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Energies and Properties of Ions Involved in Electrophilic Halogenations: Singlet and Triplet States of Halogen Cations (X^+, X_3^+, and X_4^{2+}) and Hydrohalonium Ions (HX_2^+ and H_2X^+)

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Abstract: The geometries and relative energies of the singlet and triplet states of halogen cations, X^+ (X = F, Cl, Br), X_3^+ (X = F, Cl), and hydrohalonium ions, H_2X^+ and HX_2^+ (X = F, Cl), were studied with ab initio molecular orbital calculations. The monatomic halogen cations have triplet ground states, but most of the triatomic cations and hydrohalonium ions have singlet ground states. The optimization of the corresponding triplet complexes led to geometries of diatomic radical cations associated loosely with atom. The geometries of X_4^{2+} (X = F, Cl) dications were also examined by ab initio calculations.

Halogen cations, X^+, or various complexes formed by the reaction of Lewis acids with halogen molecules, X_2, are generally believed to be intermediates in a variety of electrophilic reactions. These electrophilic cations may not only attack electron-rich substrates, but may form intermediate complexes with various lone-pair-donor solvents or halogen species. Each of these may differ in physical properties and reactivities. The mechanistic picture is complicated further by the fact that radical cations of halogens may be either singlet or triplet states.[1] Although it is well-known that the ground states of halogen cations are triplets (see below), these ground-state triplets are seldom invoked as intermediates in electrophilic halogenations. However, chemical observations imply that different species are generated under different halogenation conditions.[1b] Little is known about the multiplicities of coordinated species or the physical properties and relative energies of various coordinated halogen species. In order to provide such inside as a background to mechanistic interpretation of electrophilic halogenations,[1] we have undertaken a theoretical study to investigate the electronic states of halogen cations and various coordinated and molecular derivatives.

Computational Methods

Ab initio molecular orbital calculations have been successfully used to reproduce experimental single–triplet gaps of various reactive species.[2] The inclusion of electron correlation corrections is essential for the reliable assessment of singlet–triplet gaps by ab initio quantum mechanical calculations. Spin-projected Moller–Plesset (MP) perturbation calculations give fairly accurate results within a reasonable computational time.[3]

The lowest lying singlet states of halogen cations are even-electron systems for which either spin-restricted (RHF) or spin-unrestricted (UHF) determinantal wavefunctions can be used within the framework of Hartree–Fock theory. Since the HOMO and the LUMO of the ground-state singlet halogen cations are quite close in energy, the spin-restricted wavefunctions are internally unstable with respect to spin-unrestricted wavefunctions. Furthermore, the solution of the RHF equations using real orbitals leads to a total energy higher than that obtained with complex orbitals. With such internally unstable wavefunctions, the energy calculations are unreliable with both the RHF and the Moller–Plesset methods.[4] To insure a lowest total energy within the RHF theory, the MO's must be allowed to become complex, but the RHF wavefunction still does not achieve internal stability relative to the UHF.

The most severe problem of the UHF method, however, is the spin contamination by higher spin states.[4] The UHF wavefunction allows the α and β electrons to occupy different spatial molecular orbitals and is not an eigenfunction of the total spin operator, S^2. The expectation value of the S^2 operator, $\langle S^2 \rangle$, is a measure of the extent of spin contamination. For a pure singlet state, $\langle S^2 \rangle = 0$, while $\langle S^2 \rangle = 2$ for a pure triplet state. The energy of the spin-contaminated wavefunction can be corrected to a good approximation by subtracting out the fraction corresponding to the contamination, assessed from the value of $\langle S^2 \rangle$; this method assumes that there is no higher order spin contamination.[3a] This approach requires only the energies of the contaminated singlet and the pure triplet wavefunctions. This method can also be used for correlated wavefunctions without any further complications. When electron correlation is introduced by the Moller–Plesset many-body perturbation theory,[5] we name this spin corrected method, SCMP*n*, for wavefunctions including electron correlation up to *n*th order.[3a]

