Structure and Spectra of HOCl(H_2O)$_n$ Clusters, $n = 1-4$: A Theoretical Calculation

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The geometrical structure, binding energy, and vibrational spectra of small clusters of HOCl and water molecules, HOCl(H_2O)$_n$, $n = 1-4$, have been investigated at the MP2 level of theory, using triple-Z, 6-311++G(d,p), basis sets. The ab initio results predict for the clusters an almost planar ring skeleton, made up of the O atoms and one H atom from each molecule, linked by hydrogen bonding to the next oxygen. The species with one water unit presents two almost equally stable conformers, syn and anti, in agreement with previous calculations. Two stable structures have also been found for clusters with three and four molecules of water, one where the H atom of the HOCl molecule makes part of the ring, and another one in which the Cl atom is in the ring. The more stable in either case is found to be the H-in molecule, with a difference of 35.6 kJ/mol in optimized energy. The predicted spectra for these two species are very different. As the number of water units increases, the corresponding clusters become more stable, and a number of physical effects is predicted. The more important one is the increase in the intramolecular O−H bond length, which is responsible for a large reduction in the wavenumber of the corresponding O−H vibration. The results indicate the formation of hydrogen bonds and a partial proton transfer from HOCl to the water ring structure. In a parallel calculation, water clusters, (H_2O)$_n$, $n = 1-5$, have also been investigated. Our results agree well with those of previous authors.

Introduction

Since the first reports on the importance of chlorine on atmospheric reactions, published over a decade ago,[1−3] the topic of the interactions between water molecules and chlorine-containing molecules has been the subject of a large number of scientific contributions. The molecules of HCl and HOCl, in particular, have constituted a favorite target of these studies, since they are directly involved in chemical reactions leading to the formation of chlorine radicals, which can deplete the stratospheric ozone concentration. The speed at which these reactions occur is greatly enhanced on ice surfaces.[4] Type II polar stratospheric clouds (PSC) consist of water ice, with rapidly changing surfaces at the stratospheric temperatures. The adsorption of HOCl to such surfaces can proceed through its interaction with a small number of water molecules, similarly to what was found for HCl.[4] Thus, the study of interactions of single chlorinated molecules with small water clusters can then contribute to a better understanding of such reactions. From the several papers that have recently appeared with this approach, we quote here a few theoretical calculations performed with different aims and using also different techniques. Kroes and Clary[6] carried out classical trajectory calculations to model the physical adsorption of HCl and HOCl on single-crystal ice surfaces. Robinson-Brown and Doren[7] performed ab initio calculations using density functional theory to study the interaction of an HOCl molecule with ice surfaces made up of 4 and 26 water molecules. Packer and Clary[8] and Geiger, Hicks, and de Dios[9] studied specifically the interaction of HCl, and HOCl, HCl, and Cl_2, respectively, with water clusters made up of 1−3 and 4 molecules. At the MP2 level of theory, they obtained the optimized geometry and interaction energy of the molecular species studied. Re, Osamura, Suzuki, and Schaefer III[10] had calculated earlier HCl(H_2O)$_n$ clusters, $n = 1-5$, by density functional and Hartree−Fock methods. Dibble and Francisco[11] used large basis sets, also at the MP2 level, to optimize the geometry of the HOCl−H_2O complex. We will return to some of these references at the appropriate section below.

In this paper, we present an ab initio investigation on the changes of geometry, energy and spectra occurring when a molecule of HOCl is attached to water aggregates composed of between 1 and 4 molecules. The calculations for some of these systems had never been reported before, as far as we are aware. One of our aims was to study the extent of positive charge transfer between the O−H bond of the acid and the water molecules and its contribution to an enhanced stability of the complex. Another objective was to predict the spectra of these complexes, which could be a helpful tool to their experimental observation. To present a more comprehensive basis for comparisons between different geometries, and to test the accuracy of our results where possible, we performed also calculations on water clusters, made up of between two and five molecules. Among the many relevant and recent publications on water clusters, we will mention here the series of theoretical works of Xantheas,[12−14] following earlier calculations of Xantheas and Dunning,[15] a series of articles by Saykally with different co-workers,[16−20] and the very recent papers by Nielsen,

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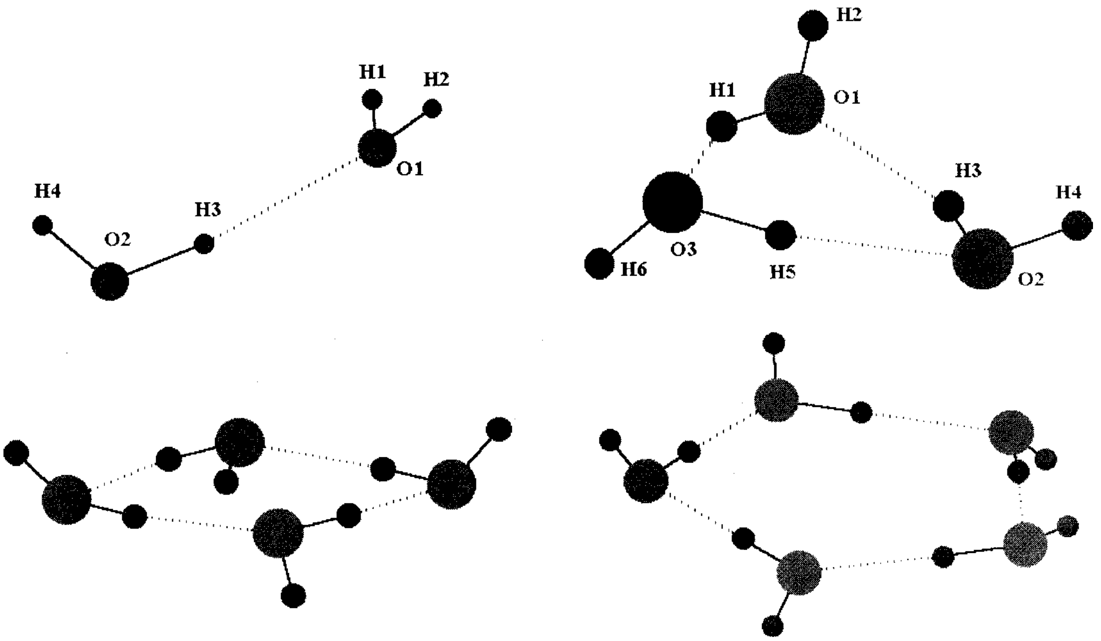

Figure 1. Schematic representation of the water clusters calculated in this article, from dimer to pentamer. Atom numbering is indicated up to the trimer as a reference for the parameters in Table 2.

Seidl, and Janssen[21] and by Leutwyler with other co-workers.[22,23] As a single example of an experimental contribution of high quality, we will quote the paper by Paul, Collier, Saykally, Scherer, and O'Keefe,[24] in which they determine absolute concentrations of water clusters up to the pentamer in a pulsed supersonic expansion by means of infrared cavity ring-down spectroscopy. Although the experimental detection of mixed HOCl−water clusters that we study in this article may be a difficult task, it could perhaps be attempted in similar conditions to those of this last paper,[24] by bubbling helium through a concentrated water solution of hypoclorous acid and making use of an extremely sensitive technique like that of cavity ring-down spectroscopy.

