HIO_x-IONO₂ Dynamics at the Air-Water Interface: Revealing the Existence of a Halogen Bond at the Atmospheric Aerosol Surface

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Supporting Information Placeholder

ABSTRACT: Iodine is enriched in marine aerosols, particularly in coastal mid-latitude atmospheric environments, where it initiates the formation of new aerosol particles with iodic acid (HIO₃) composition. However, particle formation in polluted and semi-polluted locations is inhibited when the iodine monoxide radical (IO) is intercepted by NO₂ to form the iodine nitrate (IONO₂). The primary fate of IONO₂ is believed to be, besides photolysis, uptake by aerosol surfaces, leading to particulate iodine activation. Herein we have performed Born Oppenheimer molecular dynamics (BOMD) simulations and gas-phase quantum chemical calculations to study the iodine acids-iodine nitrate (HIO_x (x = 2 and 3)-IONO₂) dynamics at the air-water interface modeled by a water droplet of 191 water molecules. The results indicate that IONO₂ does not react directly with these iodine acids, but forms an unusual kind of interaction with them within a few picoseconds, which is characterized as halogen bonding. The halogen bond-driven HIO₃-IONO₂ complex at the air-water interface undergoes deprotonation and exists as IO₃⁻-IONO₂ anion whereas the HIO₂-IONO₂ complex does not exhibit any proton loss to the interfacial water molecules. The gas-phase quantum chemical calculations suggest that the HIO₃-IONO₂ and HIO₂-IONO₂ complexes have appreciable stabilization energies, which are significantly enhanced upon deprotonation of iodine acids, indicating that these halogen bonds are fairly stable. These IONO₂-induced halogen bonds explain the rapid loss of IONO₂ to background aerosol. Moreover, they appear to work against iodide formation. Thus, they may play an important role in enhancing the amount of atmospherically non-recyclable iodine (iodate) in marine aerosol.

Introduction. Understanding the atmospheric chemistry of iodine is important because of its role in ozone depletion and new particle formation¹. A deeper

knowledge of how new particles form and nucleate in the atmosphere will help assessing their impact on human health and global climate. In the global marine boundary layer (MBL), aerosol is enriched in iodine compared to seawater², reflecting a transfer of volatile iodinated gases from the sea surface¹. In coastal environments, intense emission of iodine precursors results in high iodine monoxide (IO) mixing ratios capable of sustaining the formation of iodine oxides that grow to form iodine oxide particles (IOPs)³. This gas-to-particle mechanism is yet to be fully understood. Potentially nucleating species derived from IO are I₂O_y (y = 2,4)^{4,5}. Iodine oxide clusters may subsequently rearrange to I₂O₅, which then hydrates to form iodic acid (HIO₃)^{6,7}. However, gas phase HIO₃ has also been identified as a major nucleating species in mid latitude and polar coastal environments, while a role of HIO₂ has been suggested as well⁸. We have recently explored a mechanistic framework to explain the formation of I₂O₄ and I₂O₅ from HIO₂ and HIO₃ reactions using ab initio calculations and molecular simulations⁹. This mechanism is based on non-covalent interactions between iodine acids and oxides and results in the barrierless formation of IOPs.

Mid-latitude coastal particle formation events are generally less intense in polluted air masses^{10,11} since IO reacts with NO₂ forming iodine nitrate (IONO₂), which is a major iodine reservoir species together with hypoiodous acid (HOI). These compounds may be taken up by aqueous aerosol particles, hydrolyzing and releasing di-halogens on aqueous reaction with available halide anions in the presence of sufficient acidity, resulting in halogen activation¹². However, the I⁻/IO₃⁻ ratio, representative of the amount of recyclable iodine in fresh aerosol, is highly variable and the mechanism controlling this ratio is not understood¹. The prominent role of HIO₃ in aerosol iodine chemistry raises interesting questions: can IONO₂ interact with HIO₃ (and other species) on the aerosol surface and result in a gas-phase iodine loss process? Can other molecules such as I₂O₃ be released to the gas phase? Despite speculations about

uptake and hydrolysis of IONO_2 on aqueous aerosol in the literature¹², the different steps of this process have never been studied in detail.

In this article, we report the HIO_3 - IONO_2 and HIO_2 - IONO_2 dynamics at the air-water interface using Born-Oppenheimer molecular dynamics (BOMD) simulations. The air-water interface is a simpler model of the aqueous surfaces, which are prevalent in the atmosphere and provide a unique microenvironment for promoting chemistries, which, otherwise, may not be feasible.¹³⁻¹⁶ These simulations unexpectedly reveal the existence of a unique non-covalent bonding that holds HIO_3 or HIO_2 and IONO_2 together at the air-water interface, preventing iodide formation. This is the first time that such non-covalent bonding in the context of atmospheric chemistry has been studied in an aqueous environment via molecular simulations. Finally, we present gas-phase ab initio calculations to provide deeper insights into the non-covalent HIO_3 - IONO_2 and HIO_2 - IONO_2 bonding.