Table I. Calculated Singlet–Triplet Gaps (kcal/mol) at Various Level of Theory with the 6-31G* Basis Set for O/F^+ and S/Cl^+ and the STO-3G* Basis Set for Se/Br^+[a]

level	O	F^+	S	Cl^+	Se	Br^+
UHF	23.6 (23.8)	31.2 (30.7)	12.8	15.4	13.8	14.8
SCUHF	47.4 (47.7)	62.5 (64.6)	27.2	32.6	28.2	30.2
SCMP2	49.4 (51.7)	63.2 (66.3)	32.8	39.8	36.9	39.2
SCMP3	44.7 (50.2)	61.8 (64.4)	32.1	38.9		
SCMP4	46.9 (48.6)	60.2 (62.4)	30.9	37.4		
Exptl.	45.4[b]	59.7[c]	26.4[d]	33.3[e]	27.4[f]	33.9[g]

[a] The 6-311G* values are shown in the parentheses. [b] Reference 11. [c] Reference 10. Note this number is ~10 kcal/mol less than that calculated from experimental EAs given in Table III. [d] Reference 13. [e] Reference 12. [f] Reference 14. [g] Reference 15.

UHF wavefunctions are used for the triplet states. The triplet wavefunction involves only negligible amount of spin contamination and can be used as a good approximation of the triplet wavefunction of the pure spin state. The spin-restricted Hartree–Fock calculations on the open shell triplet states of molecular species indicate that the UHF procedure gives similar results in terms of the geometry and the energy when the spin contamination is small.[6]

The UHF singlet of the halogen cation is spin-contaminated by the triplet of lower energy, which causes the UHF energy calculated for the singlet to be lower than that of the pure spin state. Therefore, the calculated singlet–triplet gaps with the UHF method represent lower limits to the true gaps. On the other hand, the RHF calculations of the

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Table II. UHF/6-31G* Geometries (Distances in Å, Angles in Degrees), Total Energies (Hartrees) and Singlet–Triplet Gaps (kcal/mol) of H_3^+, X_3^+, HX_2^+, and H_2X^+ (X = F, Cl)[a]

