Ab Initio Study of HOCl, HCl, H_2O, and Cl_2 Interacting with Four Water Molecules

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We present an ab initio study of the interaction of the stratospherically significant compounds HOCl, HCl, H_2O, and Cl_2 with four water molecules representing an adsorption site on the surface of hexagonal ice. Using the 6-311++G(d,p) basis set and geometries optimized at the MP2 level of theory, the interaction energies of HOCl, HCl, H_2O, and Cl_2 with the water tetramer were found to be −37, −26, −17, and −11 kJ/mol, respectively. Results indicate that when a small foreign molecule interacts with a water adsorption site in these systems, both adsorbed molecule and adsorption site maintain their original geometric and electronic structure. Optimized geometries of the test molecules at the prototypical ice adsorption site are reported.

I. Introduction

The chemistry of small chlorine-containing gases on ice surfaces has received a great deal of attention in the past decade since the discovery that these materials are involved in stratospheric ozone depletion.[1−3] Stratospheric chlorine species consist of the stable reservoir species chlorine nitrate ($ClONO_2$) and hydrochloric acid (HCl) and the less stable species hypochlorous acid (HOCl) and chlorine (Cl_2).[4−6] Production of the less stable species can lead to an increase in the concentration of Cl radicals by photolysis, for example, and it is the Cl radical that catalytically converts ozone to oxygen.[3,7−9] Production of HOCl and Cl_2 from reservoir chlorine species is thought to occur heterogeneously on ice contained in polar stratospheric clouds (PSC's) at 185 K by the reactions[1−6]

$$ClONO_2 + HCl \rightarrow HNO_3 + Cl_2 \tag{1}$$

$$ClONO_2 + H_2O \rightarrow HNO_3 + HOCl \tag{2}$$

Polar stratospheric clouds are composed of small 1 μm particles consisting of nitric acid hydrates (type I) and of larger (∼10 μm) particles of hexagonal water ice (type II).[10−13] In this study, we concentrate on water ice, which forms at 188 K or less in the stratosphere, temperatures reached inside the polar vortex above Antarctica. Understanding the mechanisms of the heterogeneous reactions such as (1) and (2) is important for accurate predictions of ozone depletion chemistry in many environments, including the stratosphere and the upper troposphere on particles including ice, aerosols, and solids from aircraft emissions. Experimental data leading to molecular descriptions of the reactions are sparse due to the difficulty of performing surface experiments on a high vapor pressure material such as ice (the vapor pressure of ice at 185 K is 10^{-4} Torr, too high to allow the use of most surface techniques).[14]

In recent years, several molecular dynamics simulations and ab initio calculations on HCl and HOCl interacting with water molecules have been performed. They have included an ab initio study by Dibble and Francisco showing that the geometry of the $HOCl \cdot H_2O$ complex has C_s symmetry with preferred syn configuration.[15] Low binding energies were obtained in their work. Robinson-Brown and Doren studied the interaction of HOCl with four water molecules and a water cluster consisting of 26 water molecules using density functional theory. They found that HOCl acts as a proton donor and arrived at binding energies between 43 and 52 kJ/mol.[16] Kroes and Clary performed molecular dynamics simulations on HCl and HOCl interacting with ice, resulting in higher binding energies for HOCl.[17] The higher binding energies match experimental results obtained using amorphous ice.

Packer and Clary performed an ab initio study of HCl interacting with up to three water molecules.[18] Cyclic structures were found to correspond to the global energy minimum, and HCl retained its molecular identity. Wang and Clary examined the interaction of HCl with ice using two-dimensional quantum molecular dynamics resulting in large-amplitude vibrations for the adsorbate−surface species.[19] HCl was found to adsorb with its proton sticking toward the ice, and an interaction energy of 25 kJ/mol was obtained. Whether or not HCl ionizes on ice surfaces is an important but still controversial issue in heterogeneous stratospheric chemistry. Infrared spectroscopic studies on vacuum-deposited ice at low temperatures ($<$160 K) suggest the loss of molecular HCl.[20−25] Graham and Roberts observed molecular HCl on solid HCl hexahydrate made at 120 K.[26,27] On the other hand, two computational studies using molecular dynamics including a proton-transfer step show acid ionization on ice.[28,29] These studies include the dynamic nature of the ice surface and assume HCl gets buried by impinging water molecules, allowing for solvation of the ions.

In the available ab initio studies of adsorption of foreign molecules at ice surfaces, work concentrated on obtaining the geometries corresponding to the global minimum of the potential energy surface. Results from quantum mechanical methods combined with molecular dynamics treatments are promising and seem more convincing in representing the physical and chemical processes occurring during adsorption than pure molecular dynamics simulations. But a detailed quantum mechanical analysis of the adsorbate−surface entity has not been performed so far.

In this work, we present an ab initio calculation of the adsorption of HOCl, HCl, H_2O, and Cl_2 on a water tetramer mimicking an adsorption site on the 0001 (basal) surface of hexagonal ice. We concentrate on geometric and electronic changes in both the adsorbates and the adsorption site during their interaction.

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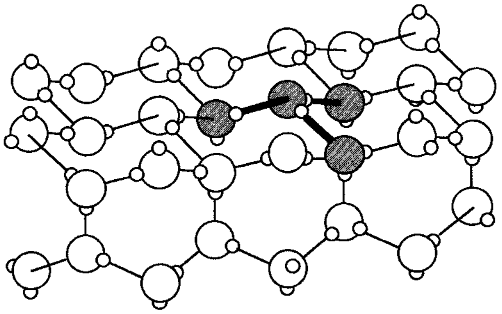

Figure 1. Basal plane of ice and plausible and abundant adsorption sites (adapted from refs 30 and 40).

II. Generating an Ice Surface Model

The surface structure of ice at various temperatures is not known. An ideal termination of the hexagonal (0001) ice surface generates water molecules oriented with one of the two free electron pairs directed away from the surface into the gas phase (see Figure 1). Supporting this picture is a recent low-energy electron diffraction (LEED) study by Materer et al. on a thin ice layer crystallized onto a Pt (111) surface at 140 K.[30] To investigate the outermost layers of the ice film, the LEED study was combined with molecular dynamics simulations and ab initio calculations at the Hartree–Fock level on two-dimensional periodic slabs of ice. A full-bilayer termination of the ice film was found.