Computational Methods. BOMD simulations were performed based on DFT implemented in the CP2K¹⁷ code. In the BOMD simulations, the droplet system contained 191 water molecules and one HIO_3 or HIO_2 molecule and one IONO_2 . The dimensions of the simulation box were $x = 35 \text{ \AA}$, $y = 35 \text{ \AA}$, and $z = 35 \text{ \AA}$, making the box large enough to avoid interactions between adjacent periodic images of the water droplet. Both types of chemistries (HIO_3 - IONO_2 and HIO_2 - IONO_2) at the air-water interface were explored by setting up fifteen different simulations for each case. The orientation of HIO_3 - IONO_2 and HIO_2 - IONO_2 with respect to the center of the droplet as well as the intermolecular distance between HIO_3 or HIO_2 and IONO_2 were altered to set up these simulations. The starting configurations of the interface-bound HIO_3 - IONO_2 and HIO_2 - IONO_2 complexes are shown in **Figures S1-S3**. Prior to the BOMD simulations, the system was fully relaxed using DFT, in which the exchange and correlation interaction was treated with the Perdew, Burke, and Ernzerhof (PBE) exchange-correlation functional.^{18,19} Grimme's dispersion correction (D3) was applied to account for the weak dispersion interaction.^{20,21} A double- ζ Gaussian basis set combined with an auxiliary basis set and Goedecker-Teter-Hutter (GTH) norm-conserved pseudopotentials were adopted to treat the valence electrons and core electrons, respectively.^{22,23} An energy cutoff of 280 Rydberg was set for the plane-wave basis set, and a cutoff of 40 Rydberg was set for the Gaussian basis set. The BOMD simulations were carried out in the constant volume and temperature (NVT) ensemble, using the Nose-Hoover chain method to control the temperature (300 K) of the system. The integration step was set as 1 fs, which has been proven to achieve sufficient energy conservation in water systems.^{9,15,16} Both systems were simulated for 40 picoseconds (ps).

All gas-phase quantum mechanical calculations reported in this work were performed using the Gaussian09²⁴ software at standard temperature (298.15 K) and pressure (1 atm). Both HIO_3 - IONO_2 and HIO_2 - IONO_2 complexes as well as their deprotonated forms were explored in the gas phase. The gas-phase geometries of all stationary points on the potential energy surfaces of both reactions were first fully optimized using the Mo6-2X²⁵ density functional theory (DFT) method and aug-cc-pVDZ^{26,27} basis set for H and O, and effective core potential LANL2DZ basis set for Iodine atoms (Mo6-2X/aug-cc-pVDZ+LANL2DZ), and subsequent normal-mode vibrational frequency analyses were performed to confirm that the stable minima had all positive vibrational frequencies. The electronic binding energies and Gibbs free energies of the gas-phase complexes were further refined using the coupled-cluster single and double substitution method with a perturbative treatment of triple excitations (CCSD(T))²⁸ and the aug-cc-pVTZ+LANL2DZ basis set. For all reactions, the Mo6-2X/aug-cc-pVDZ+LANL2DZ calculated unscaled vibrational frequencies were used to estimate the zero-point energy corrections. In addition, the natural bond orbital (NBO) analysis of these complexes was also performed. The electrostatic potential maps of individual entities involved in these complexes were also calculated at the Mo6-2X/aug-cc-pVDZ+LANL2DZ level of theory. The IR spectral analysis of HIO_3 - IONO_2 and HIO_2 - IONO_2 complexes were also performed at the Mo6-2X/aug-cc-pVDZ+LANL2DZ and MP2/aug-cc-pVDZ+LANL2DZ levels of theory. In addition to the above-mentioned iodine complexes, we have also analyzed the electrostatic potential maps of I_2O_2 and I_2O_3 here.

Scheme 1. Plausible reaction paths resulting from the interaction of HIO_3 and HIO_2 with IONO_2 .

Results and Discussion.

a) Air-Water interface inclusive BOMD simulations. We studied the HIO_3 - IONO_2 and HIO_3 - IONO_2 interactions at the air-water interface to investigate if the formation of I_2O_y ($y = 2, 3$) and nitric acid (HNO_3) from these reactions could be observed. These bi-molecular paths were not observed in any of our simulations. Surprisingly, these interactions lead to the formation of an unusual kind of bonding between HIO_3 or HIO_2 and IONO_2 (**Scheme 1**), *i.e.*, a halogen bond is formed, in which the iodine atom attached to IONO_2 behaves like a proton and resides nearly equidistant from HIO_3 or HIO_2 and IONO_2 . This halogen bonding is quite similar to hydrogen bonding except for the fact that the iodine atom in IONO_2 behaves like a proton, *i.e.*, iodonium ion, which holds together interacting species. It is important to mention here that though the halogen bonding involving HIO_3 in the gas-phase has been previously discussed in literature,²⁹ this is the first time such interactions are predicted to be feasible in an interfacial environment. The simulation results suggest that the IONO_2 -induced halogen bonding is quite strong, since it remains intact over the course of the simulated time scale of 40 ps. There are important

mechanistic distinctions between the HIO_3 - IONO_2 and HIO_2 - IONO_2 interactions at the air-water interface. For example, the halogen bond formation in the HIO_3 - IONO_2 reaction is accompanied by the deprotonation of HIO_3 , *i.e.*, $[\text{OOI}-\text{O}\cdots\text{I}\cdots\text{ONO}_2]^-$, whereas no such deprotonation occurs during the HIO_2 - IONO_2 reaction ($[\text{HO}-\text{I}-\text{O}\cdots\text{I}\cdots\text{ONO}_2]$). A more detailed description of the HIO_3 - IONO_2 and HIO_2 - IONO_2 interactions at the air-water interface is provided below.

b) HIO_3 - IONO_2 interaction at the air-water interface. Ten different simulations were set up to study the HIO_3 - IONO_2 interaction at the air-water interface. In all of simulations, the formation of halogen bonding is observed followed by deprotonation of HIO_3 . Importantly, two different channels were observed: (i) the oxygen atom in HIO_3 , which participates in halogen bonding, is different from the one undergoing deprotonation, and (ii) the oxygen atom in HIO_3 , which undergoes deprotonation, also participates in halogen bonding. The former mechanistic channel is the dominant one with 80% probability (**Figure 1** and **Movie S1**) whereas the latter one is a minor channel with a probability of 20% (**Figure 2** and **Movie S2**).