species	singlet	triplet	E_{S-T} (kcal/mol)
H_3^+	$\mathrm{H\underset{0.844}{-}H\underset{0.844}{-}H}$ (∠HHH = 60°) UHF = −1.27429 au [0] $\langle S^2\rangle = 0.000$	$\mathrm{H\underset{1.183}{-}H\underset{1.585}{-}H}$ (linear) UHF = −1.08778 au [117] $\langle S^2\rangle = 2.000$	−117.0
	$\mathrm{H\underset{0.799}{-}H\underset{0.799}{-}H}$ (linear) UHF = −1.22031 au [34] $\langle S^2\rangle = 0.000$	$\mathrm{H\underset{1.357}{-}H\underset{1.357}{-}H}$ (linear) UHF = −1.08764 au [117] $\langle S^2\rangle = 2.000$	
F_3^+	$\mathrm{F\underset{1.388}{-}F\underset{1.388}{-}F}$ (∠FFF = 108°) UHF = −297.44651 au [37] $\langle S^2\rangle = 0.000$	$\mathrm{F\underset{1.345}{-}F\underset{2.626}{-}F}$ (linear) UHF = −297.47112 au [21] $\langle S^2\rangle = 2.006$	+21.2
	$\mathrm{F\underset{1.682}{-}F\underset{1.682}{-}F}$ (linear) UHF = −297.50490 au [0] $\langle S^2\rangle = 1.422$	$\mathrm{F\underset{1.964}{-}F\underset{1.964}{-}F}$ (linear) UHF = −297.47014 au [22] $\langle S^2\rangle = 2.835$	
Cl_3^+	$\mathrm{Cl\underset{1.998}{-}Cl\underset{1.998}{-}Cl}$ (∠ClClL = 107°) UHF = −1377.95812 au [0] $\langle S^2\rangle = 0.000$	$\mathrm{Cl\underset{1.878}{-}Cl\underset{3.291}{-}Cl}$ (linear) UHF = −1377.95419 au [2] $\langle S^2\rangle = 2.018$	−2.5
	$\mathrm{Cl\underset{2.211}{-}Cl\underset{2.211}{-}Cl}$ (linear) UHF = −1377.89569 au [39] $\langle S^2\rangle = 1.299$	$\mathrm{Cl\underset{2.328}{-}Cl\underset{2.328}{-}Cl}$ (linear) UHF = −1377.93777 au [13] $\langle S^2\rangle = 2.016$	
HF_2^+	$\mathrm{H\underset{0.975}{-}F\underset{1.388}{-}F}$ (∠HFF = 107°) UHF = −198.81903 au [29] $\langle S^2\rangle = 0.000$	$\mathrm{H\underset{0.994}{-}F\underset{2.127}{-}F}$ (∠HFF = 84°) UHF = −198.86477 au [0] $\langle S^2\rangle = 2.010$	+28.7
	$\mathrm{H\underset{0.940}{-}F\underset{1.815}{-}F}$ (linear) UHF = −198.78785 au [48] $\langle S^2\rangle = 0.967$	$\mathrm{H\underset{1.004}{-}F\underset{2.652}{-}F}$ (linear) UHF = −198.85711 au [5] $\langle S^2\rangle = 2.007$	
	$\mathrm{F\underset{1.294}{-}H\underset{1.295}{-}F}$ (∠HFF = 179°) UHF = −198.74183 au [77] $\langle S^2\rangle = 0.949$		
HCl_2^+	$\mathrm{H\underset{1.287}{-}Cl\underset{2.013}{-}Cl}$ (∠HClCl = 101°) UHF = −919.10985 au [0] $\langle S^2\rangle = 0.000$	$\mathrm{H\underset{1.279}{-}Cl\underset{2.645}{-}Cl}$ (∠HClCl = 98°) UHF = −919.10581 au [3] $\langle S^2\rangle = 2.020$	−2.5
	$\mathrm{H\underset{1.293}{-}Cl\underset{3.546}{-}Cl}$ (linear) UHF = −919.08510 au [16] $\langle S^2\rangle = 1.012$	$\mathrm{H\underset{1.269}{-}Cl\underset{3.499}{-}Cl}$ (linear) UHF = −919.08156 au [18] $\langle S^2\rangle = 2.006$	
	$\mathrm{Cl\underset{1.527}{-}H\underset{1.527}{-}Cl}$ (∠HClCl = 85°) UHF = −919.03260 au [48] $\langle S^2\rangle = 0.000$		
H_2F^+	$\mathrm{H\underset{0.962}{-}F\underset{0.962}{-}H}$ (∠HFH = 114°) UHF = −100.19782 au [0] $\langle S^2\rangle = 0.000$	$\mathrm{H\underset{1.006}{-}F\underset{3.343}{-}H}$ (∠HFH = 174°) UHF = −99.98786 au [132] $\langle S^2\rangle = 2.004$	−124.5
	$\mathrm{H\underset{0.965}{-}F\underset{0.965}{-}H}$ (linear) UHF = −100.16834 au [18] $\langle S^2\rangle = 0.000$	$\mathrm{H\underset{1.462}{-}F\underset{1.462}{-}H}$ (linear) UHF = −99.90661 au [183] $\langle S^2\rangle = 2.036$	
	$\mathrm{H\underset{1.029}{-}H\underset{1.136}{-}F}$ (linear) UHF = −99.95664 au [151] $\langle S^2\rangle = 0.616$	$\mathrm{H\underset{1.303}{-}H\underset{1.089}{-}F}$ (linear) UHF = −99.99949 au [125] $\langle S^2\rangle = 2.007$	
H_2Cl^+	$\mathrm{H\underset{1.286}{-}Cl\underset{1.286}{-}H}$ (∠HClH = 97°) UHF = −460.26688 au [0] $\langle S^2\rangle = 0.000$	$\mathrm{H\underset{1.294}{-}Cl\underset{3.399}{-}H}$ (linear) UHF = −460.13248 au [84] $\langle S^2\rangle = 2.007$	−77.5
	$\mathrm{H\underset{1.326}{-}Cl\underset{1.326}{-}H}$ (linear) UHF = −460.16366 au [65] $\langle S^2\rangle = 0.000$	$\mathrm{H\underset{1.570}{-}Cl\underset{1.570}{-}H}$ (linear) UHF = −460.07934 au [118] $\langle S^2\rangle = 2.007$	
	$\mathrm{H\underset{0.827}{-}H\underset{1.411}{-}Cl}$ (linear) UHF = −460.10033 au [105] $\langle S^2\rangle = 0.000$	$\mathrm{H\underset{0.735}{-}H\underset{2.849}{-}Cl}$ (∠HHCl = 83°) UHF = −460.14340 au [78] $\langle S^2\rangle = 2.007$	

