G2 Molecular Orbital Study of the Reactions of Water with $Cl^+(^3P)$ and $Cl^+(^1D)$

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G2 *ab initio* molecular orbital calculations have been carried out to study the potential energy surfaces (PESs) associated with the reactions of Cl^+ in its ^3P ground state and in its ^1D first excited state with water. Similar to what was found for the reactions involving F^+, the $[H_2,Cl,O]^+$ triplet state cations are weakly bound species, while the corresponding singlets are covalently bound species. As a consequence, although the PES of $Cl^+(^3P)$ lies 33.0 kcal/mol below that of the $Cl^+(^1D)$, the global minimum of the singlet potential energy surface lies 34.0 kcal/mol below the global triplet minimum. We have also found significant differences between the $[H_2,Cl,O]^+$ species and their fluorine-containing homologs regarding both their bonding and relative stabilities. These differences are more pronounced in the case of the triplets where the relative stabilities of the $[H_2,F,O]^+$ minima are completely reversed when fluorine is replaced by chlorine. As a result, most of the products of the reactions of F^+ with water cannot be formed in $Cl^+ + H_2O$ reactions, although also in this case the most likely process is the single charge transfer, in agreement with the experimental evidence. However, the formation of OH^+ becomes exothermic when Cl^+ reacts in its ^1D excited state. The estimated heat of formation for the most stable H_2OCl^+ singlet state species is 193 ± 2 kcal/mol.

1. Introduction

Reactions involving open shell monocations in the gas phase, such as $P^+(^3P)$, $O^+(^2P)$, $Si^+(^2P)$, etc., have received considerable attention in the last few years,[1] among other reasons because they play an important role in interstellar chemistry or in atmospheric chemistry and because, in many instances, they present peculiar reactivity patterns, in which insertion mechanisms are very often favored with respect to the formation of simple adducts.[2] Within this set, F^+ presents the additional interest of yielding weakly bound species when it reacts in its ^3P ground state, as it has been shown recently[3] for the particular case of reactions of F^+ with water. In this respect it is worth noting that other fluoronium ions, such as F_2N-FH^+ and $FN-FH^+$, which are minima of the corresponding potential energy surfaces, have been also reported in the literature[4] to be weakly bound species, stabilized by ion−dipole interactions. The aforementioned results clearly illustrate that weakly bound species may be not only suitable intermediates in the reaction paths leading from reactants to products in many ion−molecule reactions, but also in stable systems, which in some cases are the global minima of the potential energy surfaces.

Hence, it seems to be of interest to study, on one hand whether a similar behavior should be expected for reactions involving Cl^+ and, on the other hand, what are the most important similarities and differences between both halogen monocations. In this paper we shall address both of these issues by analyzing the $[H_2,Cl,O]^+$ singlet and triplet potential energy surfaces and by comparing them with those already reported in the literature[3] for the fluorine-containing analogs.

2. Computational Details

G2 ab initio molecular orbital calculations[5] were performed by using the *Gaussian-94* series of programs.[6] Since this theory is already well-known, we shall recall here only that this formalism yields final total energies which are effectively of QCISD(T)/6-311+G(3df,2p) quality. The reader is addressed to ref 5 to have a complete description of this composite method. It must be pointed out, however, that, although in the standard G2 theory, the harmonic vibrational frequencies and by implication the zero-point energies (ZPEs) are obtained at the HF/6-31G* level. In the present application of the theory, both vibrational frequencies and ZPEs were evaluated at the MP2/6-31G* level. This is justified by the fact that the geometries of most of the minima of the triplet potential energy surface are very sensitive to the electron correlation effects, which produce significant changes in some bond lengths and therefore in the corresponding stretching frequencies. Hence, it does not seem reasonable to evaluate the harmonic vibrational frequencies associated with structures which differ significantly from those actually used to obtain the final G2 energies. The corresponding zero-point energy corrections were scaled by the empirical factor 0.93.

The bonding characteristics of the different species considered in this work were studied by means of two different theoretical schemes, namely, the atoms-in-molecules theory of Bader and co-workers[7−9] and the natural bond orbital (NBO) population analysis of Weinhold *et al.*[10] In the first case, we have located the (3,−1) critical points of the electron charge density $\rho(\mathbf{r})$, also called bond critical points (bcps). In these points, $\rho(\mathbf{r})$ is a minimum along the bond path and a maximum in the other two directions, and the values of the charge density yield some valuable information on the relative strength of homologous bonds. Further information can be obtained in terms of the characteristics of the Laplacian of the electron charge density $\nabla^2\rho(\mathbf{r})$, since in those regions where the charge density is concentrated the Laplacian is negative, while it is positive in regions where the charge density is depleted. This implies that the maxima in $-\nabla^2\rho$ are associated with bonding or nonbonding charge concentrations. The former are necessarily found in the region of space between two bonded atoms of the system, while the latter are associated with the different lone pairs of the molecule. Also, in general, when the interaction takes place between closed shell subunits, as in ionic bonds, hydrogen bonds, or van der Waals complexes, the Laplacian is positive in the region of space between both interacting subunits and the charge density at the corresponding bond critical point is

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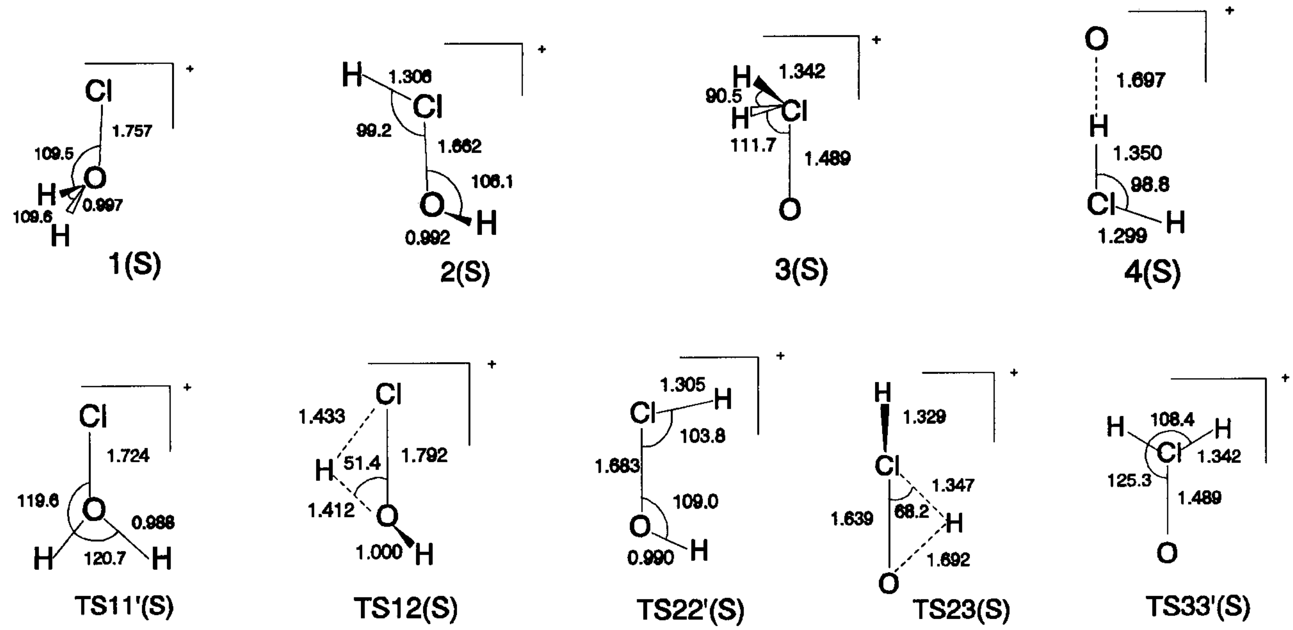