In the following section, we give details of the ab initio calculations performed, and next we discuss each cluster in detail. Finally, we summarize the results for the whole set of molecules and present the observed trends in their structure and spectra.

Ab Initio Calculations

We have performed ab initio geometry optimizations and frequency calculations for clusters of the type HOCl(H_2O)$_n$ and (H_2O)$_{n+1}$, where $n = 1-4$, at the MP2 level of theory using 6-31G(d,p), 6-311G(d,p), and 6-311++G(d,p) basis sets. Both geometries and frequencies have been studied and compared with experimental values when available. Results of the most relevant geometrical parameters are summarized in Figures 1−3. Comparison with the experimental values for H_2O and HOCl (see Table 1) indicates that both 6-311G(d,p) and 6-311++G(d,p) basis sets provide reasonably good geometries at the MP2 level of the theory, although the equilibrium angles are less well reproduced. In particular, the HOH angle of water has proved to be especially difficult to reproduce, and we found that a larger basis set, 6-311++G(2df,pd), was necessary to obtain a value closer to the experimental one (104.6° vs 104.5°, respectively, with a calculated bond distance of $r = 0.961$ Å). Also when comparing calculated harmonic frequencies with experimental ones in H_2O, HOCl, and (H_2O)$_2$, both basis sets, 6-311G(d,p) and 6-311++G(d,p), perform comparably well (the results for the former basis are not shown here), though slightly smaller errors are found when using the latter, for which the errors are always smaller than 6%, and in the case of the water dimer smaller than 2.5%. Moreover, considering that in cases where H-bond plays a role in the bonding (as in the species studied here), basis sets containing diffuse functions are more advisable, we have chosen 6-311++G(d,p) as a good compromise between quality and affordability to study this series of clusters at a uniform level of accuracy. Several previous workers (Geiger et al.[9] and Dibble and Francisco[11]) have also favored this choice, which further makes easier the comparison of results.

TABLE 1: Optimized Geometrical Parameters of the Free Molecules of H_2O and HOCl Calculated with the Basis Sets Employed in This Work and Comparison to Experimental Results (Interatomic Distances in Angstroms, Angles in Degrees)

	6-31G(d,p)	6-311G(d,p)	6-311++G(d,p)	experimental[a]
		H_2O		
r_{OH}	0.961	0.958	0.960	0.9578
α_{HOH}	103.8	102.5	103.5	104.4776
		HOCl		
r_{OH}	0.971	0.964	0.966	0.964
r_{OCl}	1.716	1.719	1.716	1.689
β_{HOCl}	102.4	101.7	102.7	102.965

[a] References 26 (H_2O) and 28 (HOCl).

We have calculated binding energies for all HOCl(H_2O)$_n$ clusters studied here, with reference to the isolated water and HOCl molecules. The energy difference was determined at the equilibrium geometry of every species, and the basis set superposition error was dealt with by performing counterpoise corrections as

$$E_{CC} = \sum_i E_i^*(c) - \sum_i E_i^*$$

where i sums over monomers, $E_i^*(c)$ is the energy of monomer i calculated using the whole cluster basis set and using the monomer's geometry corresponding to the optimized cluster, and finally E_i^* denotes the energy of the monomer calculated by using its own basis set but the same geometry as in $E_i^*(c)$.

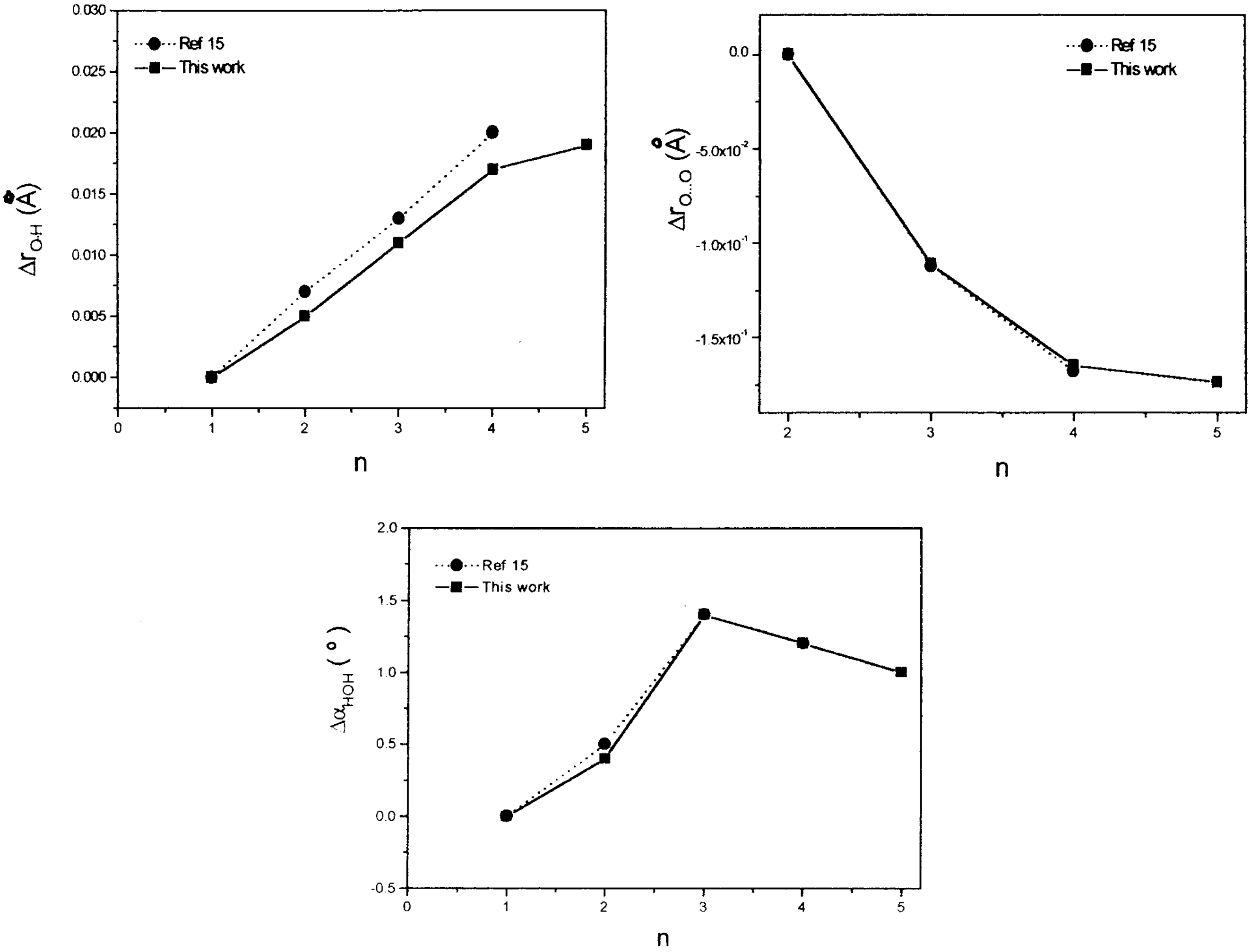

Figure 2. Increments in interatomic distances O−H and O···O and the intramolecular HOH angle, with respect to the isolated molecule, as a function of the number of water monomers in the cluster, *n*. Calculated values taken from Tables 1 and 2 (6-311++G(d,p) basis set). The corresponding calculated values of ref 15, up to the tetramer, are also indicated.