In the dominant channel (**Figure 1**), initially HIO_3 and IONO_2 are appreciably separated as indicated by the I_2 - O_1 bond distance of 3.25 Å at 0.000 ps. At this point, I_2 - O_3 bond is quite strong, *i.e.*, I_2 - $\text{O}_3 = 2.07$ Å. There is also hardly any interaction between HIO_3 and the interfacial water molecule, *i.e.*, $\text{O}_{\text{w1}}-\text{H} = 5.00$ Å at 0.000 ps. The interactions involving HIO_3 , IONO_2 and interfacial water molecules start developing very quickly. At 0.402 ps, the I_2 - O_3 bond is noticeably elongated to 2.22 Å. More importantly, HIO_3 and IONO_2 also come closer, which is indicated by a tighter I_2 - O_1 bond distance of 2.28 Å. At this point, the I_2 starts behaving like a proton and forms an unusual interaction with HIO_3 , which is described as halogen bonding ($\text{HO}-\text{OI}-\text{O}\cdots\text{I}\cdots\text{ONO}_2$). We have also performed bonding and structural analysis of HIO_3 - IONO_2 , IO_3 - IONO_2 , HIO_2 - IONO_2 and IO_2 - IONO_2 complexes in the gas-phase, which further supports our viewpoint about this interaction being a halogen bond. This will be discussed in greater detail in the next section. Until this point, the neutral HIO_3 participates in the halogen bond formation. But beyond that, HIO_3 starts deprotonating by losing its proton to the nearby water molecule. The transition state-like complex for this proton transfer step is formed at 1.808 ps, *i.e.*, both O_2 -H and O_{w1} -H bonds are equidistant at 1.22 Å, respectively. The proton transfer is deemed complete at 1.918 ps, which is indicated by O_2 -H and O_{w1} -H bond distances of 1.52 and 0.99 Å, respectively. After this proton transfer, the $[\text{O}-\text{OI}-\text{O}\cdots\text{I}\cdots\text{ONO}_2]^-$ complex is formed, in which the halogen bond ($\text{O}\cdots\text{I}\cdots\text{O}$) remains fairly stable and keeps the deprotonated HIO_3 and IONO_2 tightly bound over the

Figure 1. (a) Snapshot structures taken from the BOMD simulations, illustrating the halogen bond formation between HIO_3 and IONO_2 at the air-water interface represented by a water droplet of 191 water molecules. The topmost panel shows the atom numbering used in the discussion of BOMD simulation results. (b) Time evolution of key bond distances involved in the HIO_3 - IONO_2 interaction en route to halogen bond formation. This figure describes the dominant mechanistic channel that leads to halogen bond formation between HIO_3 and IONO_2 at the air-water interface.

Figure 2. (a) Snapshot structures taken from the BOMD simulations, illustrating the halogen bond formation between HIO₃ and IONO₂ at the air-water interface represented by a water droplet of 191 water molecules. The topmost panel shows the atom numbering used in the discussion of BOMD simulation results. (b) Time evolution of key bond distances involved in the HIO₃-IONO₂ interaction en route to halogen bond formation. This figure describes the minor mechanistic channel that leads to halogen bond formation between HIO₃ and IONO₂ at the air-water interface.

simulated time scale. This proton transfer also leads to the formation of the interfacial hydronium ion, which subsequently loses one of its protons to the nearby water molecule. The transition state-like complex for that proton transfer is formed at 3.225 ps, in which the O_{w1}-H_{w1} and O_{w2}-H_{w1} bond distances are 1.20 and 1.22 Å, respectively. This proton transfer is completed at 3.261 ps when the O_{w1}-H_{w1} bond is 1.56 Å long whereas the O_{w2}-H_{w1} bond is 1.04 Å long. At this time, the I2-O3 bond is 2.30 Å long and the I2-O1 bond is 2.35 Å long. Beyond this point, the halogen bond remains stable as indicated by the time evolution profiles of key bond distances (Figure 1 and Figure S4).

The minor channel involved in the HIO₃-IONO₂ halogen bond formation is described in Figure 2 and Movie S2. As mentioned earlier, this channel leads to the formation of the [O-OI-O...I...ONO₂]⁻ complex, but via a different mechanism, *i.e.*, the oxygen atom of HIO₃, which forms halogen bond with IONO₂, also undergoes deprotonation to nearby interfacial water molecule. At 0.000 ps, there is hardly any interaction between O₂ of HIO₃ and I₂ of IONO₂ as indicated by the I2-O2 bond distance of 5.40 Å. At this point, the I2-O3 bond is quite stable, *i.e.*, I2-O3 = 2.07 Å. Beyond this point, the I2-O3 bond starts elongating and the interaction between I₂ and HIO₃ also starts developing. At 0.794 ps, the I2-O3 bond is elongated to 2.42 Å, which represents a significant increase in the bond distance