Figure 1. MP2/6-31G*-optimized geometries for the stationary points of the $[H_2,Cl.O]^+$ singlet PES. Bond lengths are in angstroms and bond angles in degrees.

usually rather small, since the electrons accumulate preferentially at the interacting subunits rather than into the region between them.

The NBO analysis of the wave function may also help in visualizing the characteristics of the new bonds formed in terms of the natural hybrid orbitals of the interacting atoms. This analysis will be particularly useful when dealing with weakly bound species, where it is important to know whether the linkage is essentially electrostatic or has some covalent character.

Both population analysis were carried out using the MP2 charge densities in order to take explicitly into account electron correlation effects.

3. Results and Discussion

$[H_2,Cl,O]^+$ Singlet Potential Energy Surface. The MP2/6-31G* optimized geometries of the minima and transition states of the $[H_2,Cl,O]^+$ singlet potential energy surface (PES) are schematized in Figure 1. Their G2 total energies are summarized in Table 1. Hereafter, the following nomenclature will be adopted: the different minima of the singlet and triplet PESs will be identified by a number followed by (S) or (T), respectively. A similar convention will be adopted to the naming of the different transition states (TSs). In this case, the two digits indicate the two minima which are connected by a particular TS. In general, the symmetric transition structures between equivalent minima of the PES, and as **TS11′(S)**, were located in the normal searching for stationary points of the corresponding PESs by imposing the appropriate symmetry constrains. The remaining ones where found by means of the linear synchronous transit method[11] as it is implemented in the Gaussian-94 programs or alternatively by using an eigenvalue-following algorithm. All of them were characterized by a harmonic frequency calculation at the MP2/6-31G* level. An intrinsic reaction coordinate procedure[12] allowed us to establish which minima were associated with each transition structure.

In Figure 2, we present a schematic representation of the singlet PES. For the sake of a better comparison we have also included in the same figure the PES reported in ref 3 for the case of the fluorine-containing analogs. It can be seen that both PESs are rather similar. In both cases the global minimum 1(S) corresponds to the adduct of the halogen cation to the oxygen atom of the water molecule, while the species corresponding to the insertion of the halogen cation into the O−H bond of the neutral is the second stable minimum **2(S)**. However, there are some significant differences when fluorine is replaced by chlorine that deserve some comment. In the first place, it can be noted that the energy gap between **1(S)** and **2(S)** chlorine-containing species is sizeably smaller (*ca.* 4 kcal/mol) than that found[3] between the **1(S)** and **2(S)** fluorine-containing minima. This seems to bear some relation with the fact that for chlorine-containing species the Cl−O bond in the global minimum is weaker and longer than the Cl−O linkage in species **2(S)**, while for the fluorine-containing analogs the opposite situation is found. This can be explained if one considers that both minima **1(S)** and **2(S)** can be viewed as the result of protonating hypochlorous acid (ClOH) either at the oxygen or at the chlorine atoms, respectively. As it has been already shown in other similar cases,[13,14] protonation at the most electronegative atom (oxygen) to yield species **1(S)** implies a significant charge depletion of the Cl−O bond, which accordingly becomes weaker

TABLE 1: G2 Total Energies, and *E* (in hartrees) of the Stationary Points of the $[H_2,Cl,O]^+$ Singlet and Triplet Potential Energy Surfaces. Relative Energies (in kcal/mol) Are Given within Parentheses

system	*E*
1(S)	−535. 65086 (0.0)
2(S)	−535.62810 (14.3)
3(S)	−535.51827 (83.2)
4(S)	−535.46992 (113.5)
O(^{1}D)	−74.90585
TS11′(S)	−535.64587 (3.1)
TS12(S)	−535.58491 (41.4)
TS22′(S)	−535.61793 (20.7)
TS23(S)	−535.47916 (107.7)
TS33′(S)	−535.47148 (112.6)
1(T)[a]	−535.59797[b] (0.0) [2.02][c]
2(T)	−535.56897[b] (18.2) [2.03]
3(T)	−535.55219[b] (28.7) [2.01]
4(T)	−535.56714[b] (19.3) [2.01]
ClO$^+$($^3\Sigma$)	−534.36065 [2.01]
TS11′(T)	−535.59022 (4.8) [2.02]
TS12(T)	−535.54957 (30.4) [2.02]
TS22′(T)	−535.56620 (19.9) [2.03]
TS23(T)	−535.53393 (40.2) [2.02]
TS33′(T)	−535.53929 (36.8) [2.00]

[a] The **1(T)** species is 33.2 kcal/mol above the **1(S)** global minimum. [b] Values taken from ref 17. [c] Values of $\langle S^2 \rangle$ are given within brackets.

