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# Molecular Interaction and Orientation of HOCI on Aqueous and Ice Surfaces

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**ABSTRACT:** The interaction and orientation of hypochlorous acid (HOCl) on the ice surface has been of great interest as it has important implications to ozone depletion. As HOCl interacts with the ice surface, previous classical molecular dynamics simulations suggest its OH moiety orients to the outside of the ice surface, whereas the quantum calculations performed at 0 K indicate its Cl atom is exposed. To resolve this contradiction, herein, Born–Oppenheimer molecular dynamics simulations are adopted, and the results suggest that at ambient temperature, the interaction between HOCl with interfacial water is dominated by the robust H-bond of (HOCl)H–O(H<sub>2</sub>O). As a result, the HOCl mainly acts as the proton donor to the water surface, which thus can participate in proton transfer reactions via the promotion of interfacial water. Moreover, the Cl atom of HOCl is found to be exposed to the outside of the water surface. Therefore, during the heterogeneous reactions of HOCl on the water surface, the Cl atom becomes the reactive site and is easily attacked by other species.

H ypochlorous acid (HOCl) is largely generated from the heterogeneous hydration of  $ClONO_2$  taking place on ice particles in polar stratospheric clouds,<sup>1,2</sup> as shown in reaction 1

$$\text{ClONO}_2 + \text{H}_2\text{O} \rightarrow \text{HNO}_3 + \text{HOCl}$$
 (1)

Once HOCl is produced, it can either be photolyzed at wavelengths

$$HOCl + h\nu \to OH + Cl \tag{2}$$

$$HOCl + HCl \rightarrow H_2O + Cl_2(g)$$
(3)

shorter than 420 nm to generate chlorine  $(reaction 2)^{3,4}$  or participates in a heterogeneous reaction with HCl to produce active species Cl<sub>2</sub> (reaction 3);<sup>5,6</sup> both reactions can promote ozone destruction and result in the ozone hole over the Antarctic.<sup>7,8</sup> Considering the important environmental implications, the heterogeneous reactions of HOCl on ice attracted a great deal of interest.<sup>5,9,10</sup> Experimental studies suggest reactions 2 and 3 proceed extremely fast on ordinary ice.<sup>11,12</sup> However, this is unlikely to happen because of the low temperature and small diffusions of reagents on ice. Therefore, the fast reaction process of HOCl on ice is attributed to its special solvation structure.

Specifically, the solvation of HOCl can greatly affect its orientation and reactive site on ice, which thus change its reaction rates and pathways. Such solvation effects on atmospheric reactions were observed in previous studies, including the species of  $SO_2$ ,<sup>13</sup> NH<sub>2</sub> radical,<sup>14</sup> and  $SO_3$  reactions with organic acids/NH<sub>3</sub>,<sup>15,16</sup> but this has not been well understood for HOCl on the ice surface; therefore, characterizing the molecular adsorption of HOCl on ice and understanding its interactions with water are crucial for revealing important molecular details of HOCl reactions on ice. Considering that past experiments have challenges in describing dynamical conformations on the molecular scale,

several past theoretical studies attempted to address HOCl adsorption mechanisms on ice.

Kroes et al. performed molecular dynamics (MD) simulations with empirical intermolecular potential to reveal HOCl adsorption on the ice surface.<sup>17</sup> They found the OH moiety of HOCl orients to the outside of the ice surface so that its H atom can form more than one H-bond with interfacial water. However, according to the ab initio calculations performed by Dibble et al.,<sup>18</sup> HOCl forms one H-bond with the water monomer, and its OH moiety orients toward the H<sub>2</sub>O molecule. Similar results were also observed in other quantum calculation studies in water complexes of HOCl, namely HOCl·(H<sub>2</sub>O)<sub>1-4</sub><sup>19</sup> and HOCl·(H<sub>2</sub>O)<sub>26</sub>.<sup>20</sup>

The contradictory results obtained in the above studies originate from different methods used in the studies. Classical MD simulation generally performs calculations for large systems at ambient temperatures, which thus can consider the realistic ice surface and thermal effects.<sup>21,22</sup> However, the introduced artificial force field cannot describe the interactions of HOCl with ice accurately. In comparison, quantum calculations can describe the potential between HOCl and water.<sup>4,23</sup> However, they are performed at 0 K, and in many studies, only small systems are considered, which thus reveals HOCl–H<sub>2</sub>O interaction in the gas phase. Toward this end, the Born–Oppenheimer molecular dynamics (BOMD) simulations with gradient-corrected DFT (see the Supporting Information for calculation details) are performed to

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investigate the solvation structures of HOCl on ice. Considering the supercooled aqueous or quasi-liquid layer might exist on the formed ice particles, the interactions of HOCl with supercooled water droplets are also investigated.