This same LEED study found that, down to at least 90 K, the outermost water molecules undergo large rotational motions.[30] However, several studies suggest that crystalline ice has indeed a low concentration of dangling OH groups at the surface.[31–35] Using transmission IR spectra for both thin films of amorphous ice and large clusters of crystalline cubic ice at temperatures between 10 and 120 K, Devlin and co-workers observed dangling OH groups, implying there is some polar character to the ice surface.[31–33] Schaff and Roberts performed single-reflection Fourier-transform infrared spectroscopy on amorphous and crystalline ice films at 95 and 160 K. At 160 K, the crystalline ice samples were found to have a low density of dangling OH groups, corresponding to a mostly nonpolar surface.[34,35] This conclusion supports early work by Adamson and co-workers, who found that molecular adsorption on ice resembles that of a nonpolar surface.[36,37]

On the basis of these studies, we constructed an ice surface model as follows. Due to the large calculational burden of ab initio studies, we constrained the number of water molecules to four. Computational times on an IBM RS/6000 3CT computer, equipped with 2 GB of disk space and 64 MB RAM, for four water molecules and an adsorbate range from 100 to 150 h. Four water molecules were arranged in such a way that they represent the junction of three hexagonal rings in an ideal (0001) ice surface,[40] thereby mimicking a plausible and abundant adsorption site on water ice. The model geometry has the protons arranged such that the four water molecules have C_s symmetry (see Figure 2). The central water molecule (a) acts both as a hydrogen acceptor and (2-fold) donor, with one free electron pair oriented up. Two water molecules (b and c) are hydrogen acceptors, and the fourth water molecule (d) acts as a hydrogen donor.

At stratospheric temperature and pressure conditions, the ice/water vapor interface is very dynamic, with 100 monolayers of water molecules constantly exchanging per second at the interface.[41–44] Is our model of a static site relevant to the problem of adsorption of a foreign molecule on an ice surface at 180 K? The process of an HCl molecule striking an ice site and attaining an equilibrated geometry occurs on a time scale many orders of magnitude smaller than seconds: more like typical picosecond times associated with vibrations and rotations. Further, the time for diffusion of an H_2O molecule away from the adsorption site into bulk ice is approximately 5 ms while the time for desorption is approximately 90 ms at 180 K.[45] Thus, because of the large mismatch of adsorption times versus evaporation, condensation, and diffusion times, an ice surface site will appear quite static to an incoming foreign molecule.

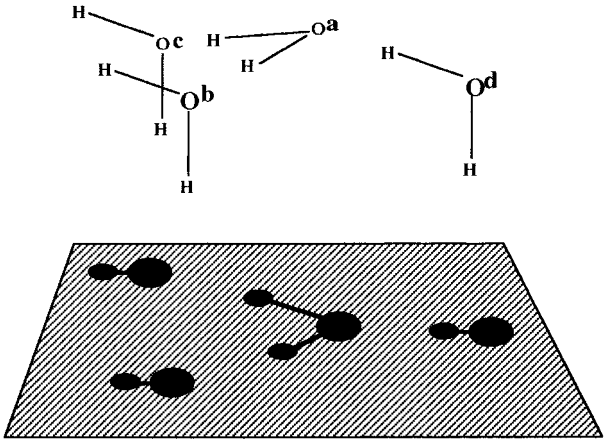

Figure 2. The water tetramer in C_s symmetry, optimized using MP2/6-311++G(d,p).

III. Methods

A preliminary study aimed at finding a method that is both economical and yet accurate enough to yield geometries close to experimental geometric parameters for the monomers was first performed. We carried out ab initio calculations at the Hartree–Fock level of theory and using second- and fourth-order Møller–Plesset perturbation theory (MP2 and MP4). The Gaussian 94 set of programs[46] was used. Geometries of H_2O, HOCl, HCl, and Cl_2 obtained by the methods using various basis sets are summarized in Table 1. With the triple-ζ basis sets, at the Hartree–Fock level of theory, both OH bond lengths of HOCl and water as well as the OCl bond length of HOCl are underestimated. This result together with the overestimation of the HOCl bond angle led us to reject Hartree–Fock level of theory for the geometry optimizations. At the MP2 level of theory, results obtained are in good agreement with the experimental geometry for HOCl, but the water bond angle is underestimated by 1° when the 6-311++G(d,p) basis set is employed. It can be seen that the use of MP4 level of theory, although computationally very expensive, does not result in a considerable improvement of the geometric parameters. Therefore, the geometry optimizations for the clusters will be performed at the MP2 level of theory.

Various standard basis sets available in Gaussian 94 were examined at the MP2 level. We examined the double-ζ basis set 6-31G(d), the triple-ζ basis set 6-311G(d,p) with p polarization functions on hydrogen and d polarization functions on all other atoms, and the triple-ζ basis set 6-311++G(d,p) with p polarization functions on hydrogen and d polarization functions on all other atoms plus diffuse functions. The results are summarized in Table 1. The double-ζ basis set overestimates both OH bond lengths in HOCl and water as well as the OCl bond length of HOCl. Even though the bond angle in water is closest to the experimental value when calculated with this basis set, it can be seen that the triple-ζ basis sets are overall more

TABLE 1: Geometries of H_2O, HOCl, HCl, and Cl_2 Calculated at the Hartree−Fock, MP2, and MP4 Levels of Theory Using the 6-31G(d), the 6-311G(d,p), and the 6-311++G(d,p) Basis Sets (All Bond Lengths in Å, All Angles in deg)

	H_2O		HOCl		HCl		Cl_2
	OH	∠HOH	OH	OCl	∠HOCl	HCl	ClCl
HF/							
6-31G(d)	0.947	105.5	0.951	1.670	105.1	1.266	1.989
6-311G(d,p)	0.941	105.5	0.944	1.673	104.9	1.269	2.003
6-311++G(d,p)	0.941	106.2	0.944	1.667	105.7	1.269	2.000
MP2/							
6-31G(d)	0.968	104.0	0.978	1.715	102.9	1.280	2.015
6-311G(d,p)	0.958	102.4	0.964	1.719	101.7	1.273	2.028
6-311++G(d,p)	0.959	103.5	0.966	1.715	102.7	1.273	2.024
MP4/							
6-31G(d)	0.971	104.0	0.980	1.732	102.5	1.286	2.035
6-311G(d,p)	0.959	102.3	0.966	1.739	101.4	1.276	2.049
6-311++G(d,p)	0.960	103.3	0.968	1.734	102.4	1.276	2.049
experimental	0.958[a]	104.5[a]	0.967[b]	1.690[b]	102.4[b]	1.274[c]	1.987[d]

[a] From ref 47. [b] From ref 48. [c] From ref 49. [d] From ref 50.

