J. Phys. Chem. A **2002,** *106,* 11271−11276

Thermochemistry of Chlorine Fluorides ClF_n, $n = 1-7$, and Their Singly Charged Cations and Anions: A Gaussian-3 and Gaussian-3X Study

Chi-Kin Law, Siu-Hung Chien, and Wai-Kee Li*

Department of Chemistry, The Chinese University of Hong Kong, Shatin, N.T., Hong Kong

Yu-San Cheung[†]

Department of Chemistry, Iowa State University, Ames, Iowa 50011

Received: April 24, 2002; In Final Form: August 22, 2002

The Gaussian-3 (G3) and Gaussian-3X (G3X) models of theory have been used to calculate the thermochemical data for chlorine fluorides ClF_n, $n = 1-7$, as well as for their singly charged cations and anions. The quantities calculated include the heats of formation (ΔH_f) and bond dissociation energies (DEs) of all of the species, as well as the ionization energies (IEs) and electron affinities (EAs) of the neutrals. By comparing the well-established experimental data of ClF and ClF_3 with the G3 and G3X results, it is found that the G3X method yields more accurate ΔH_f values. In addition, the G3 values on the IEs and EAs for ClF and ClF_3 are similar to the corresponding G3X results. On the basis of these findings, the G3X results are used to assess the sometimes conflicting experimental data. The fair to excellent agreement between the known experimental values and the G3X results also lends support to our predictions for the missing experimental thermochemical data of chlorine fluorides and their ions. Furthermore, with the results obtained in this work, a set of self-consistent thermochemical data for ClF_n and their ions is proposed. Finally, the alternating patterns of the ΔH_f, DE, IE, and EA values of the ClF_n and their ions with system size n are rationalized in terms of the electronic configuration around the central Cl atom for the species involved.

Introduction

For many years, attention has been drawn toward the chemistry of hypervalent species, such as ClF_n, SF_6, and PF_5 molecules.[1−3] Hypervalent species are defined as those molecules or ions with a central atom on which the number of valences exceeds that allowed by the traditional theory of Lewis and Langmuir.[4−5]

In addition to the structural and theoretical interests mentioned above, many members of the ClF_n series are reactive species, and they have an extensive history of interesting chemistry.[1] For instance, they are corrosive and oxidizing agents, which have vigorous reactions with both organic and inorganic compounds. To study their reactivities, it is necessary to have a better understanding of their thermochemical properties such as heat of formation (ΔH_f), ionization energy (IE), electron affinity (EA), bond dissociation energy (DE), etc.

There have been many computational studies on the thermochemical properties of chlorine fluorides ClF_n and their singly charged cations and anions at various levels of theory.[6−15] Guest et al.[6] examined the closed shell series from ClF to ClF_5 using the restricted Hartree-Fock (RHF) procedure in 1973. Peterson and Woods studied the geometry of ClF using several different methods and various basis sets.[7] The geometry and thermochemical stability of ClF_3 were investigated by Peterson et al.[8] in 1983 and Scharf et al.[9] in 1985. In 1987, Pershin and Boldyrev determined the structures, vibrational frequencies, and interconversion pathways of a series of netural, anionic, and cationic chlorine fluorides ClF_k ($k = 1-7$).[10] The geometrical structures arrived at in these studies have now been confirmed by experiments.[15−21] In 1992, Jasien et al.[11] studied the thermochemical stabilities of ClF_3, ClF_5, and ClF_7 using the RHF and MP2 methods. Their results suggested that ClF_3 and ClF_5 were likely to be stable species, while ClF_7 was probably unstable.

Ungemach and Schaefer investigated the structure of ClF_2 and ClF_4, as well as their caions and anions, using the RHF method with a double-ζ (DZ) basis set in 1976.[12] Their results confirmed the experimental finding of Mamantov et al.[17] and Morton et al.[18] Additionally, their results also supported the linear structure of ClF_2^-, which was prepared and characterized using infrared spectroscopy by Christe et al.[19,20] Furthermore, Sannigrahi et al.,[13] by estimating the full configuration interaction, predicted the EA of ClF_2 to be 4.76 eV. In 1990, Christe and co-workers[21] characterized ClF_6^- by spectroscopic method.

In 1996, Van Huis et al.[14] studied the structures and energies of the ClF_n, $n = 1-7$, and their anions using density functional theory (DFT). Three different types of prediction for electron affinities were reported. They are the adiabatic electron affinity, the vertical electron affinity, and the vertical detachment energy. And, the first Cl−F DEs for both the netural and the anion were also calculated.

Very recently, Ricca et al.[15] have used the CCSD(T) method and DFT to calculate the ΔH_f values for ClF_n, $n = 1-3$. From this work, they obtained accurate results and concluded that the accuracy of the results is strongly dependent on the basis set quality and that it is crucial to add at least one tight d function to Cl.