Figure 1A depicts the water density profile along with the direction that is perpendicular to aqueous/ice surfaces (zero



**Figure 1.** (A) The density profile of water along with the direction that is perpendicular to the aqueous/ice surfaces. (B) The distance of HOCl to the COM of the system along with the simulation time.

point is set as the center of mass (COM) of the system). The Gibbs dividing surface, which is defined as the position with 50% of bulk water density, is observed to locate at  $\sim$ 10.6 and  $\sim$ 16.8 Å for aqueous droplet and ice. Figure 1B shows the distance between HOCl and COM of the system against simulation time. It can be seen that as HOCl interacts with aqueous/ice, it always vibrates around the Gibbs dividing surfaces. This indicates HOCl tends to interact with the interfacial region of condensed water (Such a surface preference of HOCl is also revealed by the free energy profile of HOCl migrating from air to bulk water, as seen in Figure S1. The calculation details are also depicted in the Supporting Information.).

Next, the interaction of HOCl with aqueous/ice surfaces is investigated. The radial distribution function profiles between HOCl and interfacial water are calculated (see details in Figure S2); the results of which indicate the H-bond of (HOCl)H– $O(H_2O)$  is relatively strong, whereas the H-bond of (HOCl)- $H-O(H_2O)$  is weak. To reveal the detailed H-bond network, the probabilities of H-bond numbers are analyzed, as shown in Figure 2. At the aqueous surface, the H atom of HOCl tends to



**Figure 2.** Probabilities of numbers of H-bonds formed by  $(HOCl)H-O(H_2O)$ ,  $(HOCl)O-H(H_2O)$ , and  $(HOCl)Cl-H(H_2O)$  at (A) aqueous and (B) ice surfaces.

form one H-bond with interfacial  $H_2O$ , the probability of which is larger than 98%. For the O atom of HOCl, it can form 0, 1, and 2 H-bonds with interfacial water, with the probabilities of ~27%, 70%, and 3%, respectively. However, the Cl atom of HOCl cannot form any H-bond with interfacial water as the H-bond number is always 0. Overall, the H atom

of HOCl gets the largest chance to form the H-bond with aqueous water (average H-bond number is 0.98), followed by the H-bond of (HOCl)O $-H(H_2O)$  (average H-bond number is 0.76). For the H-bond network on ice, the major difference with respect to that of aqueous is that (HOCl)O $-H(H_2O)$  involves a higher chance to form two H-bonds. As a result, its average H-bond number reaches 1.03, which is slightly higher than that of (HOCl)H $-O(H_2O)$  (0.98).

The dynamic stability of H-bonds can be evaluated by the correlation function C(t). The C(t) is given by

$$\langle C(t) \rangle = \left\langle \frac{1}{N_{\rm s1}} \sum_{i=1}^{N_{\rm s1}} [h_i(0)h_i(t)] \right\rangle$$

where  $N_{s1}$  is the H-bond number, and  $h_i(t)$  is 1 or 0 for an H-bond formed or broken at time *t*.

Figure 3 shows the C(t) profiles for H-bonds of (HOCl)H– O(H<sub>2</sub>O) and (HOCl)O–H(H<sub>2</sub>O) at aqueous and ice surfaces,



Figure 3. Correlation function profiles for various H-bonds at (A) aqueous and (B) ice surfaces.

respectively. To make a comparison, the C(t) profile for Hbonds formed between aqueous waters is also analyzed, as depicted by the blue curve of Figure 3A. At the aqueous surface, the C(t) for the H-bond of (HOCl)O-H(H<sub>2</sub>O) involves the fastest decay rate, with the half lifetime (defined as the time when C(t) value reaches 0.5) ~ 1 ps. The lifetime of the H-bond formed between water molecules is found  $\sim 10$ times larger than that of  $(HOCl)O-H(H_2O)$ , suggesting the H-bonds formed by water are stronger than that of  $(HOCl)O-H(H_2O)$ . As a result, the O atom of  $H_2O$  can compete with the O atom of HOCl to form H-bonds with interfacial water and leads to the H-bond of (HOCl)O- $H(H_2O)$  being broken. However, for the H-bond of (HOCl)- $H-O(H_2O)$ , the C(t) value almost shows no decay along with BOMD simulation. The half lifetime is much longer than that of  $(H_2O)O-H(H_2O)$ . This suggests the H atom of HOCl forms a robust H-bond with interfacial water, which thus can hardly be replaced by self-interactions among water molecules. For C(t) profiles on ice (Figure 3B), the H-bond of  $(HOCl)O-H(H_2O)$  involves a smaller decay rate than that on aqueous. It suggests that compared to aqueous, the H-bond of  $(HOCl)O-H(H_2O)$  is stronger on ice.