TABLE 2: Energies of H_2O, HOCl, HCl, and Cl_2 Calculated at the Hartree−Fock, MP2, and MP4 Levels of Theory Using the 6-31G(d), the 6-311G(d,p), and the 6-311++G(d,p) Basis Sets (All Energies in hartrees, 1 hartree Corresponds to 2.626×10^3 kJ/mol)

	H_2O	HOCl	HCl	Cl_2
HF/				
6-31G(d)	−76.010 75	−534.841 97	−460.059 98	−918.912 82
6-311G(d,p)	−76.046 06	−534.888 21	−460.094 56	−918.962 22
6-311++G(d,p)	−76.053 42	−534.897 04	−460.095 46	−918.967 60
MP2/				
6-31G(d)	−76.196 84	−535.156 83	−460.192 36	−919.171 39
6-311G(d,p)	−76.263 97	−535.235 30	−460.244 02	−919.235 78
6-311++G(d,p)	−76.274 92	−535.244 87	−460.244 92	−919.240 98
MP4/				
6-31G(d)	−76.207 33	−535.182 99	−460.210 89	−919.204 53
6-311G(d,p)	−76.276 34	−535.263 67	−460.262 79	−919.269 25
6-311++G(d,p)	−76.287 25	−535.273 73	−460.263 84	−919.274 81

accurate in describing the HOCl and the water molecules. Apart from a 1°−2° difference in the water bond angle and slight overestimations of the OCl and Cl−Cl bond lengths, both triple-ζ basis sets yield results very close to the experimental values. The bond distance in the chlorine molecule calculated without the diffuse functions was overestimated by 0.041 Å and did not improve significantly upon addition of diffuse functions. Overall, the basis set yielding geometric parameters closest to the experimentally found values was the triple-ζ basis set enhanced by polarization as well as diffuse functions.

Table 2 shows the energies for the molecules calculated with the various basis sets and methods discussed above. On the basis of the small energy differences between the two triple-ζ basis sets, it can be seen that the energy is not sensitive to additional diffuse functions. Diffuse functions may improve the accuracy of calculations in cases where hydrogen-bonded oligomers or compounds with lone pairs are under investigation. Therefore, results from calculations using both the 6-311G(d,p) and the 6-311++G(d,p) basis sets will be presented, and the effect of the additional diffuse functions in the 6-311++G(d,p) basis set on both geometries and binding energies will be discussed.

IV. Geometries of the Complexes

A. Water Tetramer. Four water molecules were arranged in C_s symmetry (see Figure 2). All dihedral angles were constrained at 0°, 60°, or 120° in order to maintain C_s symmetry, whereas all bond lengths and bond angles were relaxed and optimized. Since we were only interested in model structures mimicking an adsorption site on ice, frequency calculations were not performed on the water tetramer. Using the 6-311G(d,p) basis set, the distances from O^a to O^b and from O^a to O^c are both found to be 2.901 Å, whereas the $O^a{-}O^d$ distance is only 2.817 Å (see Table 3). The HOH angle for the center water molecule is 104.9°, and the other three water molecules have HOH angles of 103.1°. The geometry optimized at the MP2 level of theory using the 6-311++G(d,p) basis set is shown in Figure 2. The $O^a\cdots O^b$ and the $O^a\cdots O^c$ distances are both larger when calculated with the addition of diffuse functions to the basis set (see Table 3), which is to be expected due to the influence of the far-reaching diffuse functions. The angles are not as sensitive. The HOH angles only change to 104.6° for the center water molecule and to 103.5° for the other three water molecules.

TABLE 3: Oxygen−Oxygen Distances in the Water Tetramer Calculated Here Using the 6-311G(d,p) and the 6-311++G(d,p) Basis Sets and Comparison to Other Values Available in the Literature

	this study		LEED	cyclic	
	6-311G(d,p)	6-311++G(d,p)	study[a]	$(H_2O)_4$[b]	$(H_2O)_4$[c]
$O^a\cdots$Ob	2.901	2.951			
$O^a\cdots$Od	2.817	2.860			
av O···O	2.859	2.905	2.74	2.77	2.743

[a] From ref 30. [b] From ref 18. [c] From ref 51.

Table 3 shows the $O^a\cdots O^b$ and $O^a\cdots O^d$ distances calculated in this work compared to some results by others. Comparing the 6-311++G(d,p) calculations to the LEED study by Materer et al.,[30] the oxygen−oxygen distances are overestimated here by 0.12 and 0.21 Å for the $O^a\cdots O^b$ and the $O^a\cdots O^d$ distances, respectively. Among others, Packer and Clary[18] as well as

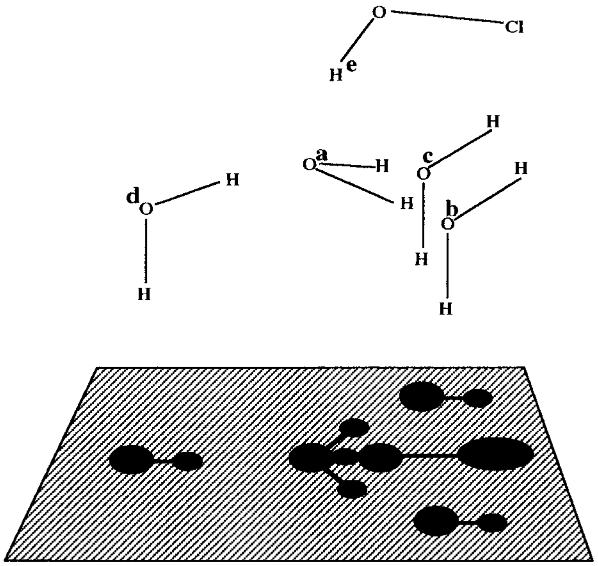

Figure 3. Geometry of the $HOCl\cdot(H_2O)_4$ cluster optimized at the MP2 level of theory with the 6-311++G(d,p) basis set.

Xantheas and Dunning[51] calculated the geometries of the cyclic water tetramer corresponding to the global minimum. In Packer and Clary's work, an average MP2/6-31g(2dp) O···O distance of 2.77 Å was found, close to the 2.743 Å distance found by Xantheas and Dunning for the water tetramer at the MP2 level of theory. Xantheas and Dunning used a basis set slightly larger than the one employed here. It can be seen that the cyclic structure of the water tetramer results in much shorter O···O distances when compared to the water tetramer investigated here.