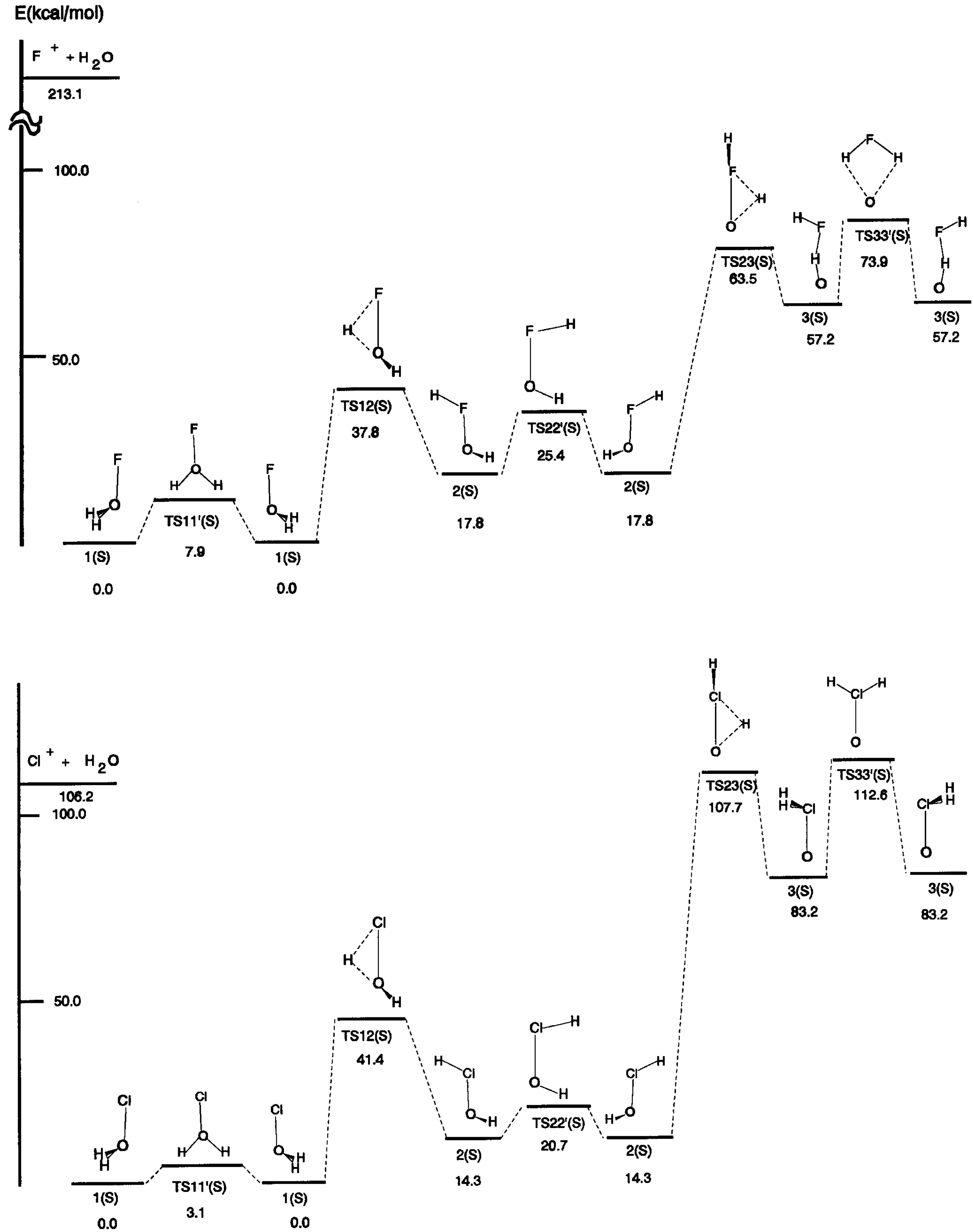

Figure 2. Energy profile for the singlet $[H_2,F,O]^+$ and $[H_2,Cl,O]^+$ potential energy surfaces. The former was taken from ref 3.

and longer. On the contrary, protonation at the less electronegative center (Cl) leads to a reinforcement of the Cl−O linkage, which accordingly becomes shorter. These charge redistributions are easily visualized by comparing the Laplacians of the charge density of ClOH and those of both protonated species. It is apparent from Figure 3 that the charge density at the Cl−O bond critical point of species **1(S)** is smaller than that found for ClOH, while the opposite is found for species **2(S)**. These results are also consistent with the corresponding harmonic vibrational frequencies. As shown in Table 2, the Cl−O stretch of species **2(S)** is blue shifted with respect to that of the ClOH molecule by 18 cm^{-1}, while that of the global minimum **1(S)** is red shifted by 77 cm^{-1}. The NBO analysis of these two species also shows substantial differences in the characteristics of the Cl−O bonding MO. For the global minimum **1(S)**, this MO involves an almost pure p orbital of the chlorine atom with a $sp^{4.8}$ hybrid of the oxygen atom which contributes 73% to the molecular orbital. For species **2(S)**, the situation is clearly different. On one hand, the chlorine hybrid has a sizeably larger s contribution (about 10%), while the s contribution in the oxygen hybrid decreases, and on the other hand the contribution of the oxygen hybrid to the bonding molecular orbital comes down to 55%. These bonding differences are also reflected in the dissociation energies of the Cl−O bonds of species **1(S)** and **2(S)** to yield $Cl(^2P) + H_2O^+(^2B_1)$ and $ClH^+(^2\Pi) + OH(^2\Pi)$, respectively. Our G2-estimated values indicate that the first process requires an energy of 66.7 kcal/mol, while the second is endothermic by 69.8 kcal/mol. Of course, the situation found for fluorine-containing species is just the opposite, since fluorine is more electronegative than oxygen. Hence, protonation at the oxygen atom to yield the global minimum **1(S)** implies a reinforcement of the F−O bond, while protonation at the fluorine atom to yield species **2(S)** leads to an important weakening of the F−O linkage.

Another important difference between $[H_2,F,O]^+$ and $[H_2,Cl,O]^+$ singlet PESs is that in the former no minimum similar to structure **3(S)** is found, since it dissociates to yield FH_2^+ and an oxygen atom in its ^1D first excited state. This may be understood if one takes into account that the chlorine containing species **3(S)** can be considered as the result of the protonation of HClO at the chlorine atom. Since the protonation takes place at the less electronegative center, a reinforcement of the Cl−O bond takes place. This is quite evident when comparing the Laplacians of the charge densities of HClO and **3(S)** species (See Figure 4). The homologous cation obtained by replacing chlorine by fluorine is not stable. In fact, the F−O bond in the HFO system is already quite weak as it corresponds to a dicoordinated fluorine atom, and, to form a species similar to **3(S)**, it must be protonated at the fluorine atom, which is the most electronegative center. Hence, the charge depletion at the F−O bond is so large that the bond breaks apart.