Despite the existence of fairly extensive experimental thermochemical data for the ClF_n, ClF_n^+, and ClF_n^- systems, there is a lack of general agreement among these measurements for many of these species. In this work, we will employ high-level

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[†] Current address: Department of Chemistry, The Chinese University of Hong Kong, Shatin, N.T., Hong Kong.

10.1021/jp0210428 CCC: $22.00

calculations to arrive at a set of self-consistent thermochemical data for ClF_n, ClF_n^+, and ClF_n^-, $n = 1-7$. For those quantities for which no experimental data are available, it is hoped that our calculated results will serve as reliable estimates.

The Gaussian-3 (G3)[22] method proposed in 1998 by Pople and co-workers provides an improvement in accuracy and a reduction in computational time when compared with the G2 method.[23] However, the G3 theory still does poorly for some of the larger non-hydrogen systems containing second-row atoms such as the hypervalent SF_6 and PF_5 molecules.[24] In light of this, a modification of the G3 theory, called Gaussian-3X (G3X),[24] has been developed. It is believed that the deficiency in the G3 basis sets is to a significant extent responsible for the large errors obtained for some of the larger non-hydrogen compounds containing second-row atoms. Hence, in the G3 method, the following new features are introduced: (i) B3LYP/6-31G(2df,p) geometry and zero-point vibrational energy (ZPVE) and (ii) addition of a g polarization function to the G3Large basis set for second-row atoms at the Hartree−Fock level. This revised method shows an improvement for the energetics of the non-hydrogen systems over the G3 theory: the G3 mean absolute deviation is 2.11 kcal mol^{-1} (8.8 kJ mol^{-1}) for the 47 non-hydrogen species in the G3/99 test set,[25] while the corresponding deviation for the G3X method is 1.49 kcal mol^{-1} (6.2 kJ mol^{-1}). Previously, we applied both G3 and G3X methods to hypervalent systems $PF_n^+/PF_n/PF_n^-$.[3] It was found that the G3X model was superior to the G3 and, on the basis of the G3X results, a self-consistent set of thermochemical data for these species was obtained. In this work, again the G3 and G3X methods are used to calculate the thermochemical properties, including the ΔH_f, IE, EA, and DE values of chlorine fluoride neutrals, cations, and anions. By comparing the experimental data with the two sets (G3 and G3X) of calculated quantities, an assessment on the relative merits of the two methods can then be made.

Methods of Calculations

All calculations were carried out on DEC 500 au, COMPAQ XP900, and COMPAQ XP1000 workstations, as well as on an SGI Origin 2000 High Performance Server, using the Gaussian 98[26] packages of programs. The computational models employed were the aforementioned G3[23] and G3X[24] levels of theory.

In the G3 model, the structure of a species is optimized at the MP2(Full)/6-31G(d) level. Based on this optimized structure, single-point calculations QCISD(T)/6-31G(d), MP4/6-31G(d), MP4/6-31+G(d), MP4/6-31G(2df,p), and MP2(Full)/G3Large are carried out. Also, this model requires higher level correction (HLC) in the calculation of total electronic energies (E_e). The MP2(Full)/6-31G(d) harmonic vibrational frequencies, scaled by 0.9661,[27] are applied for the ZPVE correction at 0 K ($E_0 = E_e + \text{ZPVE}$).

In the G3X model,[24] all of the structures are optimized at the B3LYP/6-31G(2df,p) level. In the energy calculations, apart from the five single-point calculations in the G3 model, one more single-point calculation, HF/G3XLarge, is required. Comparing the G3XLarge and the G3Large basis sets, there is an additional g polarization function in the former for second-row elements Al−Cl. In other words, there is no g function for Na or Mg. Also, HLC is added to account for the remaining basis set deficiencies. In this work, all optimized structures have been characterized by vibrational frequencies calculated at the B3LYP/6-31G(2df,p) level. A scaling factor[27] of 0.9854 was used for the ZPVE corrections.

The G3/G3X heats of formation at temperature T (ΔH_{fT}) in this work were calculated in the following manner. For molecule AB, its G3/G3X ΔH_{fT} was calculated from the G3/G3X heat of reaction $\Delta H^\circ_{rT}(A+B \rightarrow AB)$ and the respective experimental $\Delta H_{fT}(A)$ and $\Delta H_{fT}(B)$ for elements A and B. In the calculations of ΔH_{rT} for ions, we set the ΔH_{rT} value of a free electron to be zero.

Results and Discussion

The equilibrium structures of ClF_n, ClF_n^+, and ClF_n^-, $n = 1-7$, optimized at the MP2(Full)/6-31G(d) and B3LYP/6-31G(2df,p) levels are shown in Figure 1. The G3 and G3X ΔH_f at 0 and 298 K of the neutrals, cations, and anions are summarized in Tables 1−3, respectively, while the G3 and G3X IEs and EAs are listed in Table 4.