B. Optimized Geometries for Adsorbates. *1. $HOCl\cdot(H_2O)_4$.* Figure 3 shows the geometry of the $HOCl\cdot(H_2O)_4$ cluster, optimized using the 6-311++G(d,p) basis set. The calculation was performed using both the 6-311G(d,p) and the 6-311G++(d,p) basis sets in order to examine similarities and differences of the two outcomes and to assess their reliability. For both basis sets, it is found that HOCl binds to the water tetramer through its hydrogen. The formation of the hydrogen bond results in the lengthening of the OH bond in HOCl by 0.02 Å and in the contraction of the OCl bond by 0.007 Å for both basis sets. Use of the 6-311G(d,p) basis set yielded the following geometrical values: HOCl and the central water molecule establish a 1.745 Å (H^e-O^a) hydrogen bond with an angle of 167.7° ($O-H^e\cdots O^a$). The larger basis set gives similar results, with an $H^e\cdots O^a$ distance of 1.781 Å and an $O-H^e\cdots O^a$ angle of 163.7°. The $H^e\cdots O^a$ distance is well within the domain of a hydrogen bond, and the system has a slightly nonlinear hydrogen bond.

During the optimization, it was found that the potential energy surface (PES) was not very sensitive to the $Cl-O\cdots O^a\cdots O^d$ dihedral angle for values close to 180°. When the $HOCl\cdot(H_2O)_4$ cluster was optimized such that the $Cl-O\cdots O^a\cdots O^d$ dihedral angle was constrained to 170°, the system was found to be only 0.7 kJ/mol higher in energy than the cluster having C_s symmetry. We therefore scanned the PES for dihedral angles between 0° and 180°. The scan showed that a dihedral angle of 180° resulted indeed in the lowest energy. Based on this test, the geometry corresponding to the lowest energy of the $HOCl\cdot(H_2O)_4$ cluster was found to have C_s symmetry, just as the water tetramer investigated here.

TABLE 4: Geometries of the HOCl, HCl, Cl_2, and H_2O Monomers Interacting with the Water Tetramer Calculated Using MP2/6-311G(d,p) and MP2/6-311++G(d,p) (in Parentheses)[a]

molecule	parameters	this work	other
HOCl	OH*	0.985 (0.985)	0.976,[b] 0.98−1.01[e]
	OCl	1.712 (1.708)	1.709,[b] 1.71−1.77[d]
	∠HOCl	101.7 (102.5)	102.3,[b] 100.8−102.9[e]
HCl	H*Cl	1.305 (1.296)	1.287,[c] 1.6[d]
Cl_2	Cl−Cl	2.049 (2.039)	
H_2O	OH*	(0.967)	
	∠HOH	(103.0)	
	OH	(0.958)	

[a] The results for H_2O are obtained using the MP2/6-311++G(d,p) only, and the asterisk marks the hydrogen atom involved in the hydrogen bond. [b] From ref 15 for $HOCl\cdot H_2O$. [c] From ref 18 for $HCl\cdot H_2O$. [d] From ref 19. [e] From ref 16.

An ab initio study of the $HOCl\cdot H_2O$ complex by Dibble and Francisco using the same basis set and method shows that the syn conformation is more stable than the anti conformation, i.e., that the conformation having the chlorine atom of HOCl on the same side as the two hydrogens in the central water is favored.[15] This arrangement agrees with the geometries found in this work. Density functional studies by Robinson-Brown and Doren[16] yield a comparable orientation of HOCl on a small ice slab containing two water bilayers. On the other hand, Kroes and Clary found in their molecular dynamics calculation[17] that the majority of HOCl molecules have their dipole oriented at around 30°−40° with respect to the ice surface, meaning that the positive charge of HOCl points away from the surface. Table 4 compares the geometries of HOCl interacting with the water tetramer found here and in other work.[15,16] Table 5 summarizes the hydrogen bond characteristics of HOCl interacting with the water tetramer.

2. $HCl\cdot(H_2O)_4$. Figure 4 shows the geometry of the $HCl\cdot(H_2O)_4$ cluster optimized using the 6-311++G(d,p) basis set. HCl binds to the tetramer with its hydrogen, while the chlorine atom is directed away from the four water molecules. When employing the smaller basis set, the hydrogen bond distance is 1.774 Å, with an angle of 167.3°. Using the larger basis set, the $H^e\cdots O^a$ distance was found to be 1.894 Å, and the $Cl-H^e\cdots O^a$ angle was 155.9° (see Table 5). Again, these values are comparable to the normal range of hydrogen bond parameters. The $Cl-H^e\cdots O^a\cdots O^d$ dihedral angle was found to be 180°, yielding C_s symmetry for the $HCl\cdot(H_2O)_4$ cluster and corresponding to a syn conformation of HCl and the central water molecule. It can be seen that the use of diffuse functions has a greater influence on the geometrical arrangement for $HCl\cdot(H_2O)_4$ than in $HOCl\cdot(H_2O)_4$. This is probably due to the fact that the chlorine atom is now much closer to the four waters than in the case of HOCl.

Using molecular dynamics simulations, Kroes and Clary found a similar geometric arrangement for HCl colliding with an ice surface.[17] The proton was found to be directed toward the surface. In a molecular dynamics study that included HCl vibration via a quantum mechanical treatment, Wang and Clary also found that the preferred orientation for HCl upon adsorption to ice is with its proton pointing toward the surface.[19] However, a lengthening of the HCl bond from 1.3 to 1.6 Å was reported in their study, which is in disagreement with this and previous work. The arrangement of HCl with respect to the central water molecule found in our work is also comparable to the geometry of the $HCl\cdot H_2O$ cluster reported by Packer and Clary, who performed ab initio calculations on $(H_2O)_n\cdot HCl$ with $n = 1-3$.[18] In Table 4, our result for the bond length of HCl interacting with the four water molecules is given and compared to the MP2/6-31G(2dp) values found by Packer and Clary for the $HCl\cdot H_2O$ complex. In our work, it is found that the formation

TABLE 5: Values Found for the Hydrogen Bonds Established in $(H_2O)_4$, $(H_2O)_4{\cdot}HOCl$, $(H_2O)_4{\cdot}HCl$, $(H_2O)_4{\cdot}Cl_2$, and $(H_2O)_4{\cdot}H_2O$ Optimized at the MP2 Level of Theory Using the Basis Sets 6-311G(d,p) and (in Parentheses) 6-311++G(d,p)

	this work		other work	
adsorbate	H bond distance[a]	H bond angle[b]	H bond distance	H bond angle
HOCl	1.745 (1.781)	167.7 (163.7)	1.773 (1.809)[e] 1.78−1.81[h]	174.8 (175.8)[e] 169.8−177.5[h]
HCl	1.774 (1.894)	167.3 (155.9)	1.910[f]	178.7[f]
Cl_2	2.660 (2.743)[c]	174.1 (170.6)[d]		
HOH	(1.977)	(171.7)	1.913[g]	174.0[g]

