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A Theoretical Investigation of the Structure of $(Cl_2F)^+$ and Protonated ClF[1a]

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Abstract: In an attempt to resolve the controversy among experimentalists about the geometry of $(Cl_2F)^+$ cation, ab initio calculations have been carried out on the ground states of $(ClFCl)^+$ and $(ClClF)^+$ within the framework of the restricted Hartree–Fock theory. For comparison purposes, similar calculations have been performed on $(HFCl)^+$ and $(HClF)^+$. We find that, using 44-31G type basis sets, $(ClFCl)^+$ is more stable than $(ClClF)^+$, and $(HFCl)^+$ is more stable than $(HClF)^+$. The results of theoretical calculations are interpreted using Mulliken's population analysis, Morokuma's energy decomposition analysis, and the configuration analysis of Baba et al. Optimized geometries are presented for all of these molecular ions.

I. Introduction

Christe and Sawodny (CS) have shown that a new oxidizing species, $(Cl_2F)^+$, is formed in the form of a salt when ClF reacts with AsF_5 or BF_3:[2a]

$$AsF_5 + 2ClF \rightarrow (Cl_2F)^+(AsF_6)^-$$

$$BF_3 + 2ClF \rightarrow (Cl_2F)^+(BF_4)^-$$

The existence of such salts containing the novel cation, $(Cl_2F)^+$, has been confirmed by the work of Gillespie and Morton (GM).[2b] In their original paper reporting the discovery of $(Cl_2F)^+$ CS suggested that the ion was most likely to be a bent C_{2v}-symmetry molecule, $(ClFCl)^+$, with a bond angle of about 100–120°. This conclusion was challenged by GM, who suggested that $(Cl_2F)^+$ has the asymmetric, $(ClClF)^+$, structure. There has been an attempt to rationalize this suggested asymmetric structure of $(Cl_2F)^+$ using arguments based upon the frontier orbital concept.[3]

In this paper we present the results of our theoretical investigation of the structure of $(Cl_2F)^+$ using ab initio molecular orbital theory. We have also investigated the structure of protonated ClF for comparison purposes. Both of these cations can be thought of as products of interaction between ClF and the ion Cl^+ or H^+.

II. Ab Initio Geometry and Stabilization Energies

Using the standard split-valence basis set, 44-31G,[4a] with the recommended exponents and scale factors,[5] we have carried out ab initio calculations on Cl^+, ClF, $(ClFCl)^+$, $(ClClF)^+$, $(HClF)^+$, and $(ClFH)^+$ within the framework of closed-shell single-determinant Hartree–Fock theory. All geometrical parameters were optimized. The total energies, optimum geometrical parameters, and the binding energies of $(ClFCl)^+$, $(ClClF)^+$, $(ClFH)^+$, and $(HClF)^+$ are given in Table I. These results show that both $(ClFCl)^+$ and $(ClClF)^+$ are stable species with respect to isolated Cl^+ and ClF. The stability of $(ClFCl)^+$ is about 10 kcal/mol higher than that of $(ClClF)^+$. The $(ClFCl)^+$ ion has C_{2v} symmetry with a large bond angle of 140°. Our calculations show that all non-C_{2v}-symmetry structures for $(ClFCl)^+$ have higher energies. The $(ClClF)^+$ ion has a rather small bond angle of 99°.

It is interesting to note that a limited basis set, STO-3G, with recommended exponents and scale factors[4b] shows that $(ClClF)^+$ is more stable than $(ClFCl)^+$ by about 8 kcal/mol. The limited basis set also gives a rather different bond angle for $(ClFCl)^+$, although other geometrical parameters for these two cations are similar to those obtained by using the more flexible 44-31G basis. This suggests that the relative stabilities

Table I.[a] Calculated Energies and Geometrical Parameters

	Cl^+	ClF	$(ClClF)^+$	$(ClFCl)^+$
E hartrees	−458.4456	−558.2143	−1016.7358 (−1006.7120)	−1016.7509 (−1006.6999)
R_{Cl-F}, Å		1.72	1.704 (1.71)	1.80 (1.73)
R_{Cl-Cl}, Å			2.270 (2.14)	
bond angle, deg			99 (101)	140 (120)
stabilization,[b] kcal/mol			47.6	57.1

	$(HClF)^+$	$(ClFH)^+$
E, hartrees	−558.3600	−558.4174
R_{Cl-F}, Å	1.708	1.867
bond angle, deg	96	129
R_{HX}, Å[c]	1.337	0.955
stabilization, kcal/mol	91.4	127.4

[a] Results presented in this and the next table were obtained using a 44-31G basis set.[4a] Values given in parentheses were obtained by using a STO-3G basis set.[4b] [b] The stabilization energy is given with respect to the energies of isolated Cl^+ and ClF reported in this table. Stabilization = −(energy of the complex − energy of reactants). [c] X represents the atom nearest to the H atom.