Further, zero-point energy corrections (ZPEC) have been estimated and included both in clusters and in monomers by using the geometry and basis sets of the isolated species. ZPEC turned out to be an important contribution to the final binding energy. Binding energies for HOCl−water clusters are summarized in Table 6 and will be discussed later on in this paper.

All calculations have been carried out using the GAUSSIAN94 suite of programs.[25] All the results quoted in the following parts of this article refer to the more complete basis set chosen, 6-311++G(d,p), unless specifically indicated otherwise.

Discussion

$(H_2O)_n$ Clusters. Calculations on these clusters were performed with the aim of providing a basis for comparisons with previous works, and also in some cases to serve as a reference for the corresponding clusters with HOCl. Therefore, we will present here a limited discussion on these species. Figure 1 represents the structure of water clusters, from dimer to pentamer, as calculated in this work. The pictures shown, for example, in refs 15, 21, and 22 agree with the corresponding ones in this article. All clusters have a nearly planar ring structure made up of the oxygen atoms and one O−H bond of each water molecule, directed toward the following O atom, with a small deviation from linearity. The remaining O−H bonds are situated alternatively above and below the planar ring. Table 2 lists the geometical parameters refined in this work for all five water species, $(H_2O)_n$, $n = 1-5$. The more obvious trends in our results, as the number of monomers in the cluster increases, are the shortening of the adjacent O−O distances in the rings, and the lengthening of the ring O−H bonds, whereas the free O−H bonds remain practically unaltered. These results hint to the formation of stronger bonds and therefore to a larger stability in the larger clusters. They follow the same pattern as what we find for the $HOCl(H_2O)_n$ clusters, which will be discussed in more detail below, and thus we make here only a comparison with previous investigations.

We have added in Table 2 some of the values published by previous authors at similar level of computation methodology.[15,21] Our values for the water dimer agree very well with those of Xantheas and Dunning.[15] For the trimer, our values are closer to those of Nielsen et al.,[21] although we estimate a shorter ring O−H bond length, and a slightly smaller HOH angle. It is perhaps by chance that our results for the bond distances practically match those of the larger basis set (aug-cc-pVQZ) calculation of Nielsen et al. (see Table 1 of ref 21). Xantheas and Dunning[15] included the water tetramer in their high-level MP2 calculations, and investigated also the water pentamer and hexamer at a lower level of theory (HF), whereas Xantheas[12] performed similar calculations using density functional theory. Graf et al.[22] calculated the Cartesian coordinates of the pentamer using a double-Z basis set, aug-cc-pVDZ, and,

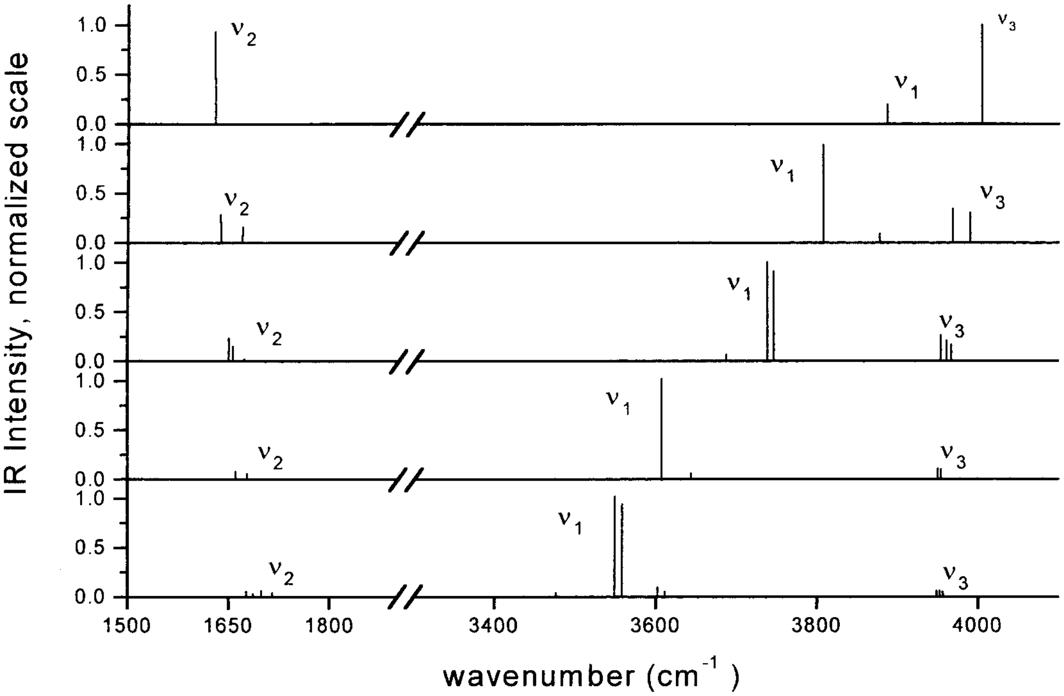

Figure 3. Stick representation of the infrared spectra of the intramolecular modes of H_2O in the water clusters calculated in this work. Top to bottom: isolated molecule, and clusters $(H_2O)_n$, with $n = 2-5$. Intensities are normalized to the more intense absorption in each spectrum.

TABLE 2: Optimized Geometrical Parameters of $(H_2O)_n$ Clusters, $n = 2-5$, Calculated in This Work Using the 6-311++G(d,p) Basis Set and Comparison to Previously Published Values at a Similar Level of Theory (Interatomic Distances in Angstroms, Angles in Degrees)

	$(H_2O)_2$		$(H_2O)_3$			$(H_2O)_4$		$(H_2O)_5$
	MP2 6-311++G(d,p) this work	MP2 aug-cc-pVTZ ref 15	MP2 6-311++G(d,p) this work	MP2 aug-cc-pVDZ ref 15	MP2 aug-cc-pVTZ ref 21	MP2 6-311++G(d,p) this work	MP2 aug-cc-pVTZ ref 15	MP2 6-311++G(d,p) this work
r_{O1H1}	0.961	0.960	0.970	0.977	0.9740			
r_{O1H2}	0.961	0.960	0.959	0.964	0.9607			
r_{O1H3}	1.950		1.918	1.901	1.891			
r_{O2H3}	0.965	0.965	0.971	0.978	0.9746			
r_{O2H4}	0.959	0.958	0.959	0.964	0.9610			
r_{O1O2}	2.914	2.898	2.810	2.800	2.7899			
α_{H1O2H2}	104.1	104.7	105.0	105.3	105.56			
α_{H3O2H4}	103.6	104.4	104.8	105.0	105.28			
r_{O2H5}			1.918	1.901	1.893			
r_{O3H5}			0.971	0.978	0.9748			
r_{O3H6}			0.959	0.965	0.9607			
r_{O3H1}			1.942	1.920	1.912			
r_{O2O3}			2.797	2.798	2.7850			
r_{O3O1}			2.803	2.799	2.7870			
α_{H5O3H6}			104.9	105.3	105.50			
$r_{OH\,in}$[b]						0.977	0.985	0.979
$r_{OH\,out}$[b]						0.959	0.965	0.959
$r_{HO\cdot\cdot HO}$[b]						1.791		1.758
r_{OO}[b]						2.749	2.743	2.731 [2.748]
α_{HOH}[b]						104.7	105.0	104.5