Comparison of the G3 and G3X Methods. Because the experimental data for ClF and ClF_3 in the literature are the most well-established among the chlorine fluorides, the comparison between the calculated and the experimental results for these two molecules are most significant to assess the relative merits of the G3 and G3X methods. The experimental ΔH_{f0} for ClF is -55.6 ± 0.4 [28] kJ mol^{-1}, while the G3 and G3X results are −52.4 and −53.8 kJ mol^{-1}, respectively. For ClF_3, the experimental, G3, and G3X results are -154.7 ± 2.9,[30] −147.0, and −153.1 kJ mol^{-1}, respectively. Hence in both instances, the G3X method gives a better results; this is expected for the non-hydrogen systems.[24] Meanwhile, as shown in Table 4, the G3 and G3X IEs for ClF are exactly the same, 12.67 eV. The experimental IEs for ClF found in the literature range from 12.65 ± 0.01 [31] to 12.66 ± 0.01 [32] eV, and the calculated results are in excellent agreement with the latter. For ClF_3, the G3 IE (12.70 eV) and G3X IE (12.58 eV) are fairly close to each other; and the experimental values range from 12.65 ± 0.05 [32] to 13.00 ± 0.02 [33] eV. On the other hand, the G3 EA (2.31 eV) and G3X EA (2.07 eV) for ClF are not in good agreement with the experimental EAs for ClF found in the literature, 1.50 ± 0.30 [34] eV and 2.86 ± 0.20 [35] eV; it is noted that these two experimental values are not in agreement at all. Apparently, the calculated EA of ClF depends greatly on the computational method adopted. For instance, as shown by Van Huis et al.,[14] for ClF, the calculated EAs range from 1.94 (BLYP/DZP) to 2.96 eV (B3LYP/DZP^{++}). For ClF_3, the EA found in the literature is only a lower bound ($>2.40 \pm 0.10$ [36] eV), and both the G3 EA (3.43 eV) and G3X EA (3.32 eV) are consistent with this value. On the basis of the above findings, we may conclude that the G3X method is more reliable to predict the ΔH_{f0} values of the ClF_n systems. However, both the G3 and G3X methods give similar IEs and EAs for ClF and ClF_3 (as noted earlier, the G3 and G3X EAs for ClF are not very close to each other). These results suggest that the G3 method underestimates the ΔH_{f0} values of the neutral and singly charged species simultaneously, and these errors cancel each other when the IEs and EAs are calculated. In the following discussion, the G3X results will thus be given more emphasis.

Assessments of the Experimental Results. In this part, with the help of the G3X results, we will appraise some widely scattered experimental results for various species to obtain a set of self-consistent thermochemical data for the ClF_n molecules and their ions.

Energetics of ClF, ClF^+, and ClF^-. The two experimental values reported for ΔH_{f0}(ClF) are -55.6 ± 0.4 [28] and -50.2 ± 0.4 [29] kJ mol^{-1}. The former value is closer to the G3X result of −53.8 kJ mol^{-1} and is hence recommended, even though the value of -50.2 ± 0.4 kJ mol^{-1} is well within the error bar of the G3X method. The experimental ΔH_{f0} value for ClF^+ is 1170.0 [29] kJ mol^{-1}, which is in very good agreement with our