[a] Distance (in Å) between hydrogen of adsorbing molecule and the oxygen atom of the central water molecule of the tetramer. [b] X−H ···O angle where X = O for HOCl, X = Cl for HCl, and X = O for H_2O. [c] Nearest Cl···O distance. [d] Cl-nearest Cl···O angle. [e] From ref 15 for $HOCl{\cdot}H_2O$. [f] From ref 18 for $HCl{\cdot}H_2O$. [g] From ref 51 for cyclic $(H_2O)_5$; values are averages of the individual reported numbers. [h] From ref 16.

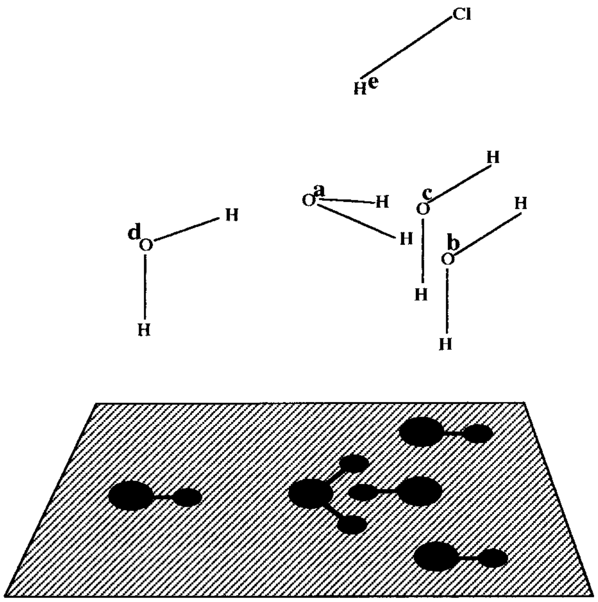

Figure 4. Geometry of the $HCl{\cdot}(H_2O)_4$ cluster optimized at the MP2 level of theory with the 6-311++G(d,p) basis set.

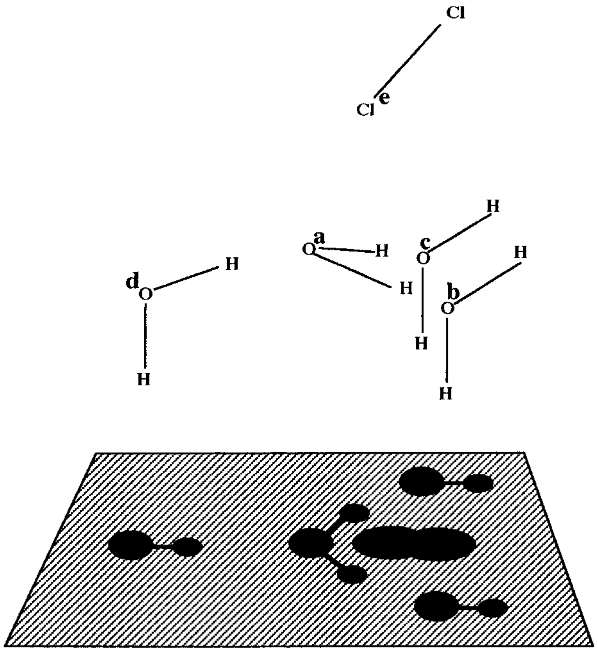

Figure 5. Geometry of the $Cl_2{\cdot}(H_2O)_4$ cluster optimized at the MP2 level of theory with the 6-311++G(d,p) basis set.

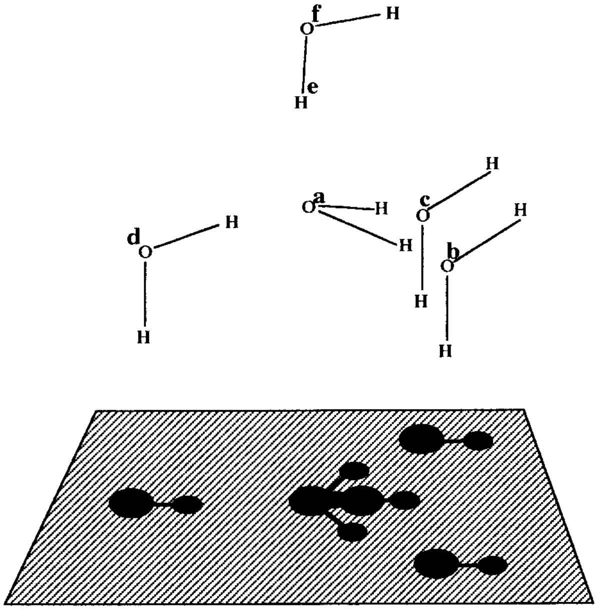

Figure 6. Geometry of the $H_2O{\cdot}(H_2O)_4$ cluster optimized at the MP2 level of theory with a 6-311++G(d,p) basis set.

of the hydrogen bond results in the lengthening of the HCl bond by 0.032 Å when the 6-311G(d,p) basis set is used. On the other hand, when the diffuse functions are added to the basis set, the HCl bond length increases only by 0.020 Å.

3. $Cl_2{\cdot}(H_2O)_4$. The optimized geometry of dichlorine interacting with the water tetramer is shown in Figure 5. Using the 6-311++G(d,p) basis set, Cl_2 interacts with the central water molecule of the tetramer via one chlorine atom, with the second chlorine atom pointing away from the surface, assuming a syn conformation with respect to the central water molecule. With the smaller basis set, the distance of Cl^e to O^a was found to be 2.660 Å, with a $Cl{-}Cl^e{\cdots}O^a$ angle of 174.1°. The basis set with the diffuse functions yields 2.743 Å for the distance of Cl^e to O^a and a $Cl{-}Cl^e{\cdots}O^a$ angle of 170.6° (see Table 5). Again in Table 4 we present the calculated bond length of dichlorine in the $Cl_2{\cdot}(H_2O)_4$ cluster. Upon adsorption, the Cl−Cl bond length was found to increase by 0.021 and 0.015 Å when calculated with the 6-311G(d,p) and the 6-311++G(d,p) basis sets, respectively.

