteworthy about this is that neither candidate structure characterization nor CCS calculations utilized input parameters which were "fit" to measurements, and it demonstrates that both the higher level and lower level computations of cluster ion structures accurately capture global structure features of clusters.

Prior work has shown that by adding condensable vapor in mobility analyzers, the sorption/binding of vapor can be examined at the molecular level, as binding, even transiently, leads to detectible mobility/CCS shifts.[20, 39-40] For iodine pentoxide-iodic acid hybrid clusters, the sorption of water vapor is of particular interest, as water facilitates the

interconversion of iodine pentoxide and iodic acid.[41-42] We examined water vapor sorption at 295 K and saturation ratios from 0.0 to 0.65 through monitoring CCS shifts for the cluster ions $(HIO_3)IO_3^-$ and $(I_2O_5)_xIO_3^-$ (x = 1 – 7). Figure 3a displays plot of the CCS as a function of saturation ratio. It is evident in the figure that CCSs for all cluster ions measured increase noticeably, but by less than 12% over the saturation ratio range examined. This is a clear indication of water vapor sorption, but not to the extent wherein cluster ions would sorb sufficient quantities of water to behave as nanometer scale droplets (i.e. where clusters, by volume, are largely composed of condensing solvent, as has been observed for cluster ions exposed to some organic species).[43] We can additionally compare the extent of observed CCS shifts to the computed change in CCS associated with the sorption of water vapor molecules. Figure 3b displays plot of the ratio CCS_g/CCS_0, where CCS_g is the DHSS computed collision cross section in CO_2 for a cluster ion with *g* water molecules attached to it. Details on cluster ion structure modeling are again provided in the *Supporting Information*. For the ions $(HIO_3)IO_3^-$ and $(I_2O_5)_xIO_3^-$ (x = 1 – 3), CCS_S/CCS_0 and CCS_g/CCS_0 fall in similar ranges for *g* = 5 and smaller (where CCS_S is the collision cross section inferred from measurement at saturation ratio *S*), and for $(I_2O_5)_4IO_3^-$ for *g* = 10 and smaller. This suggests that water vapor sorption does occur to a sufficient extent to complete the reaction $I_2O_5 + H_2O \rightarrow 2HIO_3$ for realistic relative humidity levels, but water vapor sorption beyond the level required for iodic acid formation is limited to only a few water molecules (*i.e.* fewer than 20 water molecules). We further remark that despite the apparent sorption of water vapor during mobility measurement, passage through the high pressure drop mass spectrometer inlet or through the quadrupoles appears to lead to complete loss of excess water. Ions are thus still detected at the mass channel for dehydrated $(I_2O_5)_xIO_3^-$.

Additional quantitative information on the extent of water vapor binding can be gained by comparing observed CCS_S/CCS_0 ratios to a Langmuir-like sorption model:[20, 40, 43]

$$\frac{CCS_S}{CCS_0} = \left[\sum_{g=0}^{\zeta}\left(\frac{P_g}{\left(1+S\frac{M_{H_2O}n_{sat}}{M_{CO_2}n_{CO_2}}\right)^{-1}\frac{CCS_{g,CO_2}}{CCS_0}+\left(1+\frac{1}{S}\frac{M_{CO_2}n_{CO_2}}{M_{H_2O}n_{sat}}\right)^{-1}\left(\frac{M_{CO_2}}{M_{H_2O}}\right)^{1/2}\frac{CCS_{g,H_2O}}{CCS_0}}\right)\right]^{-1} \quad (1)$$

$$P_g = \frac{S^g\prod_{j=1}^{g}\left(\frac{\zeta+1}{j}-1\right)}{1+\sum_{m=1}^{\zeta}S^m\prod_{j=1}^{m}\left(\frac{\zeta+1}{j}-1\right)} \qquad g \geq 1 \quad (2)$$

$$P_0 = \frac{1}{1+\sum_{m=1}^{\zeta}S^m\prod_{j=1}^{m}\left(\frac{\zeta+1}{j}-1\right)} \quad (3)$$