[a] Relative energies (kcal/mol) are shown in brackets.

singlet with a complex wavefunction gives a total energy higher than the "true" energy of the singlet, and this should give the upper limit of the singlet–triplet gap. The 6-311G* basis set[7a] and the 6-31G* basis set[7b] have been well tested for fluorine and chlorine atoms, respectively. They are expected to be of comparable quality for the ionic species. Our SCMP*n* calculations have been carried out with the 6-311G* basis set for the fluorine cation and the 6-31G* for the chlorine cation.

Results and Discussion

The energies of the singlet and triplet states of the monatomic halogen cations, F^+, Cl^+, and Br^+, were calculated at various levels of theory. Table I shows the singlet–triplet gaps calculated with the 6-31G* basis set for atomic oxygen, F^+, sulfur, and Cl^+, and the gaps for Se and Br^+ with the STO-3G* basis set. The 6-311G* values for oxygen and F^+ are also given in Table I. The structures of the singlet and triplet triatomic ions, the molecules which result

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Table III. Diatomic Species H_2, X_2, HX, and the Corresponding Radical Cations and X^+ (X = F, Cl) Calculated at UHF/6-31G* Level

species	lengths (Å)[a,b]	energy (au)	$\langle S^2 \rangle$	EA (kcal/mol)[a,c]	PA (kcal/mol)[a,d]
H–H	0.730 (0.742)	−1.126 83	0.000		92.5 (101)
F–F	1.345 (1.412)	−198.677 76	0.000		88.6
Cl–Cl	1.990 (1.988)	−918.912 82	0.000		123.6 (>63)[e]
H–F	0.911 (0.917)	−100.002 91	0.000		122.3 (112)
H–Cl	1.267 (1.275)	−460.059 98	0.000		129.8 (140)
H–H$^{\bullet+}$	1.041 (1.060)	−0.584 08[f]	0.750	340.6[g] (355.1)	
F–F$^{\bullet+}$	1.232 (1.322)	−198.114 19[f]	0.763	353.6 (362.0)	
Cl–Cl$^{\bullet+}$	1.874 (1.891)	−918.502 08	0.763	257.7 (265.0)	
H–F$^{\bullet+}$	1.006 (1.001)	−99.489 60[f]	0.754	322.1 (368.5)	
H–Cl$^{\bullet+}$	1.293 (1.315)	−459.633 97	0.757	267.3 (293.3)	
F^+(singlet)		−98.742 35	1.005	390.7 (459.5)	
F^+(triplet)		−98.792 06	2.004	359.5 (390.1)	
Cl^+(singlet)		−458.990 53	1.017	287.0 (332.3)	
Cl^+(triplet)		−459.015 02	2.006	271.7 (299.1)	

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Table IV. UHF/6-31G* Reaction Energies (kcal/mol)