[a] See Figure 1 for atom labeling. [b] Average values. The value in bracket for the pentamer corresponds to a r_{OO} distance quite different from the other 4.

as far as we know, our geometry for the pentamer is the first to be published using a triple-Z basis set.

It is interesting to note that our calculations match the MP2 results of ref 15 both for the reduction of the adjacent O−O bond lengths and for the increase of the ring O−H bond distance with respect to the monomer, as the number of monomer units increases. Figure 2 shows graphs with the increments in interatomic distances and the intramolecular HOH angle, with respect to the isolated molecule, as a function of the number of water monomers in the cluster. The figure reproduces also the corresponding calculated values of ref 15, up to the tetramer. The agreement can be seen to be very good. We have found that the consecutive increments for the pentamer are much smaller, pointing to convergence values of $d(O-O) \approx 2.71$ Å and $\Delta r_e(\text{ring}) \approx 0.001$ Å, respectively. A similar convergence was found in ref 15 for the HF calculations and in ref 12 for the B-LYP results. Likewise, we obtain a variation of the HOH angle which presents a peak value for the trimer and then decreases for the larger clusters, to a value of $\Delta(HOH) \approx 0.9°$, close to the B-LYP value,[12] and larger than the convergence found for the HF results, which falls nearly to the value of the monomer.[15] The same authors[12,15] also calculated that the free

TABLE 3: Optimized Geometrical Parameters of $HOCl(H_2O)_n$ Clusters, $n = 1-4$, Calculated in This Work Using the 6-311++G(d,p) Basis Set (Interatomic Distances in Angstroms, Angles in Degrees) along with Calculated Rotational Constants of Each Molecule (in GHz) and the Permanent Dipole Moment (in Debye)[a]

	$(HOCl-H_2O)_{syn}$	$(HOCl-H_2O)_{anti}$	$HOCl(H_2O)_2$	$HOCl(H_2O)_3$ H-in	$HOCl(H_2O)_4$ H-in		$HOCl(H_2O)$ Cl-in	$HOCl(H_2O)_4$ Cl-in
r_{O1H1}	0.961	0.961	0.971	0.980	0.982	r_{O1H1}	0.973	0.976
r_{O1H2}	0.961	0.961	0.960	0.960	0.960	r_{O1H2}	0.959	0.960
r_{O1H3}	1.811	1.806	1.933	1.653	1.623	r_{O1Cl3}	2.687	2.577
r_{O2H3}	0.976	0.976	0.984	0.994	0.997	r_{O2Cl3}	1.733	1.739
r_{O2Cl4}	1.710	1.711	1.710	1.708	1.707	r_{O2H4}	0.966	0.966
α_{H1O1H2}	104.3	104.6	105.3	105.3	105.0	α_{H1O1H2}	104.0	103.9
$\beta_{H3O2Cl4}$	102.3	102.8	104.0	104.6	103.6	$\beta_{Cl3O2H4}$	104.2	104.2
r_{O2H5}			1.987	1.813	1.774	r_{O2H5}	1.941	1.833
r_{O3H5}			0.968	0.974	0.975	r_{O3H5}	0.968	0.971
r_{O3H6}			0.959	0.960	0.960	r_{O3H6}	0.960	0.960
r_{O3H1}			1.765			r_{O3H1}		
r_{O3H7}				1.799	1.761	r_{O3H7}	1.883	1.808
α_{H5O3H6}			105.1	104.9	104.7	α_{H5O3H6}	104.3	104.4
r_{O4H7}				0.976	0.978	r_{O4H7}	0.973	0.975
r_{O4H8}				0.960	0.960	r_{O4H8}	0.960	0.960
r_{O4H1}				1.761		r_{O4H1}	1.865	
r_{O4H9}					1.745	r_{O4H9}		1.790
α_{H7O4H8}				104.8	104.6	α_{H7O4H8}	104.0	104.2
r_{O5H9}					0.980	r_{O5H9}		0.976
r_{O5H10}					0.960	r_{O5H10}		0.960
r_{O5H1}					1.718	r_{O5H1}		1.790
$\alpha_{H9O5H10}$					104.7	$\alpha_{H9O5H10}$		104.0
A	20.5	24.2	6.2	3.4	1.9	A	2.4	1.4
B	3.4	3.1	2.0	1.3	0.9	B	2.0	1.3
C	2.9	2.8	1.6	1.0	0.6	C	1.1	0.7
μ	4.450	4.482	1.866	1.774	1.402	μ	2.516	2.584

[a] See Figure 4 for atom labeling.

O−H bonds remain practically unaltered upon variation of the number of monomer units.

The comparison of our results for the free water molecule with the empirical values[26] gives us an indication of the degree of accuracy of our calculations, better than 0.005 Å for bond distances and ∼1° for the intramolecular angle. The differences between our results and those calculated in previous publications are then of the order of magnitude of the accuracy of our results, which gives us confidence on the quality of our calculations.

We have also estimated the harmonic vibrational frequencies for these species. Figure 3 presents a stick representation of the infrared spectra of the intramolecular modes. Our wavenumber values are systematically larger than those of refs 12, 15, and 22, but they are closer to, although still larger than, those of the aug-cc-VTZ calculation of ref 21. However, it is interesting to remark on two facts: first, that the intensity pattern predicted in our calculations matches very well that given in ref 15 for the trimer and the tetramer; and second, that the shifts in the intramolecular frequencies with respect to the average values of the monomer, as the number of water units increases, follow the same trend as that observed by Xantheas and Dunning.[15] The blue shifts of the HOH bending frequency, predicted by these authors and also in our calculations, have been very recently experimentally confirmed by Paul et al.[20] Our new values for the pentamer, giving five weak vibrations within 50 wavenumbers, anticipate the appearance of a broad feature for larger clusters.[20] We conclude that the quality of our calculation is similar to that of the previous authors, and the difference in the predicted harmonic frequencies must be due to the incomplete similarity of the basis sets used in either calculation.