In Equations (1-3), P_g is the probability that a cluster has g water vapor molecules sorbed, M_{H_2O} and M_{CO_2} are the molecular masses of water and carbon dioxide, respectively, n_{sat} is the water vapor number concentration at saturation, n_{CO_2} is the carbon dioxide number concentration at atmospheric pressure, CCS_{g,CO_2} is the computed CCS of a cluster with g water molecules bound in CO_2 bath gas, and CCS_{g,H_2O} is the computed CCS of a cluster with g water molecules bound in H_2O bath gas. ζ is a fitting parameter representing the maximum number of water vapor molecules which can bind to the cluster ion. The equation (1) calculated average collision cross section (CCS_S) is required for comparison between model and experiments because the number of water molecules sorbed to a cluster during measurement is not constant; molecules constantly sorb and desorb from a cluster ion. A more complete derivation of these equations is provided in the *Supporting Information*. Figure 3c displays comparison of the Langmuir model predictions to experimental measurements for selected cluster ions, using fit values of ζ. Results show that the Langmuir model best fits experimental results when ζ exceeds the required number of water vapor molecules needed for completion of the reaction $I_2O_5 + H_2O \rightarrow 2HIO_3$ by 7-14 water molecules. Thus, the modeling approach confirms that iodic acid clusters are only mildly

hydrated under atmospherically relevant conditions, and not hydrated to a level where ion-pairs would wholly or partially dissociate and the clusters would be described as nanodroplets.