compared to the original value of 2.07 Å. Simultaneously, the I2-O2 bond distance is also significantly reduced from 5.40 Å to 2.11 Å, indicating the formation of a halogen bond between HIO₃ and IONO₂ ([O-OI(HO)...I...ONO₂]). The I1-O2 bond (2.05 Å) is quite stable at this point. The next step involves the deprotonation of O₂ from the (O-OI(HO)...I...ONO₂) complex to the O_{w1} of the air-water interface. The transition state-like complex for this deprotonation is formed at 1.139 ps, in which the O₂-H bond is 1.23 Å long whereas the O_{w1}-H bond is 1.26 Å long. The I2-O2 bond is 2.54 Å long and the I2-O3 bond is 2.31 Å long. The deprotonation is considered complete at 1.186 ps when the O₂-H bond is 1.40 Å long and the O_{w1}-H bond is 1.04 Å long. This deprotonation results in the formation of the [O-OI-O...I...ONO₂]⁻ complex and the interfacial hydronium ion, which subsequently undergoes deprotonation to the nearby water molecule (O_{w2}). The transition state-like complex for this deprotonation is formed at 1.589 ps, in which the O_{w1}-H_{w1} bond is 1.26 Å and O_{w2}-H_{w1} bond is 1.19 Å long. This deprotonation is completed at 1.678 ps as indicated by the O_{w1}-H_{w1} and O_{w2}-H_{w1} bond distances of 1.59 and 1.00 Å, respectively. At this point, the I2-O2 bond is 2.25 Å long and the I2-O3 bond is 2.22 Å long. Beyond this point, the halogen bond remains fairly stable as indicated by the time evolution profiles of key bond distances (Figure 2 and Figure S5). For example, the I2-O2 bond is 2.25 Å long and the I2-O3 bond is 2.20 Å long at 1.683 ps. At 6.000 ps, the I2-O2 bond is 2.30 Å long and the I2-O3 bond is 2.28 Å long.

It is important to mention here that the deprotonation of IONO₂-bound HIO₃ at the air-water interface does not occur due to the presence of IONO₂, but it is due to the fact that HIO₃ is a relatively stronger acid with pK_a value of 0.78,³⁰ which tends to lose a proton in the presence of appropriate proton acceptors. We have run additional BOMD simulations to investigate the dynamics of HIO₃ at the air-water interface (Movie S3). The results suggest that HIO₃ at the air-water interface deprotonates within a couple of ps, which support the viewpoint that HIO₃ behaves as a stronger acid at the air-water interface. Since the HIO₃ deprotonation occurs very fast, we have not run HIO₃ simulations beyond 5 ps.

c) HIO₂-IONO₂ interaction at the air-water interface. The simulation results show that HIO₂ also forms halogen bonding with IONO₂. As for the HIO₃-IONO₂ ten different simulations were run to probe the HIO₂-IONO₂ interaction. The simulation data suggests that there is only one mechanistic involved in the halogen bond formation between HIO₂ and IONO₂. Unlike HIO₃, HIO₂ does not lose its proton to the nearby water molecules en route to the halogen bond formation, *i.e.*, the [HOI-O...I...ONO₂]⁻ complex is formed from the HIO₂-IONO₂ interaction whereas [O-OI-O...I...ONO₂]⁻

Figure 3. (a) Snapshot structures taken from the BOMD simulations, illustrating the halogen bond formation between HIO₂ and IONO₂ at the air-water interface represented by a water droplet of 191 water molecules. The topmost panel shows the atom numbering used in the discussion of BOMD simulation results. (b) Time evolution of key bond distances involved in the HIO₂-IONO₂ interaction en route to halogen bond formation.

complex is formed from the HIO₃-IONO₂ interaction at the air-water interface (**Figure 3** and **Movie S4**). The halogen bonding between HIO₂ and IONO₂ is formed within a few picoseconds, which remains intact over the course of simulated time scale of 40 ps (**Figure S6**). As far as the mechanistic details of the HIO₂-IONO₂ interaction are concerned, both HIO₂ and IONO₂ are relatively farther at the start of simulations, which is evidenced by the I2-O1 bond distance of 3.41 Å. The halogen bond between HIO₂ and IONO₂ starts developing immediately, i.e., the iodine atom in IONO₂ starts detaching from IONO₂ and simultaneously starts forming bonding with HIO₂. At 0.246 ps, the formation of halogen bond between HIO₂ and IONO₂ is deemed complete as indicated by the I2-O1 and I2-O3 bond distances of 2.09 and 2.27 Å, respectively. After some fluctuations, the halogen bonding remains intact. For example, at 0.559 ps, the I2-O1 and I2-O3 bond distances are 2.01 and 2.14 Å long whereas at 6.000 ps, these bonds are 2.19 and 2.28 Å long, respectively.