TABLE 4: Optimized Energy and Zero-Point Vibrational Energy (in Hartree) of $HOCl(H_2O)_n$ Clusters, $n = 0-4$, Calculated in This Work Using the 6-311++G(d,p) Basis Set[a]

n	E_T	E_0
0	−535.244870	0.0131
1_{syn}	−611.533492	0.0384
1_{anti}	−611.533408	0.0383
2	−687.825560	0.0647
3_{H-in}	−764.122743	0.0912
3_{Cl-in}	−764.107279	0.0893
4_{H-in}	−840.415142	0.1169
4_{Cl-in}	−840.400010	0.11531

[a] For reference, the optimized energy of the H_2O molecule using this same basis set was −76.274920 hartree, and the zero-point correction was 0.02168 hartree.

$HOCl(H_2O)_n$ Clusters. Figure 4 shows a schematic representation of the refined structures calculated for this series of molecules, whereas the estimated geometrical parameters are listed in Table 3. Table 4 presents the optimized energy for all these clusters, calculated with the 6-311++G(d,p) basis set. As seen in the table, two possible stable configurations are found for the clusters with one, three, and four water molecules. Details of each molecular species are given below.

HOCl−(H_2O). Dibble and Francisco[11] studied in detail this complex and found two almost equally stable conformers, syn and anti (see Figure 4). Like these authors, we also calculated the optimized structure and energy of the corresponding isolated molecules, as a test of the quality of the ab initio results. The present calculation practically matches the results of ref 11. Some of the optimized parameters are given in Table 3, with those of the rest of the molecules. The main conclusion, concerning energy, is that the accuracy of the ab initio results is smaller than the optimized energy difference between the conformers (0.22 kJ/mol) and thus we must regard both forms as isoenergetic.

The differences between the calculated values of most of the parameters for each conformer are also in general smaller than the expected accuracy of the results. One exception is the HOCl angle, where our ab initio calculations provide a value of 102.3°

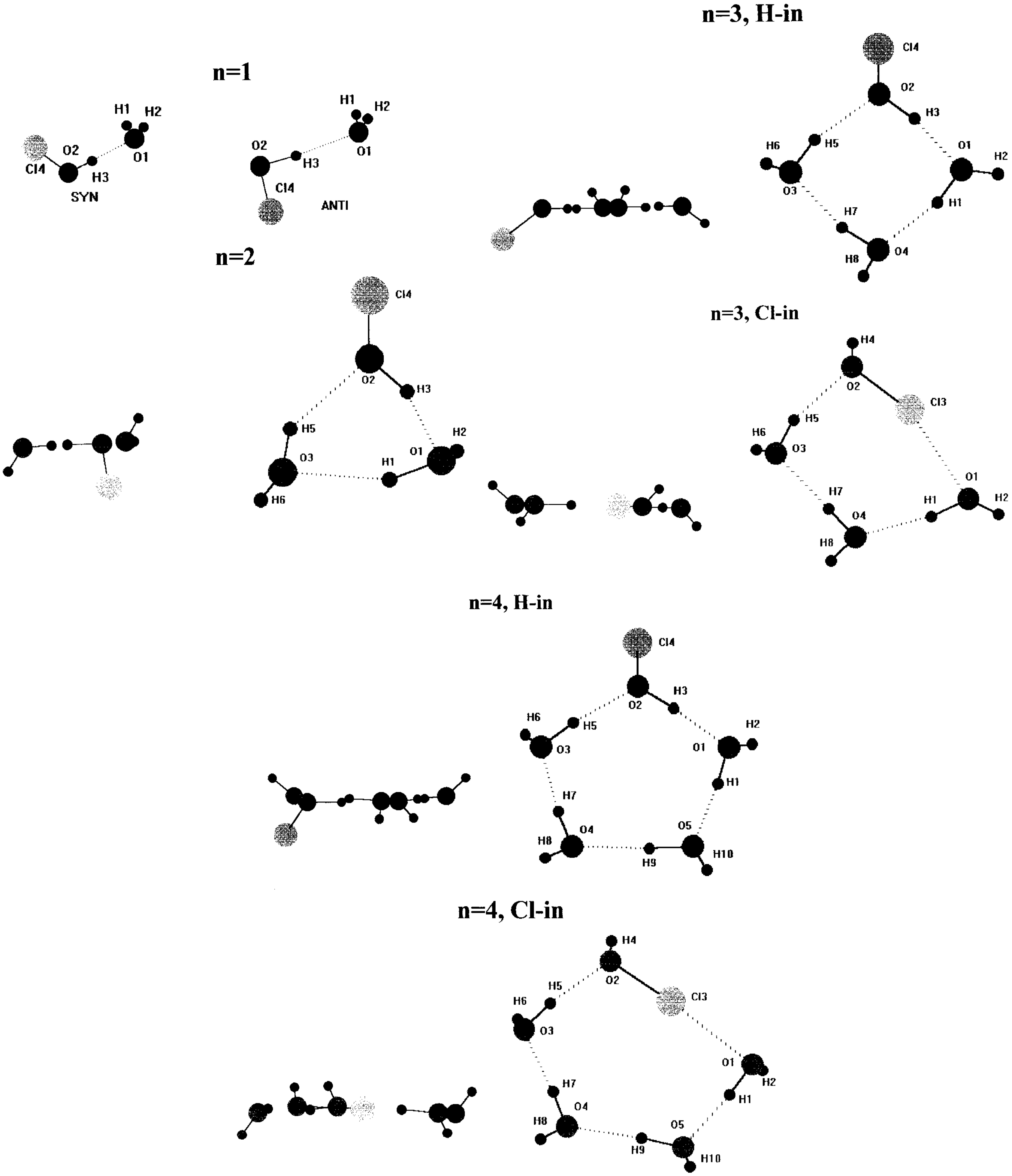

Figure 4. Schematic representation of the $HOCl(H_2O)_n$ clusters calculated in this article, for $n = 1-4$. Atom numbering is indicated as a reference for the parameters in Table 3. Top: $n = 1$, syn and anti conformers. All other structures: equatorial and top views, left and right, respectively. For the $n = 3$ and $n = 4$ molecules, the H-in structure and Cl-in structure are depicted.

for the syn conformer, which is 0.5° smaller than the value for the anti (102.8°) and 102.7° for the isolated molecule. Since the more recent determinations of this value for the molecule,[27,28] based on experimental spectra, give a value of 102.96°, we suggest that the structure of the anti conformer is probably closer to that of the isolated HOCl molecule than the syn form is.