It is also interesting to realize that species **3(S)** is the one which presents a stronger Cl−O bond in terms of the charge density at the corresponding bcp (see Figures 3 and 4). When the corresponding NBO's are analyzed, some differences are also found with respect to the bonding in **2(S)** and **1(S)**. The contribution of the oxygen hybrids decreases to 51%, and the s character of the chlorine hybrids comes up to 22%. Both pictures are consistent with the fact that species **3(S)** exhibits also the largest Cl−O stretching frequency which contributes to two absorptions at 1049 and 1096 cm^{-1}, combined with the ClH_2 wagging. The less stable minimum **4(S)** of the $[H_2,Cl,O]^+$ (not included in the PES) is apparently identical to the **3(S)** species of the $[H_2,F,O]^+$ PES. However, a detailed inspection of their bonding characteristics evidences substantial differences. As it is shown in Figure 5, the Laplacian of species **4(S)** corresponds to a hydrogen bond complex between ClH_2^+ and an oxygen atom in its ^1D first excited state. This is confirmed by the fact that the positive charge is essentially located at the ClH_2 subunit, while the oxygen atom is practically neutral. Further, from the data given in Table 1 and the G2 energies of ClH_2^+ taken from ref 5[15], an interaction energy of 8.0 kcal/mol between both subunits is estimated. Quite to the contrary, the fluorine-containing homolog can be considered as a tightly bound complex which presents a very strong hydrogen bond between FH and $OH^+(^1\Sigma)$, with the proton midway between the F and the O. This is reflected in an estimated interaction energy between both building subunits of 29.1 kcal/mol.[3] These differences are a direct consequence of the fact that FH has a proton affinity (117 kcal/mol)[16], much smaller than that of ClH (128.6 kcal/mol).[16] Hence, it is reasonable to expect that in the chlorine complex the proton is essentially attached to the

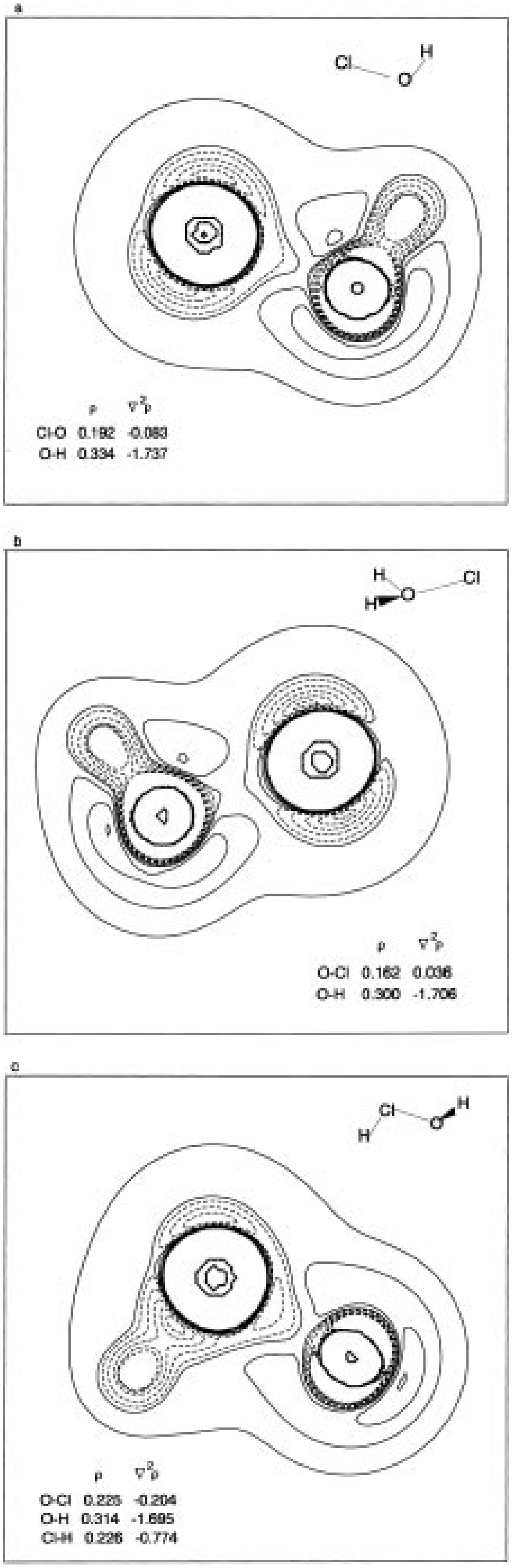

Figure 3. Contour maps of the Laplacian of the charge density of (a) ClOH, (b) species **1(S)**, (c) species **2(S)**. Positive values of $\nabla^2\rho$ are denoted by solid lines and negative values by dashed lines. Contour values au are ±0.05, ±0.25, ±0.50, ±0.75, and ±0.95. The charge density ρ in e au^{-3} and its Laplacian $\nabla^2\rho$ in e au^{-5} at the corresponding bond critical points are given.

TABLE 2: Harmonic Vibrational Frequencies (in cm^{-1}) of the [H_2,Cl,O]$^+$ Singlet State Cations.[a] Values obtained at the MP2/6-31G* Level

1(S)		2(S)		3(S)		4(S)	
ν	assignment	*ν*	assignment	*ν*	assignment	*ν*	assignment
3550	O−H asymm. stret.	3566	O−H stretch	2500	Cl−H stretch	2884	Cl−H$_a$ stretch
3452	O−H symm. stret.	2805	Cl−H stretch	2454	Cl−H stretch	2160	Cl−H$_b$ stretch
1659	OH$_2$ bending	1389	O−H bending	1348	ClH$_2$ bending	1296	ClH$_2$ bending
1093	OH$_2$ twisting	1011	Cl−H bending	1096	Cl−O stretch + ClH$_2$ wagging	550	Cl−H$_b$ bending out-of-plane
921	OH$_2$ wagging	773	Cl−O stretch	1049	Cl−O stretch + ClH$_2$ wagging	403	ClH$_2$ rocking
698	Cl−O stretch.	445	H−O−Cl−H torsion	957	Cl−H$_2$ twisting	224	O···H$_b$ stretch

[a] The H$_a$ corresponds to the hydrogen atom which does not participate in the hydrogen bond, while H$_b$ denotes the hydrogen atom involved in the hydrogen bond. The Cl−O stretching frequency for ClOH molecule is found at 755 cm^{-1} at the same level of theory.