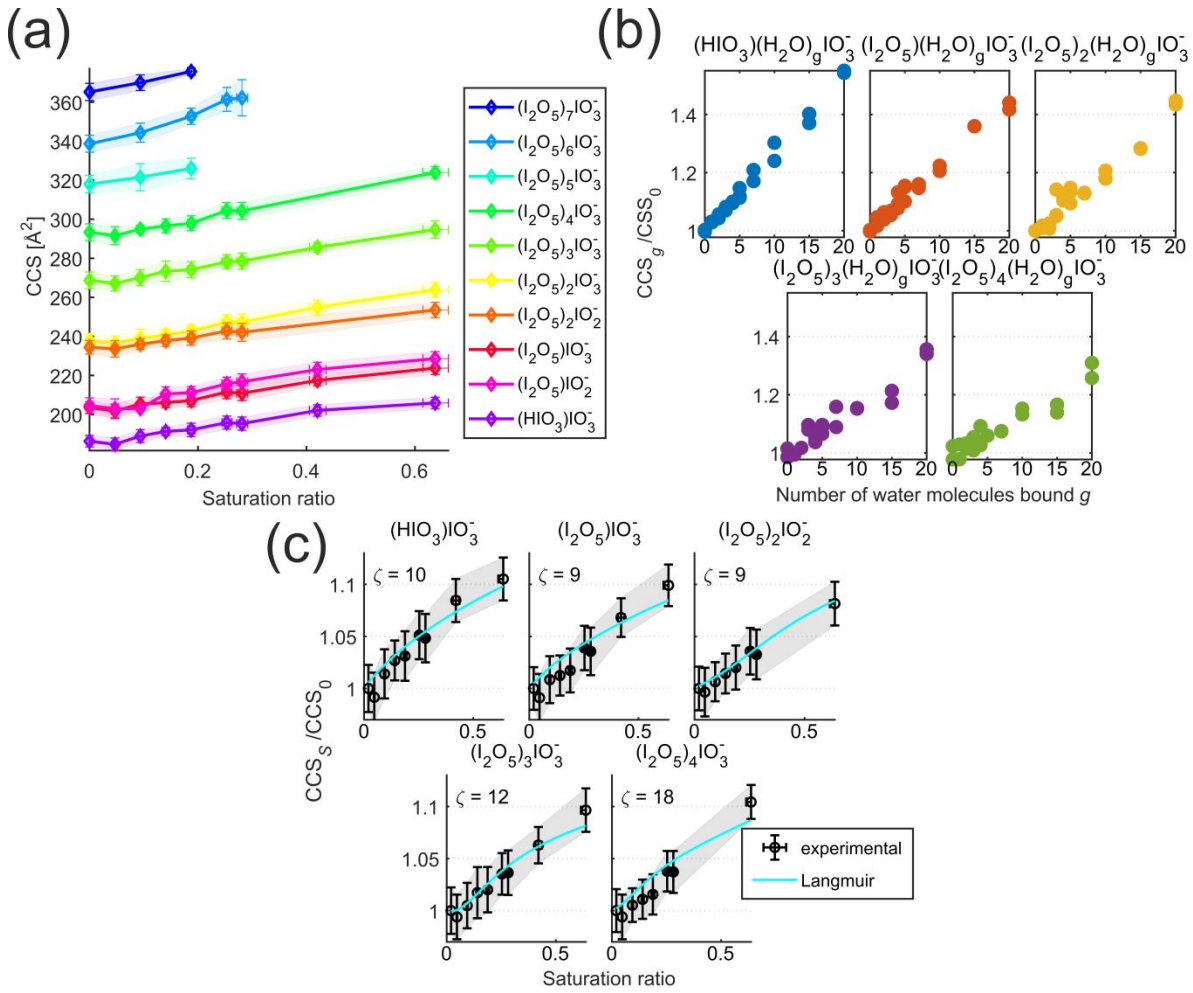


Figure 3. (a) The measured CCS as a function of saturation ratio. **(b)** The computed ratio CCS_g/CCS_0 as function of the number of water molecules (g) bound to a cluster ion. **(c)** A comparison of the CCS given by the Langmuir-model fitted to experimental data for 5 selected cluster ions. The value of the fitting parameter ζ, the maximum number of water molecules which can bind to each cluster, is noted. Error bars are based upon the uncertainty in the mobility analyzer voltage corresponding to the peak signal intensity.

In total, our results provide insight into the properties of iodine pentoxide-iodic acid hybrid clusters, similar in chemical composition to those formed in atmospheric nucleation events in coastal regions. IM-MS measurements suggest that such clusters are highly stable and at atmospherically relevant relative humidities, they can sorb sufficient quantities of water for

conversion of most iodine pentoxide to iodic acid. However, sorption of water vapor beyond this level does not appear to be substantial. Combined with similar findings for dimethylamine-sulfuric acid clusters,[21] we suggest that in many circumstances the clusters involved in atmospheric nucleation are only mildly hydrated, and hence further growth of such clusters hinges upon the interaction between these clusters and the subsequently condensing species (e.g. oxidized organic species). Comparison of measurement inferred CCSs suggest that available computational methods yield structures which capture global structural features of clusters, as modeled and measured CCSs are in good agreement. We suggest that further laboratory scale experiments (e.g. infrared spectroscopy)[44] would be important to probe iodine pentoxide-iodic acid clusters in an effort to develop models describing nucleation events driven by iodine species.

SUPPORTING INFORMATION

Descriptions of differential mobility analyzer-mass spectrometer measurements, the computational approaches used in cluster generation, and IMoS input parameters for collision cross section calculations, as well as derivation of equations (1-3) are available online. Cluster structure coordinates are additionally provided (xyz_files.zip).

AUTHOR INFORMATION

The authors declare no competing financial interests.

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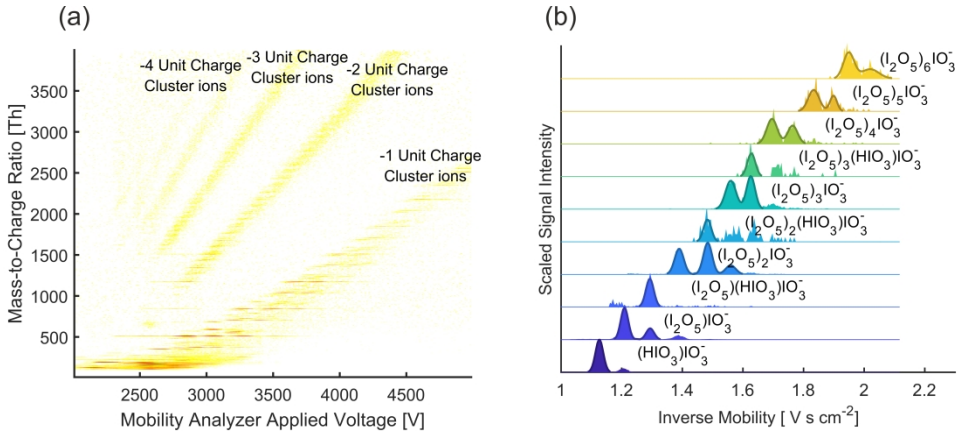

Figure 1. (a) A contour plot of measured signal intensity as a function of mass-to-charge ratio and mobility analyzer applied voltage for electrospray generated cluster anions. (b) Post-calibration inverse mobility spectra for specific mass identified cluster anions. The chemical compositions of the selected ions are noted.