d) Combined distribution plot analysis. We next calculated the combined distribution functions (CDFs) for the HIO₃-IONO₂ and HIO₂-IONO₂ complexes at the air-water interface by combining a radial distribution function (RDF) between the iodine atom of IONO₂ (I2) and the O atom of HIO₃ (O1 or O2) or HIO₂ (O1) and an angular distribution function (ADF) between the I2··O3 and I2··O1 or I2··O2 vectors (**Figure 4a**). These histograms of higher dimensionality provide further insight into the unusual O··I··O halogen bonding in an aqueous environment. Using CDFs, we could define the O··I··O halogen bonding criteria in the interfacial aqueous environment. Careful analysis of CDFs suggests that the halogen bonding between I2 of IONO₂

and O1 of HIO₃ could be characterized using a criterion with $2.05 \text{ Å} \leq \text{I2} \cdots \text{O1} \leq 2.35 \text{ Å}$ and $164^\circ \leq \theta (= \angle \text{O1} \cdots \text{I2} \cdots \text{O3}) \leq 180^\circ$ whereas the halogen bonding between I2 of IONO₂ and O2 of HIO₃ could be characterized using a criterion with $2.10 \text{ Å} \leq \text{I2} \cdots \text{O2} \leq 2.40 \text{ Å}$ and $162^\circ \leq \theta (= \angle \text{O2} \cdots \text{I2} \cdots \text{O3}) \leq 180^\circ$. The peak for the I2··O1 distance distribution in the O1··I2··O3 halogen bonding occurs at 2.20 Å and the corresponding peak for the O1··I2··O3 angle distribution occurs at 178°. The peak for the I2··O2 distance distribution in the O2··I2··O3 halogen bonding occurs at 2.25 Å and the corresponding peak for the O2··I2··O3 angle distribution occurs at 174°. This suggests that the halogen bonding in the latter case is slightly weaker, which may be due to the fact that the O2 of HIO₃ is initially directed away from I2 of IONO₂ and has to reorganize to induce I2··O2 halogen bonding. Interestingly, the halogen bonding between I2 of IONO₂ and O1 of HIO₂ follows structural criteria which is very similar to the one between I2 of IONO₂ and O1 of HIO₃. The peak for the I2··O1 distance distribution in the O1··I2··O3 halogen bonding in the HIO₂-IONO₂ occurs at 2.19 Å and the corresponding peak for the O1··I2··O3 angle distribution occurs at 178°. The CDFs of two RDFs involving I2··O1 and I2··O3 bond distances in the O1··I2··O3 halogen bonding in the HIO₃-IONO₂ complex at the air-water interface suggest that the peak for the I2··O1 distance distribution occurs at 2.22 Å whereas the corresponding peak for the I2··O3 distance distribution occurs at 2.32 Å (**Figure 4b**). For the O2··I2··O3 halogen bonding in the HIO₃-IONO₂ complex, the peak for the I2··O2 distance distribution occurs at 2.25 Å whereas the corresponding peak for the I2··O3 distance distribution occurs at 2.30 Å. Similar peak for the I2··O1 distance distribution in the HIO₂-IONO₂ complex occurs at 2.19 Å

Figure 4. Combined radial/angular distribution function (CDF). The top panels show the CDFs involving a radial distribution function (RDF) between I2 of the IONO₂ and O1 or O2 of HIO₃ (two left most panels) and O1 of HIO₂ (extreme right panel) at the air-water interface and an angular distribution function between the I2··O3 and I2··O1 or I2··O2 vectors. The lower panels show the CDFs involving a RDF between I2 and O3 of the IONO₂ and a RDF between the I2 of IONO₂ and O1 or O2 of HIO₃ (two left most panels) and O1 of HIO₂ (extreme right panel).

Figure 5. (a) Snapshot structures taken from the BOMD simulations, illustrating the halogen bond formation between H_2O and IONO_2 at the air-water interface. The topmost panel shows the atom numbering used in the discussion of BOMD simulation results. (b) Time evolution of key bond distances involved in the H_2O - IONO_2 interaction en route to halogen bond formation. (c) CDF involving a radial distribution function (RDF) between I of the IONO_2 and Ow1 of H_2O and an ADF between the $\text{I}\cdots\text{O1}$ and $\text{I}\cdots\text{Ow1}$ vectors. (d) CDF involving a RDF between I and O1 of the IONO_2 and a RDF between the I of IONO_2 and Ow1 .

Whereas the corresponding peak for the $\text{I}_2\cdots\text{O}_3$ distance distribution occurs at 2.40 Å.

e) IONO_2 dynamics at the air-water interface. We also probed the dynamics behavior of IONO_2 alone at the air-water interface to investigate whether IONO_2 could also form halogen bond with the interfacial water molecules ($\text{O}_{\text{w1}}\cdots\text{I-O1}$). As shown in **Figure 5**, the simulation results suggest that the IONO_2 -induced halogen bonding at the air-water interface is indeed possible, *i.e.*, the interfacial water oxygen interacts with the iodine atom of IONO_2 . Though the gas-phase possibility of the halogen bonding between water and IONO_2 has been previously discussed in literature,³¹ the present simulations suggest that the IONO_2 - H_2O -based halogen bonding may be formed on the aqueous surfaces that can have interesting implications for the iodine rich environments. As far as the time scale of the halogen bond formation is concerned, it occurs within a few ps. Initially, there is appreciable separation between the interfacial oxygen and iodine of IONO_2 . For example, the $\text{I}\cdots\text{O}_{\text{w1}}$ bond distance is 4.33 Å long at 0.453 ps (**Figure 5a** and **5b**). Beyond this point, the $\text{I}\cdots\text{O}_{\text{w1}}$ bond distances