4. $H_2O{\cdot}(H_2O)_4$. The structure of the optimized $H_2O{\cdot}(H_2O)_4$ cluster is shown in Figure 6. Only the larger triple-ζ basis set (6-311++G(d,p)) was used in this case. It can be seen that the fifth water molecule interacts with the central water molecule of the tetramer with one of its hydrogen atoms, maintaining C_s symmetry. The new hydrogen bond has a length of 1.977 Å, resulting in an $O^f{\cdots}O^a$ distance of 2.936 Å, which is slightly shorter than the $O^a{\cdots}O^d$ distance of 2.939 Å. The new hydrogen bond also has an angle of 171.7° which in the larger basis set calculations is the most linear hydrogen bond obtained (see Table 5). From Table 4, it can be seen that the hydrogen atom of the added water involved in the hydrogen bond is pulled

TABLE 6: Total Energies of $(H_2O)_4$, $(H_2O)_4$·HOCl, $(H_2O)_4$·HCl, $(H_2O)_4$·Cl_2, and $(H_2O)_4$·H_2O Optimized at the MP2 Level of Theory Using the 6-311G(d,p) and the 6-311++G(d,p) Basis Sets (All Energies in hartrees)

	$(H_2O)_4$	$(H_2O)_4$·HOCl	$(H_2O)_4$·HCl	$(H_2O)_4$·Cl_2	$(H_2O)_4$·H_2O
MP2/6-311G(d,p)	−305.087 22	−840.233 27	−765.347 81	−1224.332 69	
MP2/6-311++G(d,p)	−305.126 01	−840.389 01	−765.383 92	−1224.374 40	−381.409 15

TABLE 7: Interaction Energies Corrected for Basis Set Superposition Error (BSSE) of $(H_2O)_4$·HOCl, $(H_2O)_4$·HCl, $(H_2O)_4$·Cl_2, and $(H_2O)_4$·H_2O Optimized at the MP2 Level of Theory Using the 6-311G(d,p) and the 6-311++G(d,p) Basis Sets[a]

	$(H_2O)_4$·HOCl	$(H_2O)_4$·HCl	$(H_2O)_4$·Cl_2	$(H_2O)_4$·H_2O
MP2/6-311G(d,p)	−38 (20)	−31 (12)	−13 (12)	
MP2/6-311++G(d,p)	−37 (11)	−26 (8)	−11 (8)	−17 (5)
other work	−25[b]	−19[c]		−28[k]
calculations	−60[c]	−32, 30[d]		−19[l]
	−(43−52)[g]	−25[e]		
other work	−58 ± 8[h]	−46[j]		
experimental	−44 ± 8[i]	−33 ± 5[f]		

[a] All energies in kJ/mol, the counter poise correction (CPC) method was used to account for the BSSE (amount of correction in parentheses). [b] From ref 15. [c] From ref 17. [d] From ref 18; values are for $(H_2O)_n$·HCl ($n = 2, 3$). [e] From ref 19. [f] From ref 26. [g] From ref 16. [h] From ref 55. [i] From ref 56. [j] From ref 57. [k] From ref 58. [l] From ref 59.

toward the central water molecule of the water cluster, while the HOH angle decreases by 0.5° when compared to the water monomer (Table 1). Xantheas and Dunning calculated the cyclic water pentamer[51] and found hydrogen bond distances that are on average shorter than the ones reported here, similar to the findings for the water tetramer (Table 3).

All values pertaining to the hydrogen bonds formed by the adsorbate−water tetramer clusters are summarized in Table 5, which also lists other literature values for comparison. Frequency calculations on the clusters were not perfomed.

V. Interaction Energies

Tables 6 and 7 list the total energies of the clusters and the interaction energies of the adsorbates with the water tetramer obtained in this study. In addition, Table 7 compares experimental and other calculated values. All energies for $(H_2O)_4$·X (X = HOCl, HCl, Cl_2) were calculated at the MP2 level of theory with the 6-311G(d,p) and the 6-311++G(d,p) basis sets using the optimized geometries presented previously. The energy of the water pentamer was calculated using only the larger basis set. The energies were corrected for basis set superposition error (BSSE) using the counterpoise (CP) method.[52,53] Table 7 lists the estimated basis set superposition error for the systems under investigation in parentheses next to the corrected interaction energies. It can be seen that the calculations involving the larger basis set display the least BSSE. None of the energies here were corrected for zero-point vibrational energy (ΔZPE).

1. HOCl·$(H_2O)_4$. For HOCl·$(H_2O)_4$, the CP corrected interaction energies have the values of −38 and −37 kJ/mol for the 6-311G(d,p) and the 6-311++G(d,p) basis sets, respectively. The CP corrected interaction energies calculated here are approximately twice the value of a hydrogen bond.

As can be seen from Table 7, other calculated energies are generally not in agreement with our results. A molecular dynamics study by Kroes and Clary resulted in a binding energy of about −60 kJ/mol.[17] The geometry found in their work is different from the geometry found here (see previous section). In addition, the empirical potential used in their study may be the main reason for the discrepancy. An ab initio study on HOCl interacting with one water molecule by Dibble and Francisco shows an uncorrected interaction energy of about −25 kJ/mol.[15] The larger interaction energy obtained in this work is perhaps due to cooperativity, and this will be discussed later.

Table 7 also shows some experimental results concerning the interaction of HOCl on ice. Hanson and Ravishankara measured an adsorption enthalpy ΔH_{ads} which does not include the barrier to adsorption.[55] Abbatt and Molina's results measure the enthalpy of adsorption ΔH_{ads} which is in good agreement with our calculated result.[56] We have measured a maximum desorption rate of HOCl from single-crystal ice at 185 K, corresponding to an activation energy for desorption of 41−48 kJ/mol.[54] This measurement includes any barrier to desorption.