reaction	singlet	triplet
$F^+ + F_2 \rightarrow$ F–F–F^+	−53.2	−0.8
$F_2^{\bullet+} + F^\bullet$	−37.0	−5.9
$F^+ + H_2 \rightarrow$ F–H–H^+	−54.9	−50.6
H–F–H^+	−206.2	−43.3
$H_2^{\bullet+} + F^\bullet$	−50.1	−18.9
$HF^{\bullet+} + H^\bullet$	−74.5	−43.3
$F^+ + HF \rightarrow$ F–H–F^+	2.2	
F–F–H^+	−46.3	−43.8
$F_2^{\bullet+} + H^\bullet$	83.4	114.6
$HF^{\bullet+} + F^\bullet$	−68.6	−37.4
$Cl^+ + Cl_2 \rightarrow$ Cl–Cl–Cl^+	−34.4	−16.5
$Cl_2^{\bullet+} + Cl^\bullet$	−29.3	−13.9
$Cl^+ + H_2 \rightarrow$ Cl–H–H^+	10.7	−1.0
H–Cl–H^+	−93.8	5.9
$H_2^{\bullet+} + Cl^\bullet$	53.5	68.9
$HCl^{\bullet+} + H^\bullet$	−9.3	6.1
$Cl^+ + HCl \rightarrow$ Cl–H–Cl^+	11.2	
Cl–Cl–H^+	−37.2	−19.3
$Cl_2^{\bullet+} + H^\bullet$	31.5	46.9
$HCl^{\bullet+} + Cl^\bullet$	−19.7	−4.3

from reaction or complexation of F^+ and Cl^+ with H_2, X_2, or HX, were optimized with the 6-31G* basis set and UHF theory. The geometries, energies, and spin contamination of triatomic cations are summarized in Table II. The diatomic species, H_2, F_2, Cl_2, HF, HCl, the corresponding doublet radical cations calculated at the same level of theory, and the monatomic species are shown in Table III. Table IV compares the energy of the complex species with those of the separated molecules. The geometries of tetratomic dications, X_4^{2+} (X = F,Cl) were also optimized with the 6-31G* basis set.

X^+. Fluorine cation is isoelectronic with the oxygen atom. The formation of F^+ and its existence (or absence) as a reactive intermediate in the fluorination of highly electronegative compounds have recently been discussed by Cartwright and Woolf[8] and by Christe.[9] Both experimental and computational studies have been reported for the energy levels of F^+ in the gas phase. The singlet–triplet gap has been measured to be 59.7 kcal/mol.[10] Similarly, the singlet–triplet gap has been found to be 45.4 kcal/mol for atomic oxygen.[11]

The energy levels of Cl^+ have been determined spectroscopically. The singlet–triplet gap is 33.3 kcal/mol for chlorine cation.[12] The experimental singlet–triplet gap has been measured to be 26.4 kcal/mol for the isoelectronic sulfur atom.[13]

As shown in Table I, all species have triplet ground states. At the SCMP4 level, the calculated singlet–triplet gaps are only slightly higher (3–5 kcal/mol) than the experimental results, while the UHF calculations underestimate the singlet–triplet gap significantly. The singlet–triplet gap for Se and Br^+ could be calculated only at the STO-3G* level. For both species the ground state is a triplet. Because of the size of the calculation, we are unable to obtain energies including electron correlation beyond MP2. The STO-3G* basis is less flexible than desirable, but there are few high quality basis sets for the fourth row elements. The experimental singlet–triplet gap for Se has been measured to be 27.4 kcal/mol.[14] The singlet–triplet gap for Br^+ was calculated to be 39.2 kcal/mol at the SCMP2 level, which was 5 kcal/mol higher than the experimental value.[15]

Both singlet and triplet states of halogen cations are highly electron-deficient species. Both can undergo electrophilic reactions, although the triplet might also give radical behavior. Radical reactions are not commonly observed, which might appear surprising in light of the much greater stability of the triplet states. However, the free cations are unlikely to be formed in solution, and complexation alters the relative energy of singlet and triplet states, as described below.

X_3^+. H_3^+ has been previously studied by a variety of methods.[16] The ground state of H_3^+ is a singlet, 117.0 kcal/mol lower in energy than the lowest triplet. The ground-state singlet is triangular, with ∠HHH = 60° and HH = 0.844 Å. By comparison, the H–H bond length of H_2 is 0.730 Å at this level. The linear structure of the singlet is calculated to be 33.9 kcal/mol higher in energy than the D_{3h} structure. The latter is 92.5 kcal/mol more stable than H^+ plus H_2. The $\langle S^2 \rangle$ values are zero for both linear and bent singlet structures.