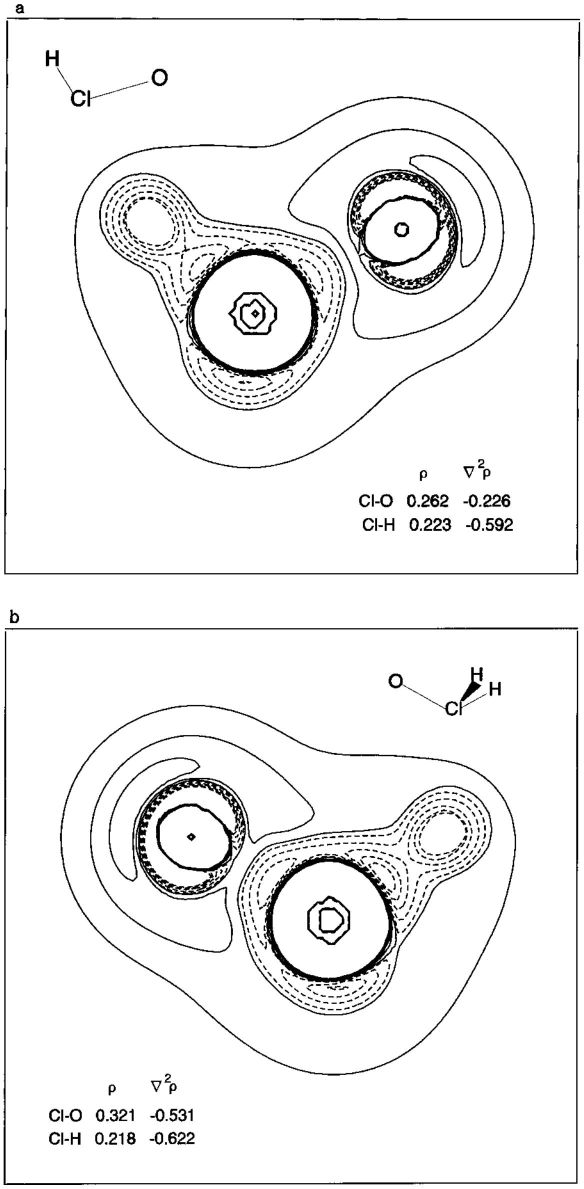

Figure 4. Contour maps of the Laplacian of the charge density of (a) HClO, (b) species **3(S)** of the [H_2,Cl,O]$^+$ PES. Same conventions as in Figure 3.

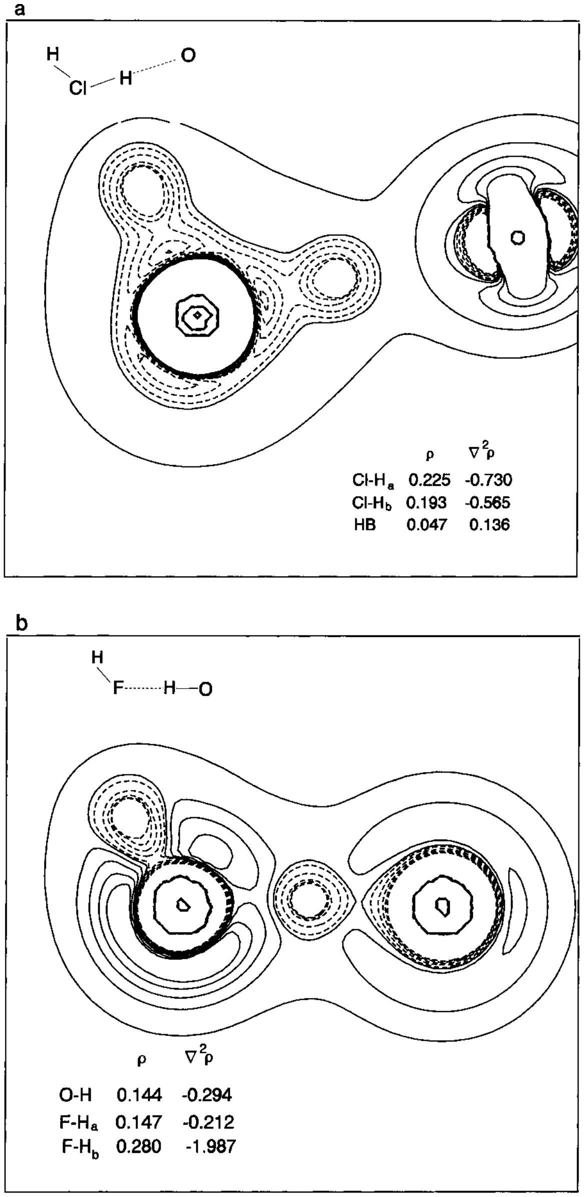

Figure 5. Contour maps of the Laplacian of the charge density of (a) species **4(S)** of the [H_2,Cl,O]$^+$ PES, (b) species **3(S)** of the [H_2,F,O]$^+$ PES. Same conventions as are in Figure 3. The H$_a$ corresponds to the hydrogen atom which does not participate in the hydrogen bond, while the H$_b$ denotes the hydrogen atom involved in the hydrogen bond.

chlorine atom, while in the fluorine complex, it remains bound to the OH subunit, although, as shown in Figure 5, the O−H linkage becomes quite weak. These differences are also responsible for the much lower stability of the chlorine-containing species. The vibrational modes of species **4(S)** are consistent with the bonding discussed above. As shown in Table 2, and due to the existence of a strong hydrogen bond, the Cl−H stretching displacements do not appear as symmetric and asymmetric combinations, because the Cl−H linkage involved in the hydrogen bond gives a much smaller stretching frequency than the other Cl−H bond, in agreement with the fact that the charge density at the bcp for the former is smaller than for the latter (See Figure 5a).

Figure 2 shows that all minima of the singlet PES should be experimentally accessible, since the barriers between them are sufficiently high. This is not the case for minimum **4(S)**, which is connected with the global minimum through a transition state **TS14(S)**, which lies only 0.3 kcal/mol above **4(S)**.