Table II. Energy Decomposition Analysis[a]

	$(ClFCl)^+$	$(ClClF)^+$	$(ClFH)^+$	$(FClH)^+$
DEF	2.2	0.05	6.3	0.02
INT	−59.2	−47.7	−133.7	−91.5
ES	−39.0	−30.9	−1.4	34.0
CT	−39.9	−31.6	−61.6	−104.2
PL	−33.3	−18.0	−70.4	−18.0
EX	57.0	108.4	0	0
MIX	−4.1	−75.6	−0.3	−3.3

[a] All energies are in kcal/mol.

of molecules obtained by using the STO-3G basis set should be interpreted with caution.

Our optimized results for ClF agree well with those reported by other workers using comparable size basis sets.[6a,7] For $(HClF)^+$ and $(ClFH)^+$ we find that the latter ion is more stable than the former one by about 36 kcal/mol. These results are in good agreement with the partially optimized results of Kollman and Rothenberg.[8] The Cl–F distances in these ions are close to those in $(ClClF)^+$ and $(ClFCl)^+$. The optimum bond angles in $(HClF)^+$ and $(ClClF)^+$ are very close to one another, and the optimum bond angles in $(ClFH)^+$ and $(ClFCl)^+$ differ by about 11°. The H–Cl distance in $(HClF)^+$ is slightly larger (by about 3%) than that in the neutral HCl molecule,[6a] and the H–F distance in $(HFCl)^+$ is also larger (by about 4%) than that in the neutral HF molecule.[6b] Finally, as expected, the H–Cl distance in $(HClF)^+$ is larger than the H–F distance in $(HFCl)^+$. These variations in geometries of $(ClFCl)^+$ and $(ClFH)^+$ on the one hand, and $(ClClF)^+$ and $(HClF)^+$ on the other, can be rationalized if one recalls that H^+ is very small compared to Cl^+ and that F is more electronegative than Cl.

It has been argued that no species in which fluorine behaves as the central atom except when forced (e.g., in HF_2^+, H_2F^+) are stable.[9] Our calculations, at the 44-31G basis-set level, give results which contradict such arguments. Our results show that the ions $(HFCl)^+$ and $(ClFCl)^+$ are more stable than the corresponding ions $(HClF)^+$ and $(ClClF)^+$, respectively, i.e., the most electronegative atom occupies the central position.

III. Energy Decomposition Analysis (EDA)

In order to understand the nature of interaction between Cl^+ and ClF, and between H^+ and ClF, we have carried out an analysis of the interaction energy, using the scheme developed by Morokuma et al.,[10-12] for $(ClFCl)^+$, $(ClClF)^+$, $(ClFH)^+$, and $(HClF)^+$. In this scheme the total stabilization energy is first divided into two parts: (1) the intramolecular deformation energy of the monomers, DEF, and (2) the intermolecular interaction energy of the deformed monomers to form the complex, INT. The INT is further subdivided into various chemically meaningful components: electrostatic (ES), charge-transfer (CT), exchange (EX), polarization (PL), and the coupling term (MIX). The results of our EDA for the above-mentioned four cations are summarized in Table II.

The interaction of Cl^+ and $Cl^{\delta+}$–$F^{\delta-}$ to form $(ClFCl)^+$ should have attractive ES (negative), CT, and PL. The EX is expected to be repulsive (positive). Our calculations show that for this cation the ES, CT, and PL terms are all attractive and are about equally important. The large contribution of the CT and PL terms suggest that considerable charge reorganization takes place during the formation of $(ClFCl)^+$. The coupling between various interaction terms is about 7% of INT. The deformation repulsion is also quite small.