We reproduce in Figure 5 the predicted infrared spectrum of the anti conformer (that of the syn being quite similar), directly below a composite of the computed spectra of the free HOCl and H_2O molecules. The main changes in the predicted spectrum are a red shift of the OH stretching vibration of HOCl, which also gains intensity relative to all other vibrations, and a blue shift in the HOCl bending. These changes indicate a weakening of the stretching force constant for that O−H bond, in favor of an increased value for that of the bending of the angle. The intensity gain can also be explained in terms of the Mulliken

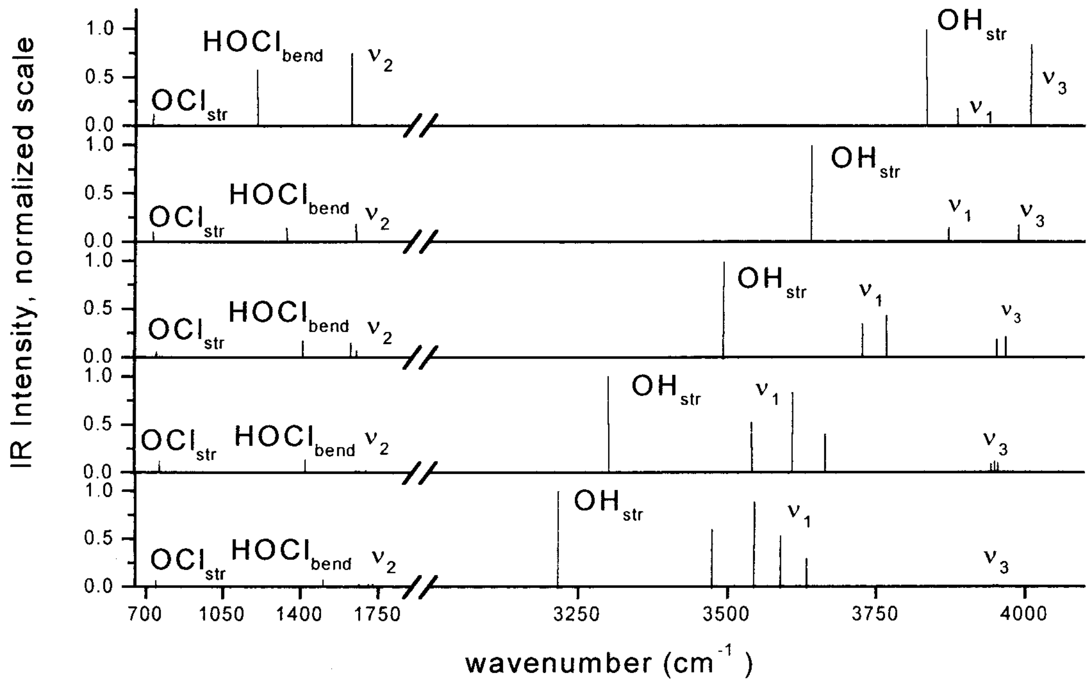

Figure 5. Stick representation of the infrared spectra of the intramolecular modes of HOCl and H_2O in the HOCl(H_2O)$_n$ clusters calculated in this work. The HOCl vibrations are indicated explicitly; those of the H_2O molecules are labeled ν_1 to ν_3. Top: composite of the computed spectra of the free HOCl and H_2O molecules. Next: clusters with $n = 1-4$; $n = 1$, spectrum of the anti conformer; $n = 3$ and 4, spectra of the H-in species. Intensities are normalized to the more intense absorption in each spectrum.

atomic charges. For the HOCl free molecule, our counterpoise corrected calculations give 0.283, −0.242, and −0.025 for the H, O, and Cl atoms, respectively. When the cluster is formed, these values (for the syn conformer) become 0.420, −0.356, and −0.047, respectively. Thus, we can expect in the cluster a larger value for the variation of the charge distribution, or effective bond charge, with the stretching of the O−H bond and therefore an increased intensity of the observed infrared transition.

As some of these effects will be found for the rest of the clusters, we will discuss them in more detail below.

HOCl(H_2O)$_2$. This is the only cluster for which one single stable structure is obtained in our calculations, which are in fact the first ones to be published on this molecule, within our knowledge. The chlorine atom is placed off the planar ring made up of three oxygen and three hydrogen atoms, as depicted in Figure 4. The optimized geometrical parameters are listed in Table 3. As the ring structure is formed, several changes take place with respect to the geometries of the isolated molecules, as calculated in this work. In the first place, all three intramolecular bending angles, the HOCl angle and both HOH, open by around 1.5° from their equilibrium isolated values. In HOCl, the O−H bond length is largely increased, and the same happens, although in lesser amount, to the O−H bonds of either water molecule. On the other hand, the free O−H bonds that are not involved in the ring remain practically unchanged. The stability of this molecule is then due to the formation of hydrogen bondings between the atoms of the ring. The separation between the H atom of HOCl and the nearest O atom is also smaller than its value in the HOCl−H_2O species described above, which implies that a stronger bonding has been formed in the present molecule.

The predicted spectrum, shown in Figure 5, presents the same trends as that of the one-water cluster mentioned above.

HOCl(H_2O)$_3$. The calculations for this species predict two stable structures, which differ in the bond of HOCl that makes part of the ring. In the more stable one, the O−H bond is placed in the ring, giving rise to a hydrogen bonding similar to that in the two-water molecule described previously, whereas in the second one, it is the O−Cl bond that takes part in the ring. They are both shown in Figure 4. The ring in the H-in species appears very planar and regular, whereas in the Cl-in molecule it is still planar but much more distorted. The calculated rotational constants for either structure reveal that the former is close to a prolate top ($A > B \approx C$, asymmetry parameter $\kappa = -0.751$, see Table 3), whereas the latter is closer to an oblate top ($A \approx B > C$, $\kappa = 0.359$), whereas they are both strongly asymmetrical. Their optimized energies, with zero-point vibrational correction included, show that the H-in species is more stable by 35.6 kJ/mol (see Table 4).

In the remaining part of the article, for the sake of simplicity, we will refer to the water molecule to which the HOCl is attached via either the O−H bond or the O−Cl bond, as ortho; the following clockwise water unit will be called meta, and those to the opposite side of the ring from the HOCl molecule will be designated, anticlockwise, as ortho′ and meta′, when present, respectively.

With respect to the geometrical parameters of the two structures of the trimer, we can point out the following aspects. In the H-in species, the ortho water molecule bears larger changes than the other two, with respect to isolated water. In all three water molecules, the O−H bond in the ring is larger than in isolated water, but the increase is larger for the ortho molecule. The HOH angle is also opened. As in the two-water complex, the O−H bond of HOCl is largely increased, indicating the attraction to the ortho oxygen atom with which hydrogen bonding is formed, and the HOCl angle is again opened. In the Cl-in structure, on the other hand, it is the ortho′ water molecule which appears different from the other two, in the sense that it is least altered from the free molecule. The ring O−H bond of the ortho′ molecule is shorter than in any previous case, closer to the value of the isolated molecule. The H atom stays tightly

TABLE 5: Predicted Wavenumber (in cm^{-1}) and Intensity (in km/mol) of the Intramolecular H_2O and HOCl Vibrations in the H-in and Cl-in Structures of the $HOCl(H_2O)_3$ and $HOCl(H_2O)_4$ Clusters Calculated in This Work Using the 6-311++G(d,p) Basis Set

		$HOCl(H_2O)_3$, H-in		$HOCl(H_2O)_3$, Cl-in		$HOCl(H_2O)_4$, H-in		$HOCl(H_2O)_4$, Cl-in	
	mode	wavenumber	intensity	wavenumber	intensity	wavenumber	intensity	wavenumber	intensity
H_2O	sym OH str	3664	475	3770	255	3638	388	3719	430
		3616	949	3708	411	3589	793	3655	169
		3542	616	3665	467	3543	1255	3632	1108
						3474	847	3576	676
	bend	1698	13	1699	45	1722	11	1714	39
		1674	51	1676	54	1701	67	1694	62
		1666	65	1667	44	1686	38	1679	15
						1675	64	1673	69
	antisym OH str	3955	102	3956	63	3953	82	3954	65
		3953	95	3955	145	3952	98	3953	98
		3948	98	3955	86	3951	94	3952	115
						3945	89	3950	90
HOCl	OH str	3299	1136	3838	86	3220	1440	3844	89
	bend	1429	93	1190	41	1513	43	1193	42
	ClO str	753	61	699	59	744	24	677	31

bound to this ortho′ oxygen, and hydrogen bonding between this H and the O atom of HOCl is weaker than in all other cases. Seen from the point of view of HOCl, as the Cl atom joins the ring, it takes part of the electron density of the oxygen and thus reduces its ability to create hydrogen bonding links.