The lowest triplet state has a linear structure with alternating bond lengths, but the surface is very flat. It is only 0.1 kcal/mol more stable than the linear structure with equal bond lengths, and the optimized triplet structure is only 3.4 kcal/mol more stable

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than $H_2^{\bullet +}$ cation radical plus a hydrogen atom.

UHF optimization of the singlet F_3^+ led to a bent structure with equal bond lengths and $\langle S^2 \rangle$ equal to zero. A linear constrained UHF singlet structure with FF = 1.682 Å was also located. The linear structure was 37 kcal/mol more stable than the bent structure, but the linear structure was heavily spin-contaminated with $\langle S^2 \rangle = 1.422$. RHF optimization of the linear-constrained structure gave a structure (FF = 1.462 Å) which was 46.5 kcal/mol less stable than the bent. Semiempirical CNDO calculations predicted a bent C_{2v} singlet ground state.[17] The UHF results for singlet F_3^+ were surprising, because UHF calculations reproduce the experimentally observed bent structure of the isoelectronic OF_2 molecule. It is likely that F_3^+ is also a bent singlet.

The optimized triplet structure is linear. At the UHF level, the lowest triplet state is 21.2 kcal/mol higher in energy than the linear singlet. This number is unreliable since UHF calculations may overestimate the stability of the linear singlet structure as a result of the heavy spin contamination. The F_3^+ cation can be formed by coupling singlet or triplet F^+ with the F_2 molecule. The heat of reaction for the coupling of the singlet state is 53.2 kcal/mol, while the triplet state is bound by only 0.8 kcal/mol.

Burdett and Marsden have reported calculations of the singlet Cl_3^+ cation which has a bent geometry (ClCl = 2.010 Å, 105.6°).[18] Both IR and Raman spectra of this cation have been reported.[19] Our calculations predicted that the Cl_3^+ cation is a ground-state singlet, but the calculated singlet–triplet gap was only 2.5 kcal/mol. The singlet ground state is bent with a ClCl distance of 1.998 Å. The linear constrained singlet has a slightly longer ClCl bond (ClCl = 2.211 Å). As for F_3^+, spin contamination is observed for the linear singlet ($\langle S^2 \rangle = 1.299$), but not for the bent one. In contrast to the F_3^+, the bent singlet is much more stable than the linear structure. Both the singlet and triplet states of Cl_3^+ are strongly bound relative to Cl^+ and Cl_2, by 34.4 kcal/mol for the singlet state and 16.5 kcal/mol for the triplet state.

HX_2^+. There are two possible bonding arrangements for the HX_2^+, symmetrical, X–H–X^+, and unsymmetrical, H–X–X^+. For the symmetrical arrangement, bond alternation can also take place.

The HF_2^+ cation has been studied by Dekock et al.[20] Our calculations predict that the HF_2^+ cation has a triplet ground state, which is 28.7 kcal/mol lower in energy than the lowest singlet state. Both structures are bent. The geometry of the triplet, although formally protonated F_2, resembles a complex of F^+ with HF, while the singlet state has both HF and FF lengths somewhat longer than in the HF and F_2 molecules. The linear constrained HFF^+ singlet is 19.6 kcal/mol less stable than the bent and has substantial spin contamination. The most stable singlet is less stable than the $HF^{\bullet +}$ radical cation plus F atom. The calculated proton affinity of F_2 is 88.6 kcal/mol, which is in the range of previously calculated values.[20,21] The FHF arrangement is very unfavorable for the singlet cation, which has a nearly linear structure of equal bond lengths with $\langle S \rangle = 0.949$. The triplet ground state of HF_2^+ is 43.8 kcal/mol more stable than HF plus the triplet F^+ and 6.4 kcal/mol more stable than $HF^{\bullet +}$ radical cation plus a fluorine atom. The latter is much more stable than $F_2^{\bullet +}$ radical cation plus a hydrogen atom.