The behavior of the interaction energies for the formation of $(ClFH)^+$ from $Cl^{\delta+}$–$F^{\delta-}$ and H^+ interaction is dominated by PL as is expected due to the small size of H^+. The CT is next in importance—contributing about 46% of INT. The large CT and PL interactions essentially neutralize the ES interaction which contributes very little (~1%) to INT. Since H^+ has no electrons for exchange, EX is zero. There is small deformation repulsion (about 5% of INT) and almost zero coupling term in $(ClFH)^+$.

The EDA data for $(HClF)^+$ formed from H^+ and $Cl^{\delta+}$–$F^{\delta-}$ has repulsive ES due to the interaction of H^+ with the positive end of the molecule. There is large CT stabilization, and PL contributes about 20% to the net INT. Here again MIX and DEF are quite small.

For $(ClClF)^+$ our EDA results show that the coupling term contributes about 48% to the stabilization energy with the remaining coming from ES (20%), CT (20%), and PL (12%). The exchange repulsion is also quite large (almost twice that obtained for $(ClFCl)^+$ formation from Cl–F and Cl^+). *Unlike the case of* H^+ + *ClF interaction to form* $(HClF)^+$, *the ES term here is attractive.* These results suggest that the separated molecular states of ClF and Cl^+ must have undergone considerable change, e.g., level crossing, during the formation of $(ClClF)^+$. This means that the normal interpretation of the EDA results in terms of the initial interacting components is

Table III. Expansion Coefficients for the Top Four HOMOs of $(ClFCl)^+$ and $(ClClF)^+$ in Terms of the MOs of ClF and Cl^+ as Determined by Configuration Analysis

MOs of ClF					MOs of Cl^+				
9	10	11	12	13	7	8	9		
0	0.1	0	0.4	−0.6	0	−0.7	0	ψ_{21}	
0	0	−0.1	−0.6	−0.4	0.6		−0.4	ψ_{20}	$(ClFCl)^+$
0.2	0	0.1	−0.6	−0.4	−0.5	0	−0.5	ψ_{19}	
0	0.2	0	−0.4	0.6	0	−0.7	0	ψ_{18}	
0	0	0	0.4	0.4	0	0	−0.9	ψ_{21}	
0	0	−0.2		0	−0.2[a]	0	0.96	ψ_{20}	$(ClClF)^+$
0	0.1	0.1	−0.5	0.6	0.4	0	0.1	ψ_{19}	
0	0	0	0.6	0.6	0	0.5	0	ψ_{18}	

[a] This is the coefficient of MO 6 of Cl^+ in ψ_{20} $(ClClF^+)$.

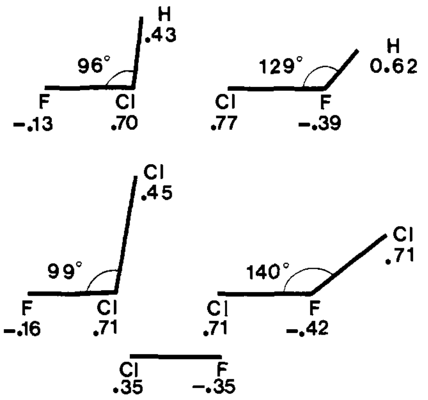

Figure 1. Net electronic charge on atoms calculated using the population analysis technique of Mulliken. The geometries of all molecules in this figure are drawn to scale, and represent the best calculated geometries within the approximation used. (See Table I.)

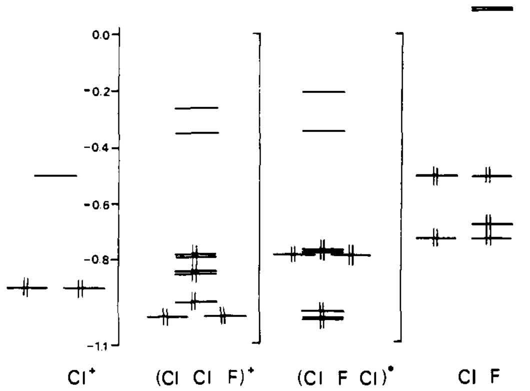

Figure 2. Orbital energies of reactants and products. Only high-lying occupied levels and low-lying unoccupied levels are depicted here. Double vertical lines are used to indicate that a given orbital is doubly occupied. The scale shown is in units of hartree (1 hartree = 27.2107 eV).

not applicable in this case. Further clue to this explanation is provided by the results of configuration analysis discussed in section V.