As in the previous complex, all bonds outside the ring keep approximately the length they had in the corresponding free molecules; that is, they contribute little to the formation and stability of the clusters.

The confirmation of the preceding remarks is very obvious in the computed spectra of these species. The O−H stretching of HOCl in the Cl-in structure is predicted at 3838 cm^{-1}, close to the value of the isolated molecule, 3832 cm^{-1}, calculated in this work (3609.48 cm^{-1} experimental value, which includes anharmonicity effects[29]), indicating that this bond is practically unchanged in the cluster. On the other hand, in the H-in structure, where the H atom is hydrogen bonded to the ortho oxygen, the predicted wavenumber is much smaller, 3299 cm^{-1}. The HOCl bending vibration differs also largely in both structures (see Table 5), and besides, although the O−Cl stretch wavenumber does not change so much, the predicted relative intensity is very different: a weak band in the H-in molecule (like in free HOCl) and a stronger band, compared to the intensity of the other vibrations, in the Cl-in species, where the chlorine displacement in the ring induces a larger dipole moment variation. Thus, the infrared spectrum would provide an immediate tool to characterize the structure of this complex when it is observed.

$HOCl(H_2O)_4$. The situation encountered for the three-water cluster is repeated here with similar characteristics. Two stable structures are found, the more stable one with the O−H bond of HOCl included in the ring, and the second one with the O−Cl bond in the ring. The optimized energy difference, including zero-point vibrational corrections, is 35.6 kJ/mol. Both species are depicted in Figure 4. The rings are less planar now than they were for the previous molecules, but whereas the ring in the H-in species is fairly regular, that in the Cl-in molecule is quite irregular. Again the rotational constants, shown in Table 3, indicate that the former structure is of prolate type ($\kappa = -0.62$) and the latter of oblate type ($\kappa = 0.60$).

Changes in the structural parameters with respect to the individual molecules follow similar patterns to those in previous clusters, although the variations between the three-water cluster and the present one are less marked than for the other molecules studied here. The actual parameters are listed in Table 3. For the H-in species, the O−H bond of HOCl is only slightly enlarged, the free O−Cl bond is almost unaltered, and the hydrogen bonding separation between the H atom of HOCl and the ortho oxygen is reduced. The physical meaning that we deduce is that the bonding structure in the five-oxygen ring is still more favorable than that in the four-oxygen species, but a convergence is being reached, either to the number of molecules that give increasingly stable structures, or to values of the parameters which could remain constant when more water molecules are added. The water O−H bonds in the ring follow also a similar trend as in the previous case; the ortho O−H bond is the largest one, and the next ones in the cycle become consecutively shorter. This reflects a stronger hydrogen bonding between the H atom of HOCl and the ortho oxygen than between each other H atom and the next oxygen. The free O−H bonds keep the length of the free water molecule.

With respect to the Cl-in molecule, we notice that all bonds in the ring are longer than in the three-water species of the similar structure. Again the ortho′ water molecule has the shorter O−H bond, but even this one is much longer than that in individual water. The hydrogen bondings in this structure are weaker than those in any previously studied molecule of this series, and as usual, free bonds retain their length from the isolated molecules.

The predicted spectra present also similar characteristics as the three-water cluster described above. Large differences are calculated in wavenumber and intensity for the HOCl vibrations between the H-in and the Cl-in structures. Table 5 shows the predicted results, and we will only stress again here the importance of the infrared spectrum to characterize the more stable configuration of this cluster.

All previous publications on the $HOCl(H_2O)_4$ molecule that we are aware of[6,7,9] refer to a very different configuration, in which the HOCl molecule is located above a $(H_2O)_4$ structure which is not planar, but has a bridged configuration instead. That structure provides a closer representation of the ice surface than the planar clusters we have studied in this work. It is nonetheless interesting to make a few remarks when comparing the results of former works with the present ones. Both Robinson-Brown and Doren[7] and Geiger et al.[9] obtain a lengthening of the O−H bond of HOCl of ∼0.025 Å with respect to the free molecule, as it acts as a proton donor to a hydrogen bonding with the nearest water molecule. We calculate an increase of 0.03 Å when HOCl is in the H-in structure of the ring. Similarly, they observe a contraction of the O−Cl bond by ∼0.007 Å, and we estimate 0.009 Å for this reduction. The distance between the H atom of HOCl and the O atom of the

TABLE 6: Counterpoise Correction, Zero-Point Energy Correction, and Binding Energy (all in kJ/mol) for $HOCl(H_2O)_n$ Clusters, $n = 1-4$, Calculated in This Work Using the 6-311++G(d,p) Basis Set

n	counterpoise correction	zero-point energy correction	binding energy
1_{syn}	−9.8	−9.4	16.8
2	−22.3	−21.5	37.2
3_{H-in}	−39.5	−34.2	65.8
4_{H-in}	−52.3	−44.7	88.3

next water molecule, with which hydrogen bonding is formed, is much shorter in the ring structures calculated in this work, than in the nonplanar molecules of the previous authors (1.62 Å compared to 1.81 or 1.78 Å from refs 7 and 9, respectively). Finally, the HOCl angle opens by almost 1° in the ring structure, whereas it remains practically unaltered in the nonplanar calculations (103.6° in this work, 102.9° and 102.5° from refs 7 and 9, and 102.7° for the free molecule in this work). All this shows the stronger binding that takes place in the rings, in agreement with the large stability predicted for these planar clusters. In any case, we can thus confirm the proton donor character of the O−H bond in HOCl when approaching water structures, either of small planar cluster type, or more similar to nonplanar ice surfaces.

Binding Energies. Table 6 presents the calculated binding energies of the $HOCl(H_2O)_n$ clusters studied in this paper. The values show that addition of a water molecule to the previous species increases the binding energy of the cluster, and therefore its stability, by about 20−25 kJ/mol. This is in agreement with all results on interatomic distances and hydrogen bonding formation discussed in the preceding paragraphs. Extrapolating from the values of Table 6, we would conclude that an increase in the number of members in the cluster would be still more energetically favorable, but we find it speculative to propose actual numbers for the consecutive binding energies.