starts dropping very fast, which is also accompanied by the simultaneous stretching of the I-O1 bond. This results in the formation of an $\text{O}_{\text{w1}}\cdots\text{I-O1}$ halogen bond at 1.394 ps, in which the $\text{I}\cdots\text{O}_{\text{w1}}$ bond is 2.35 Å and the $\text{I}\cdots\text{O1}$ bond is 2.26 Å. The halogen bond angle ($\angle\text{O}_{\text{w1}}\cdots\text{I}\cdots\text{O1}$) at this point is 170.5°. The near linearity of the $\text{O}_{\text{w1}}\cdots\text{I}\cdots\text{O1}$ interaction further suggests it to be a halogen bond, which remains intact over the simulated time scale of 40 ps. For example, the $\angle\text{O}_{\text{w1}}\cdots\text{I}\cdots\text{O1}$ at 15 ps is 178.4°, and the $\text{I}\cdots\text{O}_{\text{w1}}$ and I-O1 bonds are 2.32 and 2.29 Å, respectively. Similarly, the $\angle\text{O}_{\text{w1}}\cdots\text{I}\cdots\text{O1}$ at 20 ps is 167.5°, and the $\text{I}\cdots\text{O}_{\text{w1}}$ and I-O1 bonds are 2.36 and 2.34 Å, respectively. The average $\text{I}\cdots\text{O}_{\text{w1}}$ and I-O1 bond distances over 40 ps time scale are 2.35 Å and 2.27 Å, respectively. Among the N-O bonds, the N-O1 bond is the longest one with an average value of 1.37 Å. The N-O_2 and N-O_3 bond distances have average values of 1.24 and 1.25 Å, respectively.

We next analyzed CDFs of the interfacially-bound IONO_2 to gain deeper insights into the $\text{O}_{\text{w1}}\cdots\text{I-O1}$ halogen bonding (**Figures 5c** and **5d**). Specifically, we analyzed a CDF combining an RDF between I of IONO_2 and O_{w1} atom of H_2O and an ADF between the $\text{I}\cdots\text{O}_{\text{w1}}$ and $\text{I}\cdots\text{O1}$ vectors. The halogen bonding between I of IONO_2 and the interfacial water molecules could be characterized using a criterion with $2.10 \text{ Å} \leq \text{I}\cdots\text{O1} \leq 2.50 \text{ Å}$ and $164^\circ \leq \theta (= \angle\text{O}_{\text{w1}}\cdots\text{I}\cdots\text{O1}) \leq 180^\circ$. The peak for the $\text{I}\cdots\text{O1}$ distance distribution in the $\text{O}_{\text{w1}}\cdots\text{I-O1}$ halogen bonding occurs at 2.27 Å and the corresponding peak for the $\angle\text{O}_{\text{w1}}\cdots\text{I}\cdots\text{O1}$ angle distribution occurs at 177°. The CDFs of two RDFs involving $\text{I}\cdots\text{O1}$ and $\text{I}\cdots\text{O}_{\text{w1}}$ bond distances in the $\text{O}_{\text{w1}}\cdots\text{I}\cdots\text{O1}$ halogen bonding suggest that the peak for both the $\text{I}\cdots\text{O}_{\text{w1}}$ and $\text{I}\cdots\text{O1}$ distance distribution occurs at 2.27 Å. These structural signatures are typical for a halogen bonding system.³¹⁻³³

Figure 6. Upper panel: molecular electrostatic potential maps of HIO_2 , IO_2^- , HIO_3 , IO_3^- , and IONO_2 . Red indicates negative electrostatic potential; blue refers to positive electrostatic potential. The electrostatic potential surfaces were calculated at an isovalue of 0.004. Lower panel: M06-2X/aug-cc-pVDZ+LANL2DZ optimized structures of HIO_2 - IONO_2 , IO_2^- - IONO_2 , HIO_3 - IONO_2 and IO_3^- - IONO_2 . Key bond distances and bond angles are shown. The calculated natural bond orbital (NBO) charges are also mentioned in blue color. See also **Figure S7** for detailed NBO charge distribution. The CCSD(T)/aug-cc-pVTZ+LANL2DZ//M06-2X/aug-cc-pVDZ+LANL2DZ calculated electronic binding energies of these complexes are also mentioned. Gibbs free energies are given in parentheses. Ball-stick representation was used for all structures. Iodine is shown in magenta, oxygen in red, nitrogen in blue, and hydrogen in white.

f) Bonding and structural analysis in the gas-phase.