IV. Mulliken Population Analysis[13]

The behavior of the net electronic charge on atoms in ClF, $(ClFCl)^+$, $(ClClF)^+$, $(ClFH)^+$, and $(HClF)^+$ is shown in Figure 1. In ClF, Cl is the positive end of the molecule. The F atom in $(ClFCl)^+$ and $(ClFH)^+$ is somewhat electron richer than it was in ClF. It also acts like a transmitter of positive charge between the incoming positive ion Cl^+ (or H^+) and the Cl of ClF. The net result is that both $(ClFH)^+$ and $(ClFCl)^+$ have a high degree of polarization resulting in highly polar, hence rather stable, bonds.

In $(ClClF)^+$ and $(HClF)^+$ the positive charge is located on atoms near one end of the molecule. The negative charge on F has decreased by 50% of what it was in ClF. The Cl–F bond in these cations is thus less polar than it is in $(ClFH)^+$ and $(ClFCl)^+$, and should thus be somewhat weaker. Further, the Cl–Cl (or H–Cl) bond should be much weaker because both atoms involving this bond carry a net positive charge.

This qualitative analysis thus suggests that the cations with F in the center should be more stable than the corresponding ions where F is at the end of the molecule.

V. Nature of HOMOs and Configuration Analysis for $(ClFCl)^+$ and $(ClClF)^+$

Let us now take a look at the high-lying MOs of ClF and Cl^+, and the new MOs generated by their interaction during the formation of $(Cl_2F)^+$ (see Figure 2). In ClF the two HOMOs (highest occupied MOs) are degenerate π orbitals ($\epsilon = -0.495$ hartree). The top two MOs of Cl^+ are also degenerate ($\epsilon = -0.898$ hartree). The LUMO (lowest unoccupied MO) of Cl^+ has the same energy as the HOMO of ClF. In addition, the three MOs below the degenerate HOMO pair of ClF have orbital energies quite close to that of the HOMO pair (see Figure 2). The LUMO of ClF has $\epsilon = +0.08$ hartree. All these MOs are expected to mix significantly during the formation of $(Cl_2F)^+$. The changes in the orbital energies of these MOs during the formation of $(Cl_2F)^+$ are also shown in Figure 2. One important point that emerges from this diagram is that all of the five HOMOs of ClF are affected by the interaction with the HOMOs and the LUMO of Cl^+. Thus any conclusion regarding the nature of bonding in $(Cl_2F)^+$ arrived at by considering only the HOMO of ClF would be inadequate.

In order to understand the nature of the mixing of the MOs of Cl^+ and ClF during the formation of $(Cl_2F)^+$ we have carried out a configuration analysis (CA)[14-16] for both molecular cations—$(ClClF)^+$ and $(ClFCl)^+$.[17] The configuration analysis gives two types of information which are of interest to us here. First, it shows how the MOs of the complex are formed from the MOs of the monomers. Second, it tells us the contribution of the ground and various single and double excited states of monomers to the total ground state wave function of the complex when it is expanded in a CI form (in terms of the ground and excited states of the monomers).

In Table III are given the expansion coefficients for the top four HOMOs of $(ClFCl)^+$ and $(ClClF)^+$ in terms of the MOs of ClF and Cl^+ as determined by the configuration analysis. The ψ_{21} and ψ_{18} of $(ClFCl)^+$ are nonbonding MOs formed by coupling of χ_{12} (ClF), χ_{13} (ClF), and χ_8 (Cl^+). The ψ_{20} and ψ_{19} of $(ClFCl)^+$ are bonding MOs formed by coupling of the χ_{12} (ClF), χ_{13} (ClF), χ_7 (Cl^+), and the vacant χ_9 (Cl^+).

The cation $(ClClF)^+$ HOMOs are of markedly different composition than those of the symmetric $(ClFCl)^+$ ion. Here

Table IV. Configuration Coefficients: $(ClFCl)^+$

Ground State: 0.49

Single Excitations

$ClF \rightarrow Cl^+$	$ClF \rightarrow ClF$	$Cl^+ \rightarrow Cl^+$
9 → 9 (0.17)	11 → 14 (−0.15)	7 → 9 (0.55)
11 → 9 (−0.2)		
12 → 9 (0.1)		

Double Excitations

$Cl^+ \rightarrow Cl^+$	$ClF \rightarrow Cl^+$ $Cl^+ \rightarrow Cl^+$	$ClF \rightarrow ClF$ $Cl^+ \rightarrow Cl^+$
7,7 → 9,9 (0.31)	9,7 → 9,9 (0.14) 11,7 → 9,9 (−0.16)	11,7 → 14,9 (0.18)