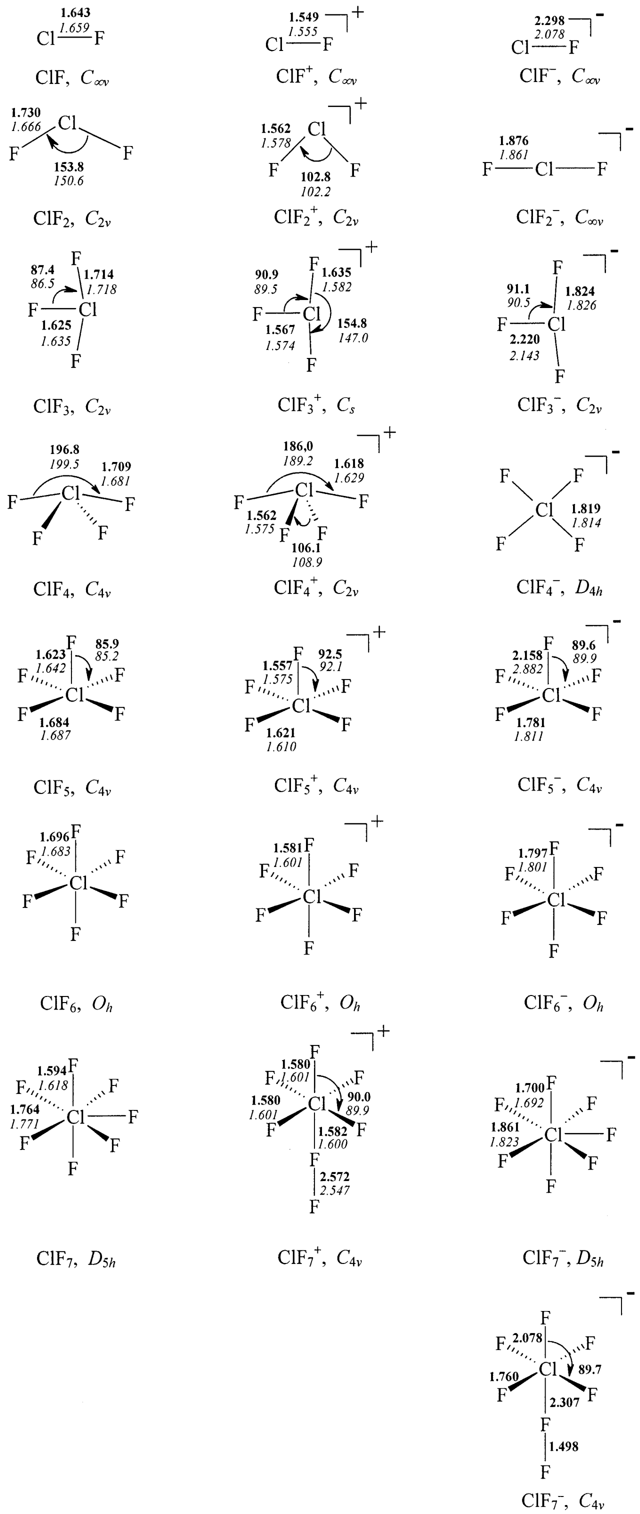

Figure 1. Theoretical equilibrium structures of chlorine fluorides and their singly charged cations and anions optimized at the levels of MP2-(Full)/6-31G(d) (italic font) and B3LYP/6-31G(2df,p) (bold font).

TABLE 1: G3 and G3X Total Energies (E_0), Enthalpies (H_{298}), and Standard Heats of Formation at 0 K (ΔH_{f0}) and 298 K (ΔH_{f298}) of Chlorine Fluorides[a]

species	E_0 (hartree)	H_{298} (hartree)	ΔH_{f0} (kJ mol^{-1})	ΔH_{f298} (kJ mol^{-1})
ClF	*−559.770 16*	*−559.766 77*	*−52.4*	*−52.2*
	−559.774 56	**−559.770 69**	**−53.8**	**−52.3**
			[−55.6 ± 0.4][b]	[−55.7 ± 0.3][b]
			(−50.2 ± 0.4)[c]	(−50.3 ± 0.4)[c]
ClF$_2$	*−659.474 80*	*−659.470 53*	*−28.6*	*−30.3*
	−659.487 34	**−659.482 68**	**−46.3**	**−46.9**
ClF$_3$	*−759.233 58*	*−759.228 33*	*−147.0*	*−150.3*
	−759.243 67	**−759.238 37**	**−153.1**	**−156.3**
			[−154.7 ± 2.9][d]	[−158.9 ± 2.9][d]
			(−159.0)[c]	(−163.0)[c]
			(−160.5)[b]	(−164.6 ± 5.0)[b]
ClF$_4$	*−858.930 72*	*−858.924 88*	*−103.6*	*−109.5*
	−858.946 27	**−858.939 64**	**−118.9**	**−122.8**
ClF$_5$	*−958.682 37*	*−958.675 52*	*−203.2*	*−210.7*
	−958.698 64	**−958.691 68**	**−215.4**	**−222.6**
			[−229.3][b]	[−238.0 ± 7.0][b]
			(−229.8 ± 63.0)[d]	(−238.5 ± 63.0)[d]
ClF$_6$	*−1058.372 41*	*−1058.365 00*	*−141.1*	*−151.4*
	−1058.392 11	**−1058.383 05**	**−157.2**	**−163.1**
ClF$_7$	*−1157.996 80*	*−1157.987 76*	*93.3*	*83.2*
	−1158.017 02	**−1158.008 05**	**81.0**	**70.7**

[a] G3X results are shown in bold font, and G3 results are in italic font. Experimental values are given in parentheses; those given in square brackets are the recommended values. [b] Reference 28. [c] Reference 29. [d] Reference 30.