To gain deeper insights into the IONO_2 -induced halogen bonding in HIO_3 - IONO_2 and HIO_2 - IONO_2 complexes, we next performed bonding and structural analysis of the HIO_2 - IONO_2 , IO_2 - IONO_2 , HIO_3 - IONO_2 and IO_3 - IONO_2 complexes in the gas-phase using Mo6-2X/aug-cc-pVDZ+LANL2DZ and MP2/aug-cc-pVDZ+LANL2DZ levels of theory. The anionic complexes were also considered here because the BOMD simulations suggest that HIO_3 at the air-water interface undergoes deprotonation and exists as IO_3^- while interacting with IONO_2 . As a first step, we calculated the molecular electrostatic potential surfaces of HIO_2 , IO_2^- , HIO_3 , IO_3^- , IONO_2 at the Mo6-2X/aug-cc-pVDZ+LANL2DZ level of theory (Figure 6). The Mo6-2X and MP2 calculated geometries are given in Tables S1 and S2, respectively. The calculations suggest that the electrostatic potential around the iodine atom of IONO_2 is positively charged, which gives rise to the σ -hole, a typical signature of halogen bond donors.³¹⁻³³ This explains why IONO_2 acts as a halogen bond donor when interacting with HIO_3 or HIO_2 . On the other hand, oxygens in HIO_3 and HIO_2 are negatively charged, which is significantly enhanced in their deprotonated forms. This suggests that deprotonated HIO_3 and HIO_2 will form stronger halogen bonds with IONO_2 . It is important to mention here that iodine atom in HIO_3 and HIO_2 also bear positive charges implying that both these iodine compounds can also act as halogen bond donors under appropriate conditions. However, we did not explore that mode of interaction in the gas-phase or at the air-water interface. Next we optimized the HIO_2 - IONO_2 , IO_2^- - IONO_2 , HIO_3 - IONO_2 and IO_3^- - IONO_2 complexes at the Mo6-2X/aug-cc-pVDZ+LANL2DZ level of theory and analyzed key structural parameters and NBO charges on key atoms in these complexes. The calculated halogen bond distances and their near linear nature is consistent with previous literature reports on halogen bonding.³²⁻³⁴ The calculated NBO charges provide further insight into the IONO_2 -induced halogen bonding. In all the IONO_2 complexes, iodine atom of IONO_2 bears ~ 0.50 NBO charge indicating proton-like behavior. The oxygen atoms of HIO_3 , HIO_2 , IO_3^- , IO_2^- and IONO_2 , which directly interact with the positively charged iodine of IONO_2 , bear negative charge. All the halogen bond acceptor oxygens bear nearly one-unit negative charge whereas the halogen bond donor oxygen of IONO_2 bears nearly 0.60 unit of negative charge. For a more detailed NBO picture in these complexes, see Figure S7. The electronic binding energies of these complexes were next calculated at the CCSD(T)/aug-cc-pVTZ+LANL2DZ//Mo6-2X/aug-cc-pVDZ+LANL2DZ level of theory to investigate whether these halogen bonds are actually viable or not. See Table S3 for more details. The calculations suggest that the IONO_2 -induced halogen bonds are quite stable in nature. The HIO_2 - IONO_2 and HIO_3 -

Figure 7. The M06-2X/aug-cc-pVDZ+LANL2DZ calculated IR spectra of free HIO_2 , IO_2^- , HIO_3 and IO_3^- as well as their IONO_2 complexes. The blue and red curves represent the spectra of iodine species before and after complexation, respectively. See also Table S1.

IONO_2 complexes have 13.9 and 10.3 kcal/mol electronic binding energies, respectively. HIO_3 and HIO_2 could undergo deprotonation and give rise to the IO_2^- - IONO_2 and IO_3^- - IONO_2 complexes in the troposphere. The calculated binding energy of the IO_2^- - IONO_2 complex is 50.7 kcal/mol whereas that of the IO_3^- - IONO_2 complex is 35.6 kcal/mol. Clearly, the deprotonation of iodine acids could lead to stronger halogen bonding interactions. This gas-phase analysis suggests that the IONO_2 -induced halogen bonding observed at the air-water interface is indeed possible.

We next analyzed harmonic vibrational frequencies to better understand the bonding structure of iodine species upon complexation. These frequencies were calculated at the Mo6-2X/aug-cc-pVDZ+LANL2DZ and MP2/aug-cc-pVDZ+LANL2DZ levels of theory. Table S4 lists the calculated harmonic frequencies whereas Figure S8 shows the labeling scheme used in the discussion of frequency results. The Mo6-2X calculated spectra is shown in Figure 7 whereas the MP2 calculated spectra is shown in Figure S9. See Tables S2-S3 for the Mo6-2X- and MP2-optimized geometries of all species studied here. Results from both methods show that all species are global minima on their potential energy surface. Inspection of Table S4 reveals that the I-O_2 bond length in free HIO_2 and HIO_3 were predicted to be 1.8036 and 1.7476 Å respectively. These distances were increased by 0.02 Å upon complexation. The I-O bond distance in IONO_2 (2.2556 Å) also increased by 0.2 Å upon complexation. The I-O_2 distance in the IO_2^- was predicted to be 1.8653 Å, which increased by 0.044 Å upon complexation. Similarly, the calculated I-O_2 distance in IO_3^- was 1.7838 Å, which increased by 0.058 Å upon complexation. The I-O_3 and I-O_4 distances

in the IO_3^- - IONO_2 complex did not change much relative to their value in free IO_3^- . This change in the equilibrium geometries will affect the harmonic frequencies. The I_2O_2 bond elongation results in redshift in the frequencies (Figure 7). For instance, the calculated I_2O_2 stretching mode in free HIO_3 and HIO_2 were 877 and 782 cm^{-1} , respectively. These were redshifted by 41 cm^{-1} upon complexation. The I_2O_3 stretching mode does not change much and shows only a slight shift of 3 cm^{-1} . The I_2O_2 stretching mode in IO_3^- - IONO_2 complex is redshifted by 108 cm^{-1} , which is the largest redshift among all iodine complexes. Note that it is relatively harder to estimate the shift in the complexed IO_2^- due to the mixing between the symmetric and asymmetric stretching modes. The OH stretching mode in free HIO_3 and HIO_2 were predicted to be 3780 and 3827 cm^{-1} , respectively. Upon complexation, these are redshifted by 72 and 52 cm^{-1} (Figure 7), indicating a noticeable elongation of the HO bond length. The Mo6-2X calculated OH bond length in free HIO_3 and HIO_2 were predicted to be 0.9720 and 0.9677 Å, respectively. Upon complexation, these distances are increased by 0.0045 and 0.0042 Å, respectively. Similar conclusions were drawn from the MP2 results (Figure S9 and Table S4).