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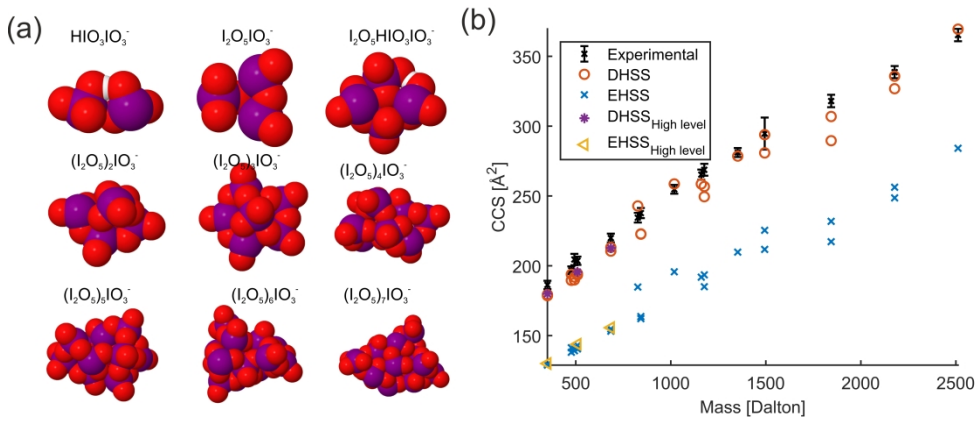

Figure 2. (a) Depictions of selected cluster ion candidate structures. Purple: Iodine atoms. Red: Oxygen Atoms. (b) Experimentally inferred and calculated CCSs as a function of cluster ion mass. The subscript "High Level" refers to structures obtained from density function theory (ωB97xD//aug-cc-pVTZ-PP level) using a sufficiently large basis set. Error bars are based upon the uncertainty in the mobility analyzer voltage corresponding to the peak signal intensity.

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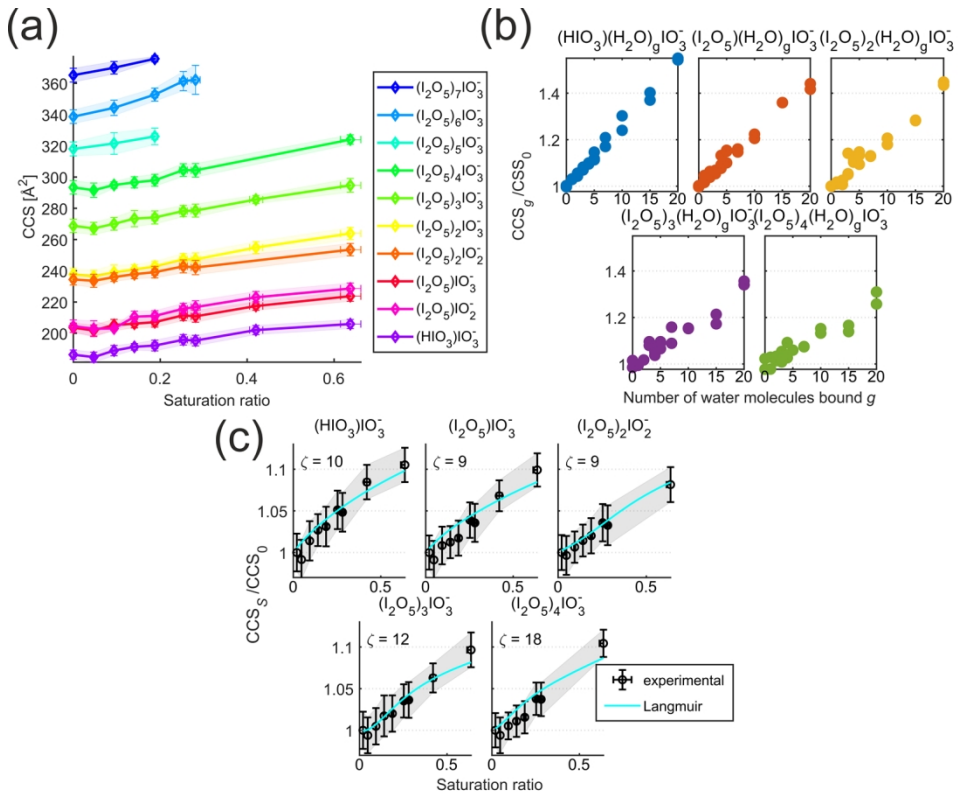

Figure 3. (a) The measured CCS as a function of saturation ratio. (b) The computed ratio CCS_g/CCS_0 as function of the number of water molecules (g) bound to a cluster ion. (c) A comparison of the CCS given by the Langmuir-model fitted to experimental data for 5 selected cluster ions. The value of the fitting parameter ζ, the maximum number of water molecules which can bind to each cluster, is noted. Error bars are based upon the uncertainty in the mobility analyzer voltage corresponding to the peak signal intensity.

291x230mm (150 x 150 DPI)