TABLE 2: G3 and G3X Total Energies (E_0), Enthalpies (H_{298}), and Standard Heats of Formation at 0 K (ΔH_{f0}) and 298 K (ΔH_{f298}) of Chlorine Fluoride Cations[a]

species	E_0 (hartree)	H_{298} (hartree)	ΔH_{f0} (kJ mol^{-1})	ΔH_{f298} (kJ mol^{-1})
ClF$^+$	*−559.304 54*	*−559.301 19*	*1170.1*	*1170.2*
	−559.309 02	**−559.305 19**	**1168.5**	**1169.9**
			(1170.0)[b]	(1170.0)[b]
ClF$_2^+$	*−659.079 08*	*−659.074 79*	*1010.3*	*1008.7*
	−659.087 31	**−659.083 02**	**1004.0**	**1002.4**
ClF$_3^+$	*−758.766 89*	*−758.762 00*	*1078.3*	*1074.0*
	−758.781 34	**−758.776 01**	**1060.7**	**1057.6**
			(1061.0)[b]	(1057.0)[b]
ClF$_4^+$	*−858.522 66*	*−858.516 81*	*967.8*	*961.9*
	−858.537 68	**−858.531 84**	**953.8**	**947.9**
ClF$_5^+$	*−958.208 94*	*−958.202 67*	*1039.8*	*1030.7*
	−958.226 97	**−958.220 14**	**1023.0**	**1015.4**
ClF$_6^+$	*−1057.980 88*	*−1057.973 93*	*886.8*	*875.4*
	−1057.998 83	**−1057.991 98**	**875.4**	**863.7**
ClF$_7^+$	*−1157.668 87*	*−1157.659 40*	*954.3*	*945.3*
	−1157.689 41	**−1157.679 98**	**941.1**	**932.0**

[a] G3X results are shown in bold font, and G3 results are in italic font. Experimental values are given in parentheses; those given in square brackets are the recommended values. [b] Reference 29.

G3X result, 1168.5 kJ mol^{-1}. As shown in Table 4, there are two experimental IEs (12.66 ± 0.01 [32] and 12.65 ± 0.01 [31] eV) for ClF. While both are consistent with the G3X value, 12.67 eV, the one reported by DeDock et al.[32] (12.66 ± 0.01 eV) is in excellent agreement and hence is our recommended value. The experimental ΔH_{f0} value for ClF$^-$ is −200 ± 29 [32] kJ mol^{-1}, which is fairly close to the G3X value, −253.5 kJ mol^{-1}. However, it is stressed that the experimental uncertainty for this quantity is exceedingly large. Therefore, it may be believed that the G3X result gives a more reliable estimate. The two EAs for ClF found in the literature are 1.50 ± 0.30 [34] and 2.86 ± 0.20 [35] eV. While the G3X result is calculated to be 2.07 eV and is in agreement with neither, it falls almost right in the middle of the range spanned by the two experimental values. Clearly, the EA of ClF deserves further examination, both experimentally and computationally.

Energetics of ClF$_2$, ClF$_2^+$, and ClF$_2^-$. There are no experimental data reported for the ΔH_f of ClF$_2$, ClF$_2^+$, and ClF$_2^-$. The G3X ΔH_{f0}(ClF$_2$) and ΔH_{f0}(ClF$_2^+$) are −46.3 and 1004.0 kJ mol^{-1}, respectively. In the literature, there are only two experimental IEs found for the ClF$_2$, which are 12.77 ± 0.05 [35] and 12.80 ± 0.30 [33] eV. Both of them are fairly close to our G3X value, 10.89 eV. Considering the former result has a smaller experimental uncertainty, it is therefore our recommended value. In addition, the G3X ΔH_{f0}(ClF$_2^-$) and EA(ClF$_2$)

TABLE 3: G3 and G3X Total Energies (E_0), Enthalpies (H_{298}), and Standard Heats of Formation at 0 K (ΔH_{f0}) and 298 K (ΔH_{f298}) of Chlorine Fluoride Anions[a]

species	E_0 (hartree)	H_{298} (hartree)	ΔH_{f0} (kJ mol^{-1})	ΔH_{f298} (kJ mol^{-1})
ClF^-	*−559.855 10*	*−559.851 53*	*−275.4*	*−274.7*
	−559.850 63	**−559.846 39**	**−253.5**	**−251.0**
			(−200 ± 29)[b]	
ClF_2^-	*−659.656 39*	*−659.651 78*	*−505.4*	*−506.2*
	−659.663 18	**−659.658 47**	**−507.9**	**−508.5**
ClF_3^-	*−759.359 72*	*−759.353 26*	*−478.2*	*−478.3*
	−759.365 60	**−759.359 29**	**−473.3**	**−473.8**
ClF_4^-	*−859.142 91*	*−859.135 92*	*−660.7*	*−663.6*
	−859.154 04	**−859.146 93**	**−664.4**	**−667.0**
ClF_5^-	*−958.831 98*	*−958.824 18*	*−596.0*	*−601.0*
	−958.847 29	**−958.838 48**	**−605.7**	**−608.0**
ClF_6^-	*−1058.589 36*	*−1058.579 84*	*−710.7*	*−715.4*
	−1058.605 93	**−1058.595 97**	**−718.6**	**−722.1**
ClF_7^-				
D_{5h}	*−1158.196 75*	*−1158.187 65*	*−431.6*	*−441.6*
D_{5h}	**−1158.226 33**	**−1158.215 46**	**−468.6**	**−473.9**
C_{4v}	**−1158.274 03**	**−1158.261 72**	**−593.8**	**−595.3**