Table V. Configuration Coefficients: $(ClClF)^+$

Ground State: 0.02

Single Excitations

$ClF \rightarrow Cl^+$	$Cl^+ \rightarrow Cl^+$
13 → 9 (0.06)	7 → 9 (−0.15)
12 → 9 (−0.05)	

Double Excitations

$Cl^+ \rightarrow Cl^+$	$ClF \rightarrow Cl^+$	$ClF \rightarrow Cl^+$ $Cl^+ \rightarrow Cl^+$
7,7 → 9,9 (0.63)	12,13 → 9,9 (−0.13)	12,7 → 9,9 (0.32) 13,7 → 9,9 (−0.36)

MO 21 is again a nonbonding type. The MO 20 is primarily centered on Cl and is weakly bonding, and MO 19 is a bonding orbital. The MO 18 is nonbonding between Cl and F but is bonding between Cl and Cl.

The results of analysis of the total ground state wave function of $(ClFCl)^+$ in terms of a CI-type expansion are shown in Table IV. The small value of the coefficient for the ground-state configuration suggests that the characters of Cl^+ and ClF have undergone considerable change during the formation of $(ClFCl)^+$. This is usually expected to occur in all strong interactions among reactants. The dominant configurations are ones involving single excitation $Cl^+(7) \rightarrow Cl^+(9)$ and the double excitation $Cl^+(7,7) \rightarrow Cl^+(9,9)$. These local excitations account for the large polarization stabilization observed in our EDA results for this ion. Notice that in almost all important configurations the vacant $Cl^+(9)$ MO plays a major role. This is consistent with the fact that this MO makes large contributions to the bonding MOs of $(ClFCl)^+$.

The results of a similar analysis of the total wave function of $(ClClF)^+$ in terms of the wave functions of ClF and Cl^+ are given in Table V. First we note that the coefficient of the ground-state configuration is essentially zero. This implies that the ClF and Cl^+ have lost their initial identity—that is to say, the $(ClClF)^+$ cation *cannot* be thought of as being formed as a result of interaction between ground state of ClF and the singlet-p $Cl^+(p_x{}^2, p_y{}^2, p_z)$. The vacant MO of $Cl^+(9)$ plays a dominant role (as a charge acceptor) in all of the important configurations. This suggests that the most likely dissociation products of $(ClClF)^+$ would be the triplet $Cl^+(p_x{}^2, p_y{}^1, p_z{}^1)$, and the ground state of ClF. The large coefficients of the double excitations involving $Cl^+(9)$ MO support this argument. This means that the energy decomposition analysis of $(ClClF)^+$ that was done with the assumption that this cation is formed by the interaction of the ground states of ClF and singlet-p Cl^+ is not expected to yield reasonable results. This situation has already been recognized earlier.

VI. Conclusions

We have thus shown that the $(ClFCl)^+$ and $(ClClF)^+$ ions have very different geometries as is also found to be true for the $(HFCl)^+$ and $(HClF)^+$ ions. The fluorine-centered ions, $(ClFCl)^+$ and $(ClFH)^+$, are more stable than the corresponding chlorine-centered ions, $(ClClF)^+$ and $(HClF)^+$. Our results thus support the qualitative suggestions of CS regarding the structure of the $(Cl_2F)^+$ cation.[1] We have also shown that the protonation of ClF should occur at the F end as was suggested by the partially optimized results of Kollman and Rothenberg.[8] The EDA results suggest that the charge transfer and polarization are two dominant components responsible for the stability of the F-centered ions: $(ClFCl)^+$ and $(HFCl)^+$.

It should be pointed out that the SCF results presented here, with 44-31G level basis sets, may be improved upon (1) by inclusion of d orbitals in basis sets and (2) by carrying out CI-type calculations. We are currently investigating the possible effects of including d orbitals in our basis sets on the relative stabilities of ions discussed in this paper. There is little experimental data available regarding the ground-state electronic structure of these molecular ions. We have assumed that all molecular species investigated here have closed-shell singlet ground states. It would, however, be desirable to carry out calculations similar to those reported here on the lowest triplet states before the question of the relative stabilities of the ground states of $(ClFCl)^+$ and $(ClClF)^+$ is unambiguously settled.

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