Atmospheric implications. The role of halogen bonding in drug design, material discovery and catalysis is well appreciated.³²⁻³⁶ Some studies have explored the role of halogen bonding in gas phase atmospheric chemistry, e.g. in the formation of hydrated HOX clusters ($X = \text{Cl}, \text{Br}$)³⁷, iodine oxide clusters and hydrated iodine oxide clusters⁴, and others³⁸. It has been recently proposed that halogen bonding may play a role in chemical transformations in particles³⁸. Our work is the first inspecting in detail these unusual interactions in the context of atmospheric aerosol surface chemistry.

Our dynamic simulations indicate that the iodine atom of IONO_2 interacts with interfacial water oxygen through halogen bonding, supporting the high accommodation coefficient assumed in atmospheric models¹². In addition, IONO_2 can act as a halogen bond donor and interact with oxygen-rich iodine acids or oxides or other species in the air-water interface. We have shown that IONO_2 can interact with gas phase HIO_2 or HIO_3 , or with IO_3^- present at the aerosol surface. Similarly, it could also interact with iodine oxides such as I_2O_y ($y = 2 - 4$), resulting in new complexes. The calculated electrostatic potential maps for I_2O_2 and I_2O_3 suggest that these interactions are viable and are expected to be relatively stronger in I_2O_3 (Figure 8). This also indicates a high IONO_2 reactive uptake coefficient. The ability of IONO_2 to stick to aqueous aerosol surface may also modify substantially its photochemistry.

Previous atmospheric modelling studies have assumed that IONO_2 would hydrolyze on aqueous

Figure 8. The calculated molecular electrostatic potential maps of I_2O_2 and I_2O_3 . Red indicates negative electrostatic potential; blue refers to positive electrostatic potential. The electrostatic potential surfaces were calculated at an isovalue of 0.004 .

aerosol, resulting in iodide ions¹². These react in the aqueous phase with available halide anions in the presence of sufficient acidity, forming di-halogens, and thus resulting in halogen activation. Future studies should investigate the fate of halogen-bound complexes at the air-water interface. After uptake, they may result in the formation of iodate rather than iodide. For example, IO_3^- - IONO_2 may decompose into I_2O_3 , which could subsequently hydrolyze, forming HIO_3 and eventually IO_3^- . Currently the factors controlling the iodate to iodide ratio in aerosol and rain water are not understood¹, although recent particulate iodine observations in the upper troposphere and lower stratosphere show this fraction to be dominated by iodate³⁹. Furthermore, as gas phase molecules, HIO_x - IONO_2 may photolyze or, in coastal environments, participate in new particle formation. Our work should open up new research avenues in further exploring the role of these unusual non-covalent interactions in atmospheric chemistries.

A related aspect is the role of halogen bonding in the formation of cluster anions in ambient chemical ionization mass spectrometry (CIMS). A popular CIMS ionization scheme employs iodine for the detection of di-halogens (excluding I_2), nitric acid (HNO_3), and organic acids. This is achieved by the formation of complexes that can be easily identified in the mass spectra, provided that a primary standard is available. Some of these complexes show halogen-bonding³⁸. Other ionization schemes employing bromide, acetate or nitrate ions are more suitable for the detection of ambient iodine species, e.g. of gas phase HIO_3 by nitrate CIMS as IO_3^- has been reported⁸. The halogen-bonded IO_3^- - IONO_2 adduct studied in the present work may be as well reached from $\text{I}_2\text{O}_3 + \text{NO}_3^-$, in such a way that these reagents connect without barriers with the products $\text{IO}_3^- + \text{IONO}_2$ (a bimolecular nucleophilic substitution). Thus, a major iodine oxide such as I_2O_3 ⁵ is also likely to produce IO_3^- , potentially confounding the interpretation of nitrate CIMS mass spectra. Considering that the existing field measurement techniques are very sensitive, but not entirely selective to establish the chemical composition of molecular clusters, computational chemistry could play a crucial role in illuminating the interpretation of observations.

CONCLUSIONS

The HIO_3 - IONO_2 and HIO_2 - IONO_2 interactions as well as the dynamics behavior of IONO_2 at the air-water interface were explored using molecular simulations. Interestingly, the iodine atom of IONO_2 interacts with HIO_2 or IO_3^- present at the aerosol surface or interfacial water molecules through halogen bonding. The gas-phase analysis of IONO_2 complexes suggest that the iodine atom of IONO_2 in these complexes behave like a proton, which contributes towards its halogen bonding behavior. This halogen bonding may result in a high IONO_2 reactive uptake coefficient at the aqueous aerosol surface, which may also modify substantially its photochemistry. The IONO_2 -induced halogen bonding with potential iodine species could also result in new particle formation in coastal environments. In short, our work should open up new research avenues in further exploring the role of these unusual non-covalent interactions in atmospheric chemistries.

ASSOCIATED CONTENT

Supporting Information. Movies showing the trajectories of the aqueous phase dynamics of the HIO_3 , IONO_2 , HIO_3 - IONO_2 , and HIO_2 - IONO_2 at the air-water interface, time evolution profiles of key distances involved in the interfacial HIO_3 - IONO_2 and HIO_2 - IONO_2 complexes, Mo6-2X calculated NBO charges, rotational constants, zero-point correction, thermal correction to Gibbs free energy, CCSD(T) calculated electronic energies, MP2 calculated IR spectra of key iodine species, tables containing Mo6-2X and MP2 calculated harmonic vibrational frequencies, and optimized geometries of various species examined in the present work. The Supporting Information is available free of charge on the ACS Publications website.

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