[a] G3X results are shown in bold font, and G3 results are in italic font. Experimental values are given in parentheses; those given in square brackets are the recommended values. [b] Reference 32.

TABLE 4: G3 and G3X IEs and EAs of Chlorine Fluorides[a]

species	IE (eV)	EA (eV)
ClF	*12.67*	*2.31*
	12.67	**2.07**
	[12.66 ± 0.01][b]	(1.50 ± 0.30)[f]
	(12.65 ± 0.01)[c]	(2.86 ± 0.20)[d]
ClF_2	*10.77*	*4.94*
	10.89	**4.78**
	[12.77 ± 0.05][d]	(>3.23 ± 0.19)[g]
	(12.80 ± 0.30)[e]	(>0.9 ± 0.2)[d]
ClF_3	*12.70*	*3.43*
	12.58	**3.32**
	(12.65 ± 0.05)[b]	(>2.40 ± 0.10)[g]
	(13.00 ± 0.02)[e]	
ClF_4	*11.10*	*5.77*
	11.12	**5.65**
ClF_5	*12.88*	*4.07*
	12.84	**4.05**
ClF_6	*10.65*	*5.90*
	10.70	**5.82**
ClF_7	*8.92*	*5.44*
	8.91	**5.70**[h]
		6.99[i]

[a] G3X energies are shown in bold font, and G3 energies are in italic font. Experimental values are given in parentheses; those given in square brackets are the recommended values. [b] Reference 32. [c] Reference 31. [d] Reference 35. [e] Reference 33. [f] Reference 34. [g] Reference 36. [h] Using the D_{5h} structure for ClF_7^-. [i] Using the C_{4v} structure for ClF_7^-.

are −507.9 kJ mol^{-1} and 4.78 eV, respectively. While the two experimental EAs for ClF_2 (>3.23 ± 0.19 [36] and >0.9 ± 0.2 [35] eV) are lower bounds and are rather disparate, it is difficult to assess the accuracy of our G3X result. In fact, our result is greater than 3.2 eV and is reasonably close to the Sannigrahi's computational estimate of 4.67 [13] eV. According to this result, it may be claimed that the lower limit given by Dudlin et al. (0.9 ± 0.2 [35] eV) is well below the computational EAs and hence can be considered meaningless.

Energetics of ClF_3, ClF_3^+, and ClF_3^-. As mentioned before, there is a very good agreement between experimental and the G3X results for $\Delta H_{f0}(ClF_3)$ and IE(ClF_3). Therefore, no further discussion is required here. The experimental $\Delta H_{f0}(ClF_3^+)$ value is 1061.0 [29] kJ mol^{-1}, which is in excellent agreement with the G3X value of 1060.7 kJ mol^{-1}. The G3X $\Delta H_{f0}(ClF_3^-)$ and EA(ClF_3) are calculated to be −473.3 kJ mol^{-1} and 3.32 eV, respectively. The experimental EA(ClF_3) reported in the literature is >2.40 ± 0.10 [36] eV. Clearly, the G3X EA for ClF_3 is much greater than the experimental lower bound.

Energetics of ClF_4, ClF_4^+, and ClF_4^-. Experimental thermochemical data are not available for any of these three species. Our calculated G3X results show that $\Delta H_{f0}(ClF_4)$ and $\Delta H_{f0}(ClF_4^+)$ are −118.9 and 953.8 kJ mol^{-1}, respectively. Hence, the G3X IE(ClF_4) is calculated to be 11.12 eV. Meanwhile, the G3X $\Delta H_{f0}(ClF_4^-)$ is calculated to be −664.4 kJ mol^{-1}, while the G3X EA(ClF_4) is 5.65 eV. The excellent agreement between the experimental and G3X values in the previous discussion can support our results, even though there are no experimental data available for ClF_4 and its ions.