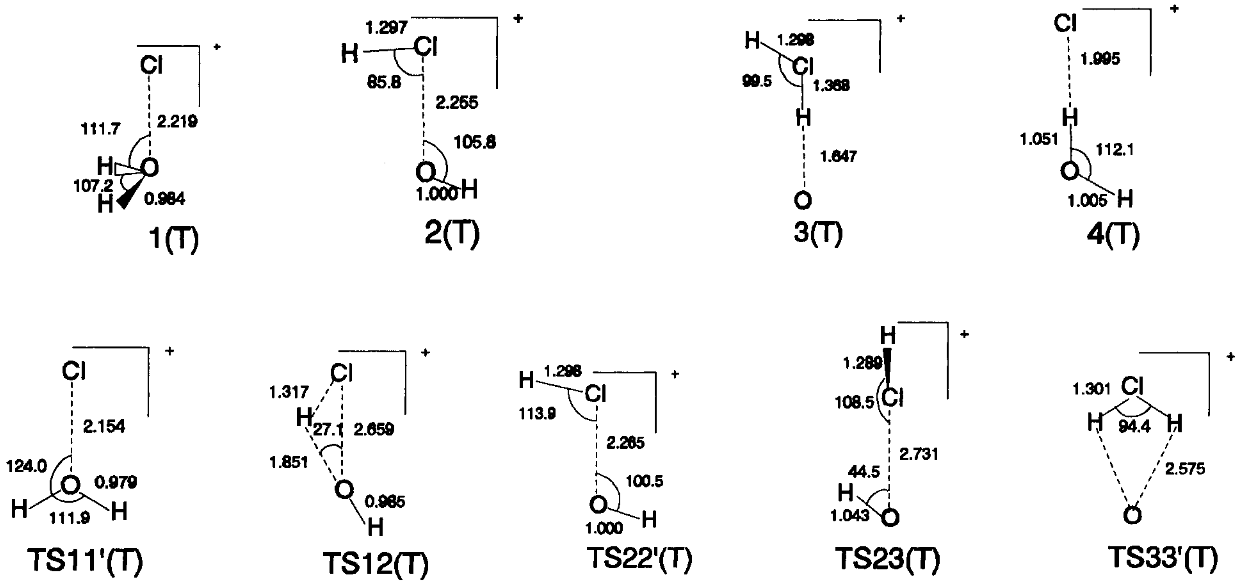

Figure 6. MP2/6-31G*-optimized geometries for the stationary points of the $[H_2,Cl,O]^+$ triplet PES. Bond lengths are in angstroms and bond angles in degrees. Those of the different minima were taken from ref 17.

The global minimum **1(S)** is connected with the second stable minimum by a 1,2-H shift. Similar to what was found for the fluorine-containing analogs, the equivalent *trans* isomers of species **2(S)** are connected by the *cis* isomer, whose imaginary frequency corresponds to the HClOH torsion. A further 1,2-H shift connects the **2(S)** minimum with the **3(S)** one.

$[H_2,Cl,O]^+$ Triplet Potential Energy Surface. The MP2/6-31G*-optimized geometries of the stationary points of the $[H_2,Cl,O]^+$ triplet PES are schematized in Figure 6. It must be mentioned that some of the minima have been reported before in the literature,[17] but they are included here for the sake of a better comparison with the corresponding singlets. The G2 total energies of the different stationary points have been also included in Table 1. The corresponding PES is compared with the PESs of the fluorine-containing systems in Figure 7. The first conspicuous fact of Figure 6 is that the triplet state systems are weakly bound species. All of them can be described, in a first approximation, either as ion−dipole or hydrogen bond complexes involving different building blocks, very much in the same way as their fluorine-containing analogs.[3] There are, however, differences between the bonding characteristics of $[H_2,F,O]^+$ and $[H_2,Cl,O]^+$ triplet state cations which were pointed out elsewhere.[3,16] We will summarize here the most important ones. Species **1(T)** of the $[H_2,Cl,O]^+$ PES is apparently similar to species **4(T)** of the $[H_2,F,O]^+$ PES. However, it is important to realize that the Cl−O distance in the former is slightly shorter than the F−O distance in the latter, even though Cl^+ is more voluminous than F^+. This difference reflects substantial bonding differences. While the fluorine-containing cation is a polarization complex between H_2O^+ and F, the chlorine analog closely resembles a Cl^+ interacting with a water molecule. Furthermore, as explained in ref 17, the Cl−O interaction has a nonnegligible covalent character, which results in a smaller bond length. Minima **2(T)** of both PESs present also important differences. The fluorine-containing species is an ion−dipole complex between FH and $OH^+(^3\Sigma)$, with the two unpaired electrons located at the OH^+ subunit. In the chlorine analog, the interaction between both subunits is stronger. Both unpaired electrons are shared by both moieties, and again the Cl−O linkage has a covalent character similar to that found for species **1(T)**. The difference between the proton affinities of FH and ClH is again responsible for the differences between species **3(T)** of the $[H_2,Cl,O]^+$ PES and structure **1(T)** of the $[H_2,F,O]^+$ one. The former is a hydrogen bond complex between ClH_2^+ and an oxygen atoms in its ^3P ground state, while the latter is a hydrogen bond complex between FH and OH^+.

Figure 7 clearly illustrates the dramatic differences between both PESs as far as the relative stabilities of the different minima are concerned, which are completely reversed. The global minimum **1(T)** of the $[H_2,F,O]^+$ PES becomes the less stable one **3(T)** when fluorine is replaced by chlorine, while the opposite is found for the less stable complex.

Three key factors are responsible for these significant differences. First, as it was already pointed out above, the proton affinity of FH is much smaller than that of ClH,[16] but, what is more important, it is also smaller than the proton affinity of the oxygen atom in its ground state. Second, the ionization potential of FH is much greater than that of ClH, and third, F^+ has an exceptionally large recombination energy, only surpassed by the recombination energies of He^+ and Ne^+, while that of Cl^+ is significantly smaller.

The latter factor implies that in $F^+ + H_2O$ interactions the first step corresponds to a charge transfer yielding $F + H_2O^+$. Actually, as mentioned before, the **4(T)** complex is the result of the interaction between these two subunits. In $Cl^+ + H_2O$ reactions the charge transfer process is also energetically favorable, but once the H_2O^+ system is formed its electronegativity becomes greater than that of neutral chlorine and a back charge donation from the latter to the former takes place. This is reflected in the fact that while in FOH_2^+ **4(T)** species the positive charge is associated almost exclusively with the OH_2 subunit; in the homolog $ClOH_2^+$ **1(T)** the chlorine atom still retains a positive net charge of 0.64.

Table 3 summarizes the relative energies of the different noninteracting building subunits one can define for both systems, which clearly reflect the effects of the three different factors aforementioned. From this table it seems reasonable to expect the global minimum of the $[H_2,Cl,O]^+$ triplet PES to be the result of the intimate interaction between Cl and H_2O^+, while for the $[H_2,F,O]^+$ PES it should correspond to the complex between FH and OH^+.