2. HCl·$(H_2O)_4$. After CP correction, the interaction energies for HCl·$(H_2O)_4$ are −31 and −26 kJ/mol using the basis sets without and with diffuse functions, respectively. Elliot et al. interpreted experimental data found by Hanson and Ravishankara[55] and arrived at an experimental binding energy for HCl of −46 kJ/mol,[57] which is 15−20 kJ/mol higher than the values we have obtained. Graham and Roberts reported a −33 ± 5 kJ/mol activation energy for the desorption of molecularly bound HCl on thin films of HCl·$(H_2O)_6$,[26] which includes the barrier to desorption. This activation energy for HCl desorption is in excellent agreement with the corrected interaction energy found here. In another molecular dynamics study by Kroes and Clary, the interaction energy of HCl with an ice slab was found to be about −19 kJ/mol.[17] This value is somewhat smaller than the energies obtained here, even though the geometry reported in their work is comparable. In a fully CP corrected ab initio study at the MP2 level of theory using a 6-31G(2dp) basis set, Packer and Clary found zero-point energy corrected interaction energies for the systems $(H_2O)_n$·HCl of −22, −32, and −30 kJ/mol for $n = 1$, 2, and 3, respectively.[18] These values are roughly comparable with the CP corrected MP2/6-311++G(d,p) energies found for the HCl·$(H_2O)_4$ cluster in this work. Molecular dynamics simulations combined with a quantum treatment resulted in an adsorption energy of −25 kJ/mol,[19] which is in excellent agreement with the CP corrected interaction energy for HCl and the water tetramer reported here.

3. Cl_2·$(H_2O)_4$. The CP corrected interaction energies for Cl_2·$(H_2O)_4$ have values of −13 and −11 kJ/mol for the smaller and the larger basis set, respectively. These low interaction energies are consistent with laboratory observations by Molina et al.[3] that dichlorine is found to immediately desorb from ice surfaces into the gas phase, even as low as 185 K. Banham et al. measure a desorption temperature of Cl_2 from ice of 110 K.[23] To our knowledge, there is no other calculated data available for comparison.

TABLE 8: Geometries of the Central Water Molecule in the Tetramer and Its Distances to the Surrounding Three Oxygens in the Tetramer Interacting with HOCl, HCl, Cl_2, and H_2O Calculated Using MP2/6-311G(d,p) and MP2/6-311++G(d,p) (in Parentheses)[a]

		water tetramer with			
	water tetramer	HOCl	HCl	Cl_2	H_2O
R(OH)	0.963 (0.965)	0.971 (0.970)	0.970 (0.970)	0.967 (0.968)	(0.967)
$\angle$(HOH)	104.9 (104.6)	105.5 (104.2)	105.7 (105.7)	105.2 (104.3)	(105.4)
$R(O^a\cdots O^b)$	2.901 (2.951)	2.796 (2.836)	2.812 (2.855)	2.844 (2.870)	(2.904)
$R(O^a\cdots O^d)$	2.817 (2.860)	2.875 (2.904)	2.875 (2.889)	2.849 (2.894)	(2.939)
av O···O	2.873 (2.921)	2.822 (2.859)	2.833 (2.866)	2.846 (2.886)	(2.916)

[a] All bond lengths are in Å, all angles in deg. The results for H_2O are obtained using the MP2/6-311++G(d,p) only.

4. $H_2O\cdot(H_2O)_4$. Using the 6-311++G(d,p) basis set, the CP corrected interaction energy for H_2O on the model water tetramer is found to be −17 kJ/mol. This interaction energy is 11 kJ/mol smaller than the energy per hydrogen bond measured for ice Ih[58] and reflects the model character of the present system. When compared to the tetrahedral (C_s symmetry) water pentamer investigated by Ojamäe and Hermansson,[59] it can be seen that the interaction energy between the central water molecule and a hydrogen donor molecule is in good agreement with the corrected interaction energy found here: using a double-ζ basis set, Ojamäe and Hermansson obtained a CP corrected MP2 energy of −19 kJ/mol.

VI. Discussion

The large interaction energies found here for HOCl and HCl are striking, since a normal hydrogen bond appears to be the primary way of interaction between the tetramer and the adsorbates. To gain a better understanding of the binding energies of the adsorbates interacting with the water tetramer, we examined the degree of distortion that the tetramer and the adsorbates undergo upon interaction with each other. The choice of the method and the model employed here allow for the analysis of the water tetramer geometry before and after HOCl, HCl, Cl_2, or H_2O are bound.

A. Geometric Distortion of the Central Water Molecule upon Adsorption. In Table 8 we present the geometry of the central water molecule within the tetramer upon interaction with HOCl, HCl, and Cl_2. One can see that the OH distance (listed as *R*(OH) in Table 8) and the HOH bond angle in the central water molecule of the water tetramer increase slightly with increasing number of partners of the central water molecule. On the other hand, the average O···O distance decreases from its value of 2.98 Å in the water dimer[60] to an average of 2.87 Å in the water tetramer when the 6-311G(d,p) basis set is used, with further shortening of this distance by 0.05, 0.04, and 0.02 Å upon addition of HOCl, HCl, and Cl_2, respectively. The calculated average O···O distance is 2.92 Å when the diffuse functions are added, which is still shorter than the dimer value, and upon interaction with HOCl, HCl, or Cl_2, this average distance decreases by 0.06 and 0.05 Å for HOCl and HCl, respectively. For the water pentamer, a decrease in the average O···O distance by 0.005 Å is found when compared to the water tetramer, showing a very small influence of the fifth water molecule on the average O···O distance of the water tetramer.

Two types of H bonds are found in the tetramer, and they will be characterized by the two sets of oxygen−oxygen distances: one type corresponds to the H bond established between the central water molecule and the H-donor water molecule (listed as $R(O^a\cdots O^d)$ in Table 8). For this H bond, the oxygen−oxygen distance is lengthened by 0.06 Å upon interaction of the tetramer with HOCl and HCl using the 6-311G(d,p) basis set. This lengthening becomes less drastic when the diffuse functions are used in the calculation. When dichlorine interacts with the tetramer, this oxygen−oxygen distance is lengthened by only 0.03 Å. For the interaction with the fifth water molecule, the oxygen−oxygen distance increases by 0.08 Å, which is considerably more than what is observed with the other three adsorbates.

The other type of H bond is established between the two acceptor water molecules and the central water molecule which acts as a 2-fold hydrogen donor. Using both basis sets, the oxygen−oxygen distance of this H bond (listed as $R(O^a\cdots O^b)$ in Table 8) is shortened by 0.11−0.09 Å when HOCl and HCl interact with the tetramer, respectively. For the interaction with dichlorine, the contraction is less, with a value of 0.06 Å obtained when the smaller basis set is used and 0.08 Å with the larger basis set. The smaller effect of dichlorine on the oxygen−oxygen distance in both types of H bonds encountered here is clearly understandable when we consider the long distance of the chlorine atom closest to the oxygen of the central water molecule in the tetramer. Finally, the interaction with the fifth water molecule shortens the oxygen−oxygen distance by only 0.005 Å.