Energetics of ClF_5, ClF_5^+, and ClF_5^-. The two experimental values for $\Delta H_{f0}(ClF_5)$ are −229.3 [28] and −229.8 ± 63.0 [30] kJ mol^{-1}; both are in agreement with the G3X result, −215.4 kJ mol^{-1}. But we should note the very large uncertainty of the experimental result. Unfortunately, there are no experimental studies for the ions of ClF_5, as well as for its IE and EA. The G3X $\Delta H_{f0}(ClF_5^+)$ is calculated to be 1023.0 kJ mol^{-1}, while the IE(ClF_5) is 12.84 eV. Meanwhile, the G3X results of $\Delta H_{f0}(ClF_5^-)$ and the EA(ClF_5) are −605.7 kJ mol^{-1} and 4.05 eV, respectively.

Energetics of ClF_6, ClF_6^+, and ClF_6^-. Again there are no experimental thermochemical data for ClF_6, ClF_6^+, and ClF_6^-. The G3X $\Delta H_{f0}(ClF_6)$ and $\Delta H_{f0}(ClF_6^+)$ are calculated to be −157.2 and 875.4 kJ mol^{-1}, respectively. Hence, the G3X IE(ClF_6) is determined to be 10.70 eV. Similarly, at the G3X level, $\Delta H_{f0}(ClF_6^-)$ and EA(ClF_6) are −718.6 kJ mol^{-1} and 5.82 eV, respectively. In addition, the equilibrium structures identified for ClF_6 and its anion (both with O_h symmetry) are in agreement with the finding of Van Huis et al.[14] and Pershin et al.[10] It is noted that the lone pair electrons in ClF_6^- may be deemed as “structurally inert”, in the sense that the structure of ClF_6^- does not deviate from octahedral geometry, as in the cases of $TeCl_6^{2-}$, $TeBr_6^{2-}$, and $SbBr_6^{3-}$.[37] In these species, all with regular octahedral symmetry, the lone electron pair is forced inside the valence shell into a spherical orbital. As a result, the observed bond length would be longer than expected.[37] Take ClF_6^- as an example. The calculated Cl−F bond length in ClF_6^- is about 1.8 Å, which is longer than the sum of the covalent radii of Cl and F, 1.63 [38] Å.

Energetics of ClF_7, ClF_7^+, and ClF_7^-. There are again no experimental thermochemical data available for any of these three species. Our calculated G3X results show that $\Delta H_{f0}(ClF_7)$ and $\Delta H_{f0}(ClF_7^+)$ are 81.0 and 941.1 kJ mol^{-1}, respectively. Hence, the G3X IE(ClF_7) is calculated to be 8.91 eV. On the other hand, at the G3X level, $\Delta H_{f0}(ClF_7^-)$ and EA(ClF_7) are −468.6 kJ mol^{-1} and 5.70 eV, respectively. For ClF_7^-, as shown in Figure 1, two equilibrium structures with D_{5h} and C_{4v} symmetry were identified at the B3LYP/6-31G(2df,p) level (with the latter being more stable), while only one structure with D_{5h} symmetry was identified at the MP2(Full)/6-31G(d) level. In the report of Van Huis et al.,[14] only the structure of C_{4v} symmetry was found in the eight levels of theory they employed. For ClF_7, only a structure with D_{5h} symmetry was identified, in agreement with the finding of Van Huis et al.[14] and Pershin et al.[10] In passing, it is noted that the C_{4v} structure of ClF_7^+ indicates that this cation may be considered as a complex of the form $ClF_6^+ \cdots F$. On the other hand, the C_{4v} structure of ClF_7^- implies that this anion may be considered as a complex of the form $ClF_5^- \cdots F_2$.

Bond Dissociation Energies of ClF_n, ClF_n^+, and ClF_n^-. The G3 and G3X bond DEs of ClF_n, ClF_n^+, and ClF_n^- are