It is also important to emphasize that due to the fact that all $[H_2,Cl,O]^+$ triplet state cations are weakly bound species while the corresponding singlet state cations are covalently bound systems, the global singlet minimum **1(S)** lies 33 kcal/mol in energy below the global triplet minimum **1(T)**, even though,

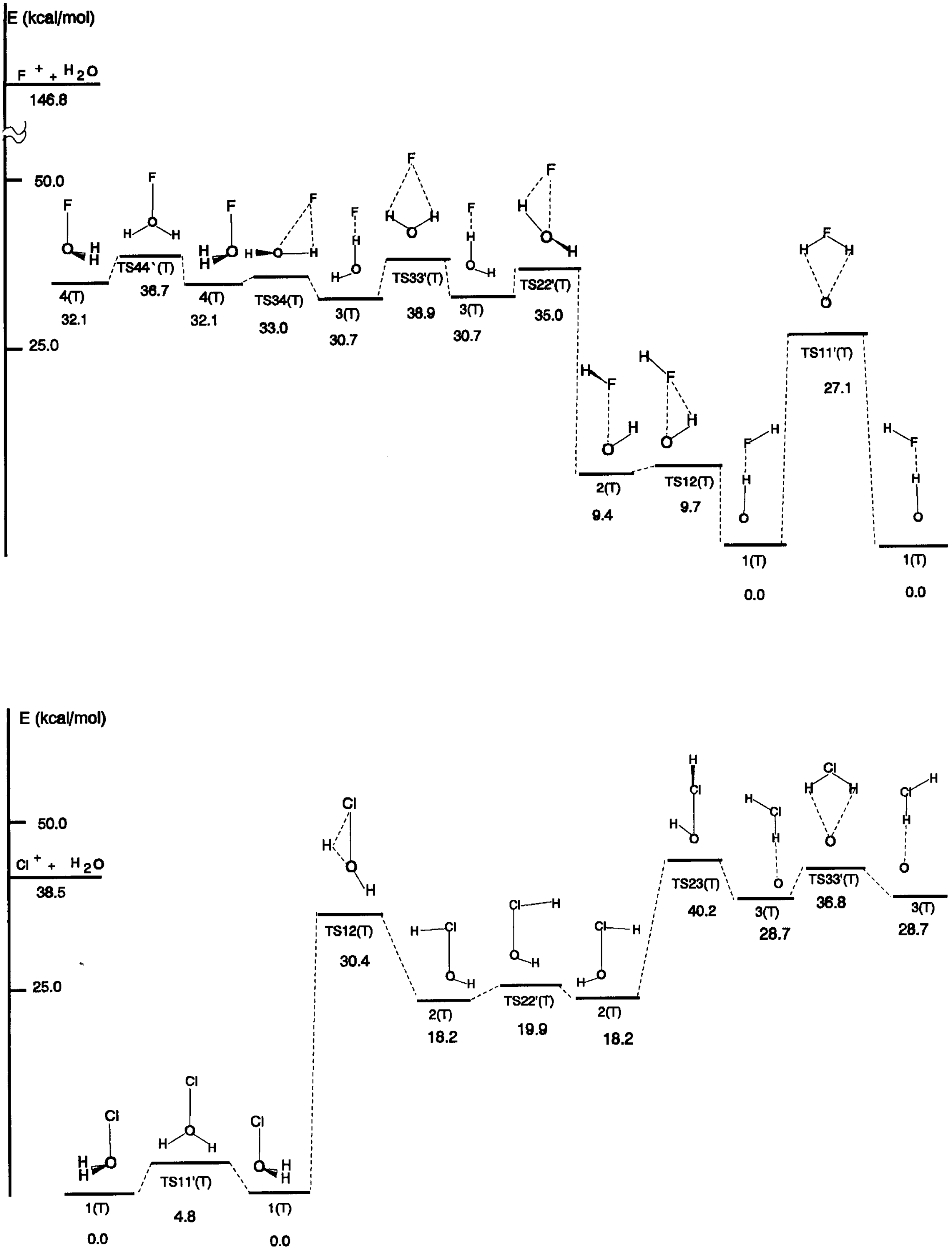

Figure 7. Energy profile for the triplet $[H_2,F,O]^+$ and $[H_2,Cl,O]^+$ potential energy surfaces. The former was taken from ref 3.

according to our G2 estimations, the $Cl^+(^3P)$ is 34.5 kcal/mol more stable than the $Cl^+(^1D)$. It is worth mentioning that this value is in very good agreement with the experimental one (33.3 kcal/mol),[18] which indicates that the possible contamination of the ^1D state by the ^1S must be very small.

Reaction Products. There is a clear difference between the

TABLE 3: G2 Relative Stabilities (kcal/mol) for the Possible Noninteracting Building Blocks of $[H_2,Cl,O]^+$ and $[H_2,F,O]^+$ Triplet State Systems

$FH + OH^+$	0.0	$ClH + OH^+$	23.5
$FH_2^+ + O$	1.6	$ClH_2^+ + O$	6.6
$F + H_2O^+$	10.2	$Cl + H_2O^+$	0.0
$FH^+ + OH$	71.7	$ClH^+ + OH$	17.5
$F^+ + H_2O$	119.9	$Cl^+ + H_2O$	5.0

reactions involving the Cl^+ in its ^3P ground state and in its ^1D first excited state. Our G2 estimations show that, in the former case, only the charge transfer process is slightly exothermic:

$$Cl^+(^3P) + H_2O \rightarrow Cl(^2P) + H_2O^+(^2B_1) \qquad \Delta H_0{}^0 = -5.0 \text{ kcal/mol} \quad (1)$$

It is worth remembering that this process is, however, highly exothermic for F^+ (*ca.* 109.7 kcal/mol) due to the high recombination energy of this cation. Hence, while, in reactions involving F^+, the H_2O^+ molecule will be produced in a vibrationally excited state, this possibility is not open for Cl^+ reactions. The formation reactions of OH^+, OH, or O^+, which are exothermic in F^+, the reactions are endothermic when Cl^+ is involved, as mentioned above and indicated below:

$$Cl^+(^3P) + H_2O \rightarrow ClH(^1\Sigma) + OH^+(^3\Sigma) \qquad \Delta H_0{}^0 = +18.4 \text{ kcal/mol} \quad (2)$$

$$Cl^+(^3P) + H_2O \rightarrow ClH^+(^2\Pi) + OH(^2\Pi) \qquad \Delta H_0{}^0 = +12.4 \text{ kcal/mol} \quad (3)$$

$$Cl^+(^3P) + H_2O \rightarrow ClH(^1\Sigma) + H + O^+(^2P) \qquad \Delta H_00 = +132.6 \text{ kcal/mol} \quad (4)$$