Overall, from perspectives of H-bond numbers, strength, and lifetimes, the interaction between HOCl and interfacial water is dominated by the H-bond of  $(HOCl)H-O(H_2O)$ . Meanwhile, the H-bond of  $(H_2O)O-H(H_2O)$  also accounts for an important type of interaction, especially on the ice surface, suggesting that HOCl mainly acts as proton donor but can also act as a proton acceptor on water surfaces.

To gain deeper insight into the hydration structures of HOCl on the water surface, we investigate the probability of

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four typical H-bond complexes. Figure 4A shows the configurations of these four solvation structures, and the



**Figure 4.** (A) Four typical complexes formed by HOCl and interfacial  $H_2O$ . The blue dashed lines represent H-bonds. The white, red, and cyan spheres represent H, O, and C atoms, respectively. Pie chart of probabilities of different H-bond complexes at (B) aqueous and (C) ice surfaces.

corresponding probabilities are depicted in Figure 4B (aqueous) and Figure 4C (ice). On both aqueous/ice surfaces, Complex 3, in which HOCl acts as both proton donor and acceptor, involves the largest probability and accounts for  $\sim$ 70%. Complex 1, in which HOCl interacts with interfacial water by only its H atom, also accounts for the large percentage ( $\sim$ 25%) on the aqueous surface. However, on the ice surface, Complex 4 is more popular than Complex 1, suggesting the O atom of HOCl involves a stronger interaction with ice. Other than these four complexes, the other hydration structures are extremely rare, with the overall percentage less than 2%.

The above analysis shows a specific interaction exists between HOCl and interfacial water. Such interactions might align the HOCl into a special orientation. Here, the orientation of HOCl on the water surface is revealed by an angular coordinate,  $\theta$ .  $\theta$  is the angle formed by the vector from the center of mass of the water droplet to the O atom of HOCl and the vector from the O atom of HOCl to the Cl atom of HOCl, as shown in Figure 5A. The probability of  $\theta$  is depicted in Figure 5B. It can be seen that  $\theta$  is mostly distributed within 90° on both aqueous and ice surfaces, suggesting the Cl atom tends to be exposed to the outside of the water surfaces.

The special solvation structure of HOCl can have important implications on its atmospheric fate on water surfaces. As shown in the reaction example of HOCl with the Cl atom (Figure 6), two possible reaction pathways can be proposed based on the adsorption mechanisms of HOCl. The corresponding potential energy surfaces for these two pathways are also depicted in Figure S3, which are calculated at the M06-2X/6-311+G(3df,3pd) //M06-2X/6-311G(d,p) level of



**Figure 5.** (A) The sketch for the angular coordinate,  $\theta$ , which is defined as the angle formed by the vector from the center of mass of the water droplet to the O atom of HOCl and the vector from the O atom in HOCl to the Cl atom in HOCl. (B)  $\theta$  distribution for HOCl at the surface of aqueous (black curve) and ice (green curve). The blue curve represents the regular (normalized) distribution 1/2  $\sin(\theta)$ .



**Figure 6.** Two possible reaction mechanisms between HOCl and the Cl atom on the water surface: (A) HOCl + Cl  $\rightarrow$  Cl<sub>2</sub> + OH and (B) HOCl + Cl  $\rightarrow$  HCl + ClO.

theory with the consideration of solvation effects (see the Supporting Information for calculation details). 1) Because the Cl atom of HOCl is exposed to the outside of the water surface, it can readily collide with the incoming Cl atom, which would lead to the formation of Cl<sub>2</sub> and the OH radical (Figure 6A). The energy barrier of this pathway is 10.5 kcal/mol (Figure S3A). 2) Considering HOCl mainly acts as a proton donor as it interacts with a water surface, it can transfer its proton and participate in a proton transfer reaction with the Cl atom, which forms the ClO radical and HCl (Figure 6B). In this proton transfer process, the interfacial water can act as a catalyst and reduce the energy barrier from 11.64 to 6.37 kcal/ mol for this pathway, as compared in Figure S3B and S3C. Such a catalysis effect of interfacial water has been observed in many proton transfer reactions.<sup>15,16</sup> The insights from this study of HOCl-aqueous/ice interactions help to better understand heterogeneous reactions of HOCl. According to these results, the actual reaction pathways and activation barriers of HOCl on ice can be investigated further, to gain more detailed molecular insight into the ozone depletion process involving HOCl in a more comprehensive manner.

# ASSOCIATED CONTENT

## **Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.0c08994.

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Computational details, free energy profile, radial distribution function profiles, and potential energy surfaces (PDF)

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#### **Author Contributions**

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The authors declare no competing financial interest.

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