The $ClHCl^+$ cation has been generated in the gas phase. It spontaneously rearranges into protonated Cl_2.[22] The singlet and triplet states of HCl_2^+ cation are predicted to be nearly degenerate. As in the case of HF_2^+, the geometry of singlet HCl_2^+ cation has the HClCl arrangement and is bent with the HCl and ClCl distances both slightly longer than those in the neutral diatomics. The linear constrained singlet is 15.5 kcal/mol less stable. There is no spin contamination for the UHF wavefunctions of the bent singlet, but the $\langle S^2 \rangle$ is 1.012 for the linear one. The unfavorable ClHCl arrangement has a bent structure with equal bond lengths. It is 48.5 kcal/mol higher in energy than the ground-state singlet. The proton affinity of Cl_2 was calculated to be 123.6 kcal/mol.

The lowest triplet state has a linear HClCl arrangement with HCl = 1.279 Å, ClCl = 2.645 Å. It is 15.0 kcal/mol more stable than HCl radical cation plus chlorine atom. The latter is 51.2 kcal/mol more stable than $Cl_2^{\bullet +}$ plus a hydrogen atom. Complexation of the singlet Cl^+ cation with HCl is exothermic by 37.2 kcal/mol, while the triplet state is stabilized by 19.3 kcal/mol by bonding to HCl.

H_2X^+. The H_2F^+ and H_2Cl^+ cations are isoelectronic with H_2O and H_2S, respectively. It is expected that both H_2F^+ and H_2Cl^+ should also have singlet ground states.[23] Our calculations predict that the singlet of H_2F^+ is the ground state. The singlet–triplet gap is calculated to be 124.5 kcal/mol. There is no spin contamination for the UHF wavefunctions of the singlet state. The geometry of the singlet H_2F^+ is very similar to that of H_2O, with ∠HFH = 113.9° and FH = 0.962 Å. Distortion to the linear structure costs 18.5 kcal/mol. Mootz and Bartmann recently reported the crystal structure of H_2F^+ salt, but the positions of hydrogen atoms were not determined due to orientational disorder.[24] The singlet state of H_2F^+ cation is formed by protonation of HF, and the calculated proton affinity of HF is 122.3 kcal/mol. The linear constrained HHF arrangement is even less stable than an unbound proton plus HF. Upon attempted optimization of HHF^+ with the HH distance initially longer than that shown in Table II, the H^+ dissociates from HF.

The H_2F^+ cation has been studied by Kendrick et al. and by Schneider et al. with ab initio MCSCF-CI calculations.[25] They found that the lowest triplet state has a linear unsymmetrical geometry F–H–H^+ (HF = 1.082 Å, HH = 1.352 Å) and that the next triplet state has a linear symmetrical geometry H–F–H^+ (HF = 1.64 Å). These two triplet states differ in energy by 5 kcal/mol. Our calculations show that the lowest triplet state is linear with F at a terminus (H–H–F^+, HF = 1.089 Å and HH = 1.303 Å), in moderate agreement with MCSCF results. However, the HFH arrangement of the triplet has alternating bond lengths (HF = 1.006 Å, FH = 3.343 Å) according to our UHF calculations. It is essentially an HF radical cation plus a hydrogen atom, which is only 7.3 kcal/mol less stable than the complex. The structure with the constrained equal bond lengths is 51.0 kcal/mol higher in energy.

H_2Cl^+ follows the same trend as H_2F^+. The ground state is a singlet which is 77.5 kcal/mol more stable than the triplet. The singlet ground state is H_2S-like with ∠HClH = 97.3° and HCl = 1.286 Å, as compared to experimental values of 94.2° and 1.304 Å.[26] Distortion to the linear structure increases the energy by 64.8 kcal/mol. The bent HHCl structure collapses into the ground-state singlet. The linear constrained HHCl structure is unfavorable, but is still 25.3 kcal/mol more stable than isolated HCl plus a proton. The proton affinity of HCl is calculated to be 129.8 kcal/mol.

The lowest triplet state is bent H–H–Cl^+ (HH = 0.735 Å, HCl = 2.849 Å). This structure is 6.9 kcal/mol more stable than the alternating HCl–H^+ structure, which is virtually the unbound $HCl^{\bullet +}$ radical cation plus a hydrogen atom. The linear HClH structure of equal bond lengths is 40.2 kcal/mol above the lowest triplet.