Analysis of the two types of oxygen−oxygen distances in the tetramer raises the question if cooperativity is strictly applicable to this system: when HCl, HOCl, Cl_2, or H_2O interact with the water tetramer, the two hydrogen-acceptor water molecules move closer to the central water molecule, whereas the one hydrogen-donor water molecule increases its distance to the central water molecule. Ojamäe and Hermansson performed ab initio studies of cooperativity in water chains, water rings, and a tetrahedral water pentamer.[59] Expanding the interaction energy over subunits of water dimers, trimers, tetramers, and pentamers, they express the total interaction energy of five waters as the sum of two-, three-, four-, and five-body terms. They define the term *strict cooperativity* as the case where all many-body terms should have a negative sign. According to their work, water molecules in a tetrahedral coordination show cooperativity, but their four- and five-body energies are positive. Hence, they conclude that the tetrahedral water pentamer does not display strict cooperativity. In contrast, water chains and rings examined in their work display strict cooperativity. The anticooperative character in the tetrahedral water pentamer that Ojamäe and Hermannson observed is consistent with our observation that the two sets of oxygen−oxygen distances do not change with the same sign when a fifth partner (i.e., HOCl, HCl, Cl_2, or H_2O) interacts with the water tetramer.

B. Effect of the Geometric Distortion of the Water Tetramer on the Binding Energy. To investigate the question of why binding energies relatively larger than that of a normal hydrogen bond result from the interaction of HOCl or HCl with the water tetramer, we calculated the energy differences between the optimized water tetramer and the water tetramer with the geometry of the $X\cdot(H_2O)_4$ clusters, (X = HOCl, HCl, Cl_2) without X. The results using the small basis set are as follows: For X = HOCl, the distortion of the water tetramer is energetically slightly unfavorable, with the optimized water tetramer being +3 kJ/mol more stable than the distorted water tetramer. (With the larger basis set, this energy difference decreases to 2.5 kJ/mol.) Even though the interaction of HOCl with the four water molecules is energetically favorable due to the formation of a hydrogen bond, the effect of HOCl on the structure of the tetramer is somewhat destructive. Nevertheless, the formation of the hydrogen bond compensates for the distortion of the adsorption site and results in a net energy gain of the system. A similar observation is made for the interaction of HCl with the water tetramer, leading to a destabilization energy for the tetramer of +2 kJ/mol. For X = Cl_2, the destabilization energy for the tetramer was found to be +1 kJ/mol and is negligible. Almost the same energy differences are found when the larger basis set is used.

C. Comparison of the Adsorbate Energies before and after Interaction with the Water Tetramer. Since the destabilization of the water tetramer does not seem to have a strong influence on the binding energies, we compared the energies of the optimized adsorbates as monomers and the adsorbate monomers in the distorted geometry which they assume upon interacting with the water tetramer. The changes in energy were calculated to be less than 2 kJ/mol for HOCl, HCl, and Cl_2. Using the larger basis set, the energy differences are less than 1 kJ/mol. This means that the geometric changes of the adsorbates indeed have no significant influence on the binding energy.

D. Atomic Charges. Changes in atomic charges of the adsorbates and the water tetramer are induced upon interaction but are found to be mainly due to basis set superposition error. This may help to explain why the CP correction turned out to be so large. The fact that the changes in atomic charges are mostly due to BSSE indicates that the adsorbate molecules and the adsorption site largely maintain the electronic structure they had prior to interaction. Clearly, the high interaction energies found in this study for HOCl and HCl are not due to changes in charge distribution.

E. H Bond Length and Effect of Permanent Dipoles. Since we found that restructuring of the adsorption site and changes in the adsorbate geometries are negligible, we looked at other causes for the high interaction energies obtained for HOCl and HCl in this study. In Table 5, the H bond distances of the $X\cdot(H_2O)_4$ (X = HOCl, HCl, Cl_2, and H_2O) complexes are listed. The hydrogen bonds established between the central water molecule of the water tetramer and HOCl, HCl, and H_2O as well as the O···Cl distance in the $Cl_2\cdot(H_2O)_4$ cluster show the following features: It can be seen that the H bond distances increase in the order HOCl (shortest) to Cl_2 (longest). This increase goes along with a decrease in the interaction energy. The dependence of the interaction energy and the H bond distance is close to a simple $1/r^3$ form, indicating that electrostatic dipole–dipole interactions are mostly responsible for binding in the clusters $X\cdot(H_2O)_4$ (X = HOCl, HCl, H_2O, Cl_2).

Looking at the dipole moments of isolated HOCl, HCl, H_2O, and Cl_2, one can observe the following trend: HOCl with a dipole moment of 1.3 D[61] has the largest interaction energy with the water tetramer. HCl with a dipole moment of 1.08 D[62] binds less strongly to the water tetramer. Finally, Cl_2 has no dipole moment, and its binding energy is smaller than a normal hydrogen bond.

The dipole moment of H_2O is 1.87 D,[40] but its interaction energy with the water tetramer is lower than the ones found for HOCl and HCl. Obviously, the interaction of H_2O with the water tetramer does not follow the observed trend mentioned above, indicating that the relatively longer H bond plays a significant role in the interaction energy of the fifth water molecule in the water pentamer.

VII. Conclusion

An ab initio study of stratospherically relevant compounds HOCl, HCl, H_2O, and Cl_2 interacting with a prototypical ice adsorption site was performed. HOCl and HCl adsorbed with hydrogens oriented toward a water oxygen with the greatest interaction energies. We conclude that the large binding energies of HOCl and HCl are not due to geometrical changes in the adsorbate or in the structure of the adsorption site. The large interaction energies are thought to be mainly due to the formation of a hydrogen bond whose interaction energy is closely related to the distance by a $1/r^3$ form. In addition, the present calculation shows that the BSSE corrected changes in electronic structure of the adsorption site and in the adsorbates are small.

The number of water molecules used in this study (four) was found to be sufficient for the calculation of binding geometries, as can be seen from the agreement of our results with the work by Robinson-Brown and Doren,[16] who used a much larger number of water molecules. The disagreement with the interaction energies obtained by Dibble and Francisco[15] strongly suggest that the binding of foreign molecules with ice cannot be calculated using the adsorbates interacting with one water molecule alone. Hence, we feel that calculation using small water clusters such as the model used in this work can already provide important insights into the adsorption behavior of small molecules onto a crystalline water ice surface. Last, we recommend the use of MP2 theory in calculating water systems similar to the one discussed above.

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