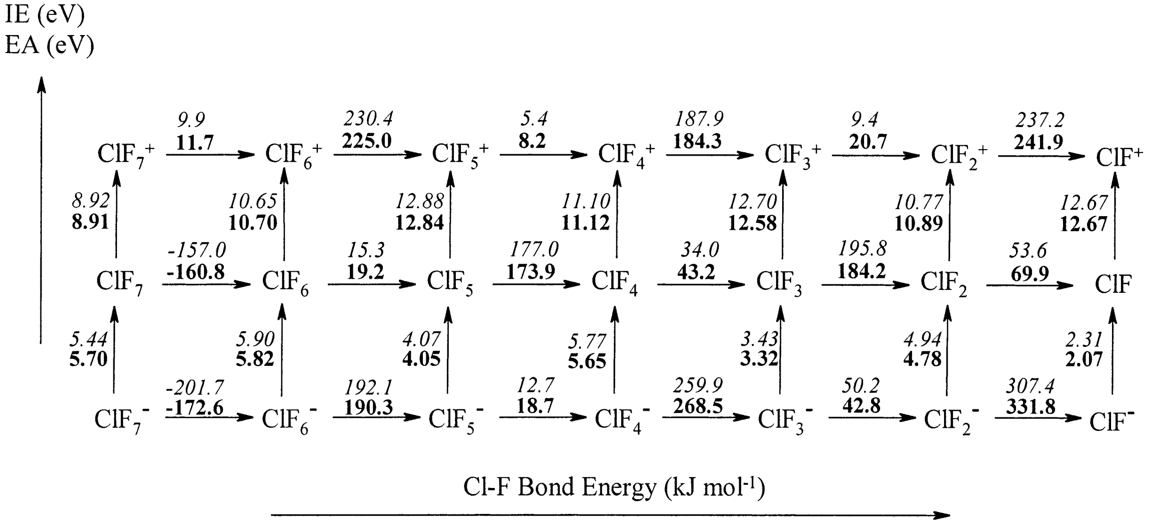

Figure 2. Summary of the G3 and G3X thermochemical data of the chlorine fluorides and their ions, illustrating the alternating patterns of the data. G3X results are shown in bold font, and G3 results are in italic font. Note that the EA of ClF_7 and DE of ClF_7^- are calculated using the D_{5h} structure of ClF_7^-.

TABLE 5: G3X and G3 Bond Dissociation Energies (in kJ mol^{-1}) at 0 K for Chlorine Fluorides and Their Ions[a]

bond	neutral	cation	anion
Cl−F	*249.4*	*270.6*	*124.2*
	250.8	**262.0**	**100.4**
	(252.5 ± 0.06)[b]		
FCl−F	*53.6*	*237.2*	*307.4*
	69.9	**241.9**	**331.8**
F_2Cl−F	*195.8*	*9.4*	*50.2*
	184.2	**20.7**	**42.8**
F_3Cl−F	*34.0*	*187.9*	*259.9*
	43.2	**184.3**	**268.5**
F_4Cl−F	*177.0*	*5.4*	*12.7*
	173.9	**8.2**	**18.7**
F_5Cl−F	*15.3*	*230.4*	*192.1*
	19.2	**225.0**	**190.3**
F_6Cl−F	*−157.0*	*9.9*	*−201.7*
	−160.8	**11.7**	**−172.6**[c]
			−47.4[d]

[a] G3X energies are shown in bold font, and G3 energies are in italic font. Experimental value for Cl−F is given in parentheses. [b] Reference 28. [c] Using the D_{5h} structure for ClF_7^-. [d] Using the C_{4v} structure for ClF_7^-.

summarized in Table 5. Only the experimental DE of Cl−F (252.5 ± 0.06 [28] kJ mol^{-1}) is available in the literature and included in the table for comparison. The G3 DE (249.4 kJ mol^{-1}) and G3X DE (250.8 kJ mol^{-1}) are close to each other, and both are in good agreement with the experiment. It is of interest to note that the value of the DEs of ClF_7 and ClF_7^- are negative. This would indicate that the molecule is thermodynamically unstable with respect to its neutral fragments. Similar finding (for ClF_7) has been reported by Van Huis et al.[14] They suggested that, for ClF_7, the D_{5h} structure is a minimum on the potential energy surface and there is an energy barrier that must be overcome for the molecule to dissociate.[14] Similar rationalization applies for ClF_7^-.

Summary of the Thermochemical Data. The G3X IEs, EAs, and DEs of ClF_n, ClF_n^+, and ClF_n^- are summarized in Figure 2. Examining these results, it is seen that there is an alternating pattern for these three sets of data. Take the DEs as an example. The larger DE values correspond to the Cl−F bond energies (in kJ mol^{-1}) for ClF_2^+ (241.9), ClF_4^+ (184.3), ClF_6^+ (225.0), ClF_3 (184.2), ClF_5 (173.9), ClF_2^- (331.8), ClF_4^- (268.5), and ClF_6^- (190.3). In all of these cases, the dissociation involves the transformation from a more stable species with a larger n value to a less stable species with a smaller n value plus a fluorine atom. Each of the stable species has a closed-shell configuration with even number of valence electrons around the central atom, whereas the unstable species do not. Similarly, a smaller DE corresponds to the transformation from a less stable species with a larger n value to a more stable species with a smaller n value plus a fluorine atom: ClF_3^+ (20.7), ClF_5^+ (8.2), ClF_7^+ (11.7), ClF_2 (69.9), ClF_4 (43.2), ClF_6 (19.2), ClF_3^- (42.8), and ClF_5^- (18.7), where the DEs given in brackets are in kJ mol^{-1}. Referring to the other data summarized in Figure 2, IE is a measure of the transition energy from the neutral to its cation, whereas EA measures the transition from an anion to its corresponding neutral. The processes $ClF \rightarrow ClF^+ + e^-$, $ClF_3 \rightarrow ClF_3^+ + e^-$, and $ClF_5 \rightarrow ClF_