Dibble and Francisco[11] give a value of 26.8 kJ/mol for the binding energy of the syn conformer of the $HOCl-H_2O$ cluster, very much in agreement with our estimation once the basis set superposition error correction has been added. Kroes and Clary[6] calculate 60 kJ/mol for the interaction energy of the $HOCl(H_2O)_4$ molecule, in the bridged configuration closer to the ice surface, as mentioned in the previous section, which is also in reasonable agreement with the value of 88.3 kJ/mol of the present work.

Summary

Figure 6 shows graphically the variation of the more interesting geometrical parameters of the $HOCl(H_2O)_n$ clusters with the number of water units. We concentrate this discussion on the structures in which the O−H bond of HOCl is integrated in the ring, that is, on the more stable clusters. The graphs included in the figure show a clear trend in bond distances as the number of water molecules increases. The H atom of the HOCl molecule becomes more attached to the ring structure, as shown both by the enlargement of the O−H bond distance of HOCl and by the decrease of the distance between this hydrogen atom and the nearest oxygen in the ring (graphs representing r_{OH} and $r_{H}\cdots O$, respectively). The interaction

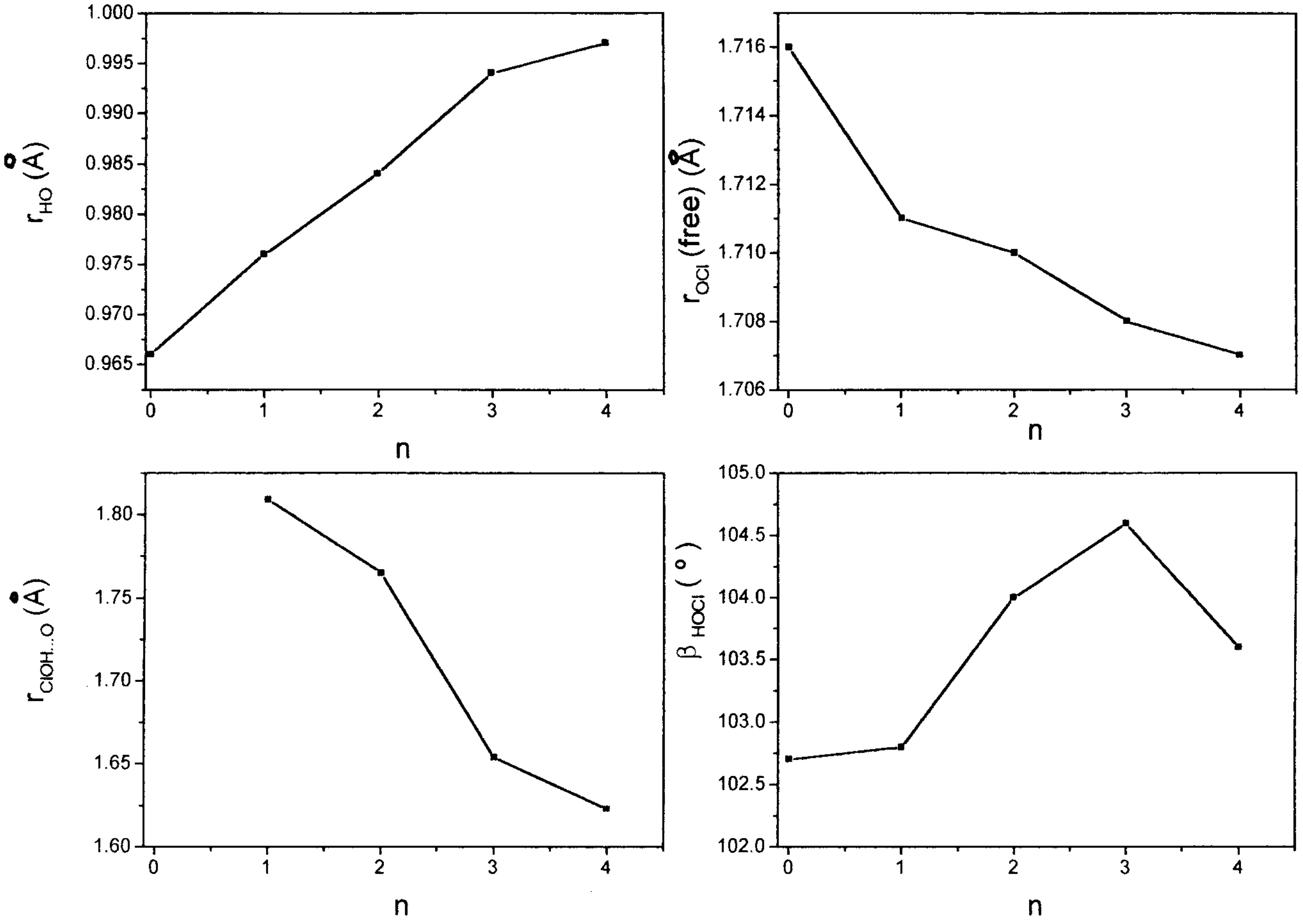

Figure 6. Variation of interatomic distances O−H, O−Cl (free bonds), and ClOH···O, and the intramolecular HOCl angle, of the $HOCl(H_2O)_n$ clusters, as a function of the number of water monomers, n: $n = 0$, isolated HOCl molecule; $n = 1$, anti conformer; $n = 3$ and 4, H-in species. Calculated values taken from Tables 1 and 3 (6-311++G(d,p) basis set).

between these two atoms must be of H-bonding character, with the HOCl molecule acting as proton donor and the next water molecule as proton acceptor. The free O−Cl bond decreases very slightly, indicating a reduced bond charge transfer within the HOCl molecule, from the O−H bond to the O−Cl. On the other hand, the HOCl angle changes in an irregular manner, although it seems to decrease when the number of water units becomes large.

The predicted spectra reflect graphically the calculated changes of the geometrical structure. Figure 5 shows stick spectra of the $HOCl(H_2O)_n$ clusters, as obtained in the ab initio calculation. The weakening of the O−H bond of HOCl as the number of water units in the cluster increases, induces a lowering of the corresponding stretching wavenumber, between 3832 cm^{-1} for the free molecule, and 3220 cm^{-1} for the four-water species. The small reduction of the O−Cl bond is reflected by the small increment of its stretching wavenumber, between 725 cm^{-1} in the free molecule and 744 cm^{-1} in the larger cluster. The increase in the HOCl bending wavenumber, also observed for the water clusters, indicates a larger impediment for the bending motion, as this molecule is more involved in the ring structure.

We present in Table 2 our results for water clusters, from monomer to pentamer, and in Figure 3 their corresponding predicted infrared spectra. The geometrical parameters for these molecules follow a similar trend to that of the heterospecies discussed above. The O−H bond in the ring increases with the number of water molecules, and the free bonds remain practically unaltered. In the spectra, the stretching vibrations of these free bonds are little affected in the series, whereas the ring O−H vibrations display marked changes both in frequency, which becomes increasingly small, and in intensity.

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