X_4^{2+}. The $I_2^{\bullet +}$ radical cation has been shown spectroscopically to dimerize to I_4^{2+} in fluorosulphuric acid solution.[27] The crystal

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structures of the dication salts have been reported recently,[28] and theoretical studies of the I_4^{2+} cation have been reported.[29] The X-ray structure reveals that the dication is a cyclic 4-membered ring in the crystal. Since little is known about other dications, such as F_4^{2+} and Cl_2^{2+}, we carried out ab initio calculations for these two species. Optimization of I_4^{2+} exceeds our computational resources even with the minimal STO-3G basis set.

The optimization of F_4^{2+} with the 6-31G* basis set showed that it has an open Z-like geometry. All the fluorine atoms are in the same plane with the FFF angles equal to 110°. The central FF bond is 1.368 Å, which is shorter than the terminal FF bonds (1.572-1.575 Å). This dication was calculated to be 202 kcal/mol less stable than two isolated radical cation $F_2^{\bullet+}$ species.

The optimized geometry of Cl_4^{2+} is nonplanar and has C_2 symmetry, with a ClClClCl torsional angle of 95°. The central ClCl bond length is 2.013 Å and the terminal ones are 2.063 Å. The ClClCl bond angles are 108°. This dication is 135 kcal/mol less stable than two $Cl_2^{\bullet+}$ radical cations. The structures of both F_4^{2+} and Cl_4^{2+} resemble those of the corresponding $[HFFH]^{2+}$ and $[HClClH]^{2+}$ dications.[30]

Conclusion

The monatomic halogen cations have triplet ground states, while most of the triatomic cations and hydrohalonium ions have singlet ground states. These singlet complexes generally have bent geometries with halogen atom at the center. The triplet complexes adopt structures resembling the most stable radical cation of the diatomic species associated to a radical.

These data should be of use for the better understanding of halogenation reactions with halogen cations, since the consequences and complications on mechanisms of the existence of low-lying triplet states has not been considered previously.

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Quenching of the Benzophenone Triplet State by Multifunctional Aromatic Quenchers

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Abstract: Enhanced quenching of the benzophenone triplet state is observed with a series of multifunctional aromatics in acetonitrile and carbon tetrachloride. After accounting for statistical differences, the multifunctional aromatic quenchers show reaction rates 3 to 13 times faster than a monofunctional model. The optimal quenching found with 1,3-diphenylpropane and 1,3,5-triphenylpentane is associated with DDA type exciplexes where the phenyl donor groups assume an excimer-like arrangement in a triple complex with the benzophenone triplet as the acceptor. The proposed mechanism involves initial formation of a DA exciplex, which undergoes conformational interchange to the DDA exciplex in competition with deactivation and dissociation. *p*-Methoxy-substituted analogues show relatively little accelerated quenching because conformation interchange is slow compared to quenching via the initially formed DA exciplex.

The quenching of the n,π* triplet state of benzophenone ($^3B^*$) and other phenyl ketones by benzene (Q) and its substituted analogues is well documented.[1-12] It is generally accepted that transient exciplexes (E) with some degree of charge transfer (CT) character are involved, with $^3B^*$ assuming either the acceptor or donor role ($E = {}^3B^*,Q \leftrightarrow B^-,Q^+$ or ${}^3B^*,Q \leftrightarrow B^+,Q^-$) depending on the redox capabilities of Q.[6,7,9,12] The kinetic scheme[8] for $^3B^*$ (Scheme I) adequately explains these observations.

Scheme I

All first-order radiative and nonradiative decays

$$^3B^* \xrightarrow{k_1} B \tag{I.1}$$

Reversible exciplex formation

$$^3B^* + Q \underset{k_{-e}}{\overset{k_e}{\rightleftharpoons}} E \tag{I.2}$$

Exciplex deactivation

$$E \xrightarrow{k_r} B + Q \tag{I.3}$$

This study explores the quenching capabilities of multifunctional aromatics, such as 1,3-diphenylpropane (**1b**) and 1,3,5-tri-

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