Also slightly endothermic is the formation of ClH_2^+:

$$Cl^+(^3P) + H_2O \rightarrow ClH_2^+ + O(^3P)\Delta H_0{}^0 = +1.5 \text{ kcal/mol} \quad (5)$$

Again, in contrast to the similar process in $F^+(^3P)$ reactions, the formation of ClOH is predicted to be endothermic:

$$Cl^+(^3P) + H_2O \rightarrow ClOH + H^+ \qquad \Delta H_0{}^0 = +80.3 \text{ kcal/mol} \quad (6)$$

as well as is the formation of ClO^+,

$$Cl^+(^3P) + H_2O \rightarrow ClO^+(^3\Sigma) + H_2 \qquad \Delta H_0{}^0 = +6.0 \text{ kcal/mol} \quad (7)$$

All these results are in agreement with the experimental evidence,[19] which indicates that H_2O^+ species is the only product in $Cl^+ + H_2O$ reactions.

The formation of $OH^+(^1\Delta)$, $H_2O^+(^2B_1)$, and $ClH^+(^2\Pi)$ are, however, exothermic when the reaction involves the Cl^+ in its ^1D first excited state:

$$Cl^+(^1D) + H_2O \rightarrow ClH(^1\Sigma) + OH^+(^1\Delta) \qquad \Delta H_0{}^0 = -11.0 \text{ kcal/mol} \quad (8)$$

$$Cl^+(^1D) + H_2O \rightarrow Cl(^2P) + H_2O^+(^2B_1) \qquad \Delta H_0{}^0 = -39.5 \text{ kcal/mol} \quad (9)$$

TABLE 4: Proton Affinities (kcal/mol)[a] of ClOH, HClO, FOH, and HFO Estimated at the G2 Level

ClOH (O)	152.0
ClOH (Cl)	137.7
HClO (O)	119.6
HClO (Cl)	188.6
FOH (O)	133.8
FOH (F)	116.0
HFO (O)	174.2

[a] Protonation of HFO at the fluorine atom leads to a F−O bond fission (see text).

$$Cl^+(^1D) + H_2O \rightarrow ClH^+(^2\Pi) + OH(^2\Pi) \qquad \Delta H_0{}^0 = -22.1 \text{ kcal/mol} \quad (10)$$

while the formation of ClH_2^+ and ClOH are still endothermic,

$$Cl^+(^1D) + H_2O \rightarrow ClH_2^+ + O(^1D) \qquad \Delta H_0{}^0 = +14.8 \text{ kcal/mol} \quad (11)$$

$$Cl^+(^1D) + H_2O \rightarrow ClOH + H^+ \qquad \Delta H_0{}^0 = +45.8 \text{ kcal/mol} \quad (12)$$

Unfortunately, we are not aware of any experimental study of reactions involving $Cl^+(^1D)$ with which to compare.

Heats of Formation and Proton Affinities. The heat of formation of the most stable singlet $[H_2,Cl,O]^+$ species was estimated using three different isogyric reactions,[20] *i.e.*, reactions with equal number of unpaired electrons on the two sides:

$$Cl_2 + H_3O^+ \rightarrow ClOH_2^+ \ \mathbf{1(S)} + HCl \qquad \Delta H_0{}^0 = +27.0 \text{ kcal/mol} \quad (13)$$

$$ClF + H_3O^+ \rightarrow ClOH_2^+ \ \mathbf{1(S)} + HF \qquad \Delta H_0{}^0 = -1.4 \text{ kcal/mol} \quad (14)$$

$$ClOH + H_3O^+ \rightarrow ClOH_2^+ \ \mathbf{1(S)} + H_2O \qquad \Delta H_0{}^0 = +11.0 \text{ kcal/mol} \quad (15)$$

The enthalpies of these reactions were obtained at the G2 level. The total G2 energies of the species involved besides the energy of **1(S)** were taken from ref 5.[15] The experimental heats of formation of ClH, OH^+, Cl, OH_2^+, ClH_2^+, and O were taken from ref 16. The average estimated heat of formation for species **1(S)** is 193 ± 2 kcal/mol, which is about 39 kcal/mol lower than that estimated[17] for the most stable triplet state cation **1(T)**.

Reactions 7 and 12, which are isogyric, can be also used to estimate the heat of formation of ClO^+ and ClOH, respectively. The former is predicted to be 276.9 kcal/mol and the latter −15.2 kcal/mol, in excellent agreement with the experimental values, 277.0[16] and −17.9 kcal/mol[1a], respectively.

The G2 values reported here can be also used to estimate the proton affinities of both isomers of hypochlorous acid, which are summarized in Table 4. For the sake of completeness, this table includes also the proton affinities of the fluorine-containing homologs. It can be noticed that in all cases these systems behave as oxygen bases and that protonation of HFO at the fluorine atom leads to a F−O bond fission, as indicated above.

Conclusions

Our survey of the $[H_2,Cl,O]^+$ singlet and triplet potential energy surfaces shows important differences between singlets and triplets regarding their bonding characteristics. The former are covalently bound species while the latter are, in general, weakly bound compounds. These bonding dissimilarities are reflected in dramatic differences in their relative stabilities, which make the most stable singlet cation to be 33 kcal/mol more stable than the corresponding triplet, even though the triplet entrance channel $Cl^+(^3P) + H_2O$ lies 34 kcal/mol below the singlet entrance channel, $Cl^+(^1D) + H_2O$.

There are also significant differences when both PESs are compared with those corresponding to the $F^+ + H_2O$ reactions. These differences are particularly important for the triplets, whose relative stabilities become completely reversed when chlorine is replaced by fluorine. They can be considered the result of three key factors. The dominant one is the extremely high recombination energy of F^+ compared with that of Cl^+. The differences in the ionization potentials, as well as in the proton affinities of FH and ClH, also play important roles in this respect.

Hence, while in $F^+(^3P) + H_2O$ reactions the formation of H_2O^+, OH^+, FH^+, and O^+ are predicted to be exothermic, for $Cl^+(^3P) + H_2O$ reactions only the formation of the former product is found to be exothermic, in agreement with the experimental evidence.

However, if the reaction involves the Cl^+ in its ^1D first excited state, the formation of both H_2O^+ and OH^+ are estimated to be exothermic, while that of ClH^+ and ClH_2^+ are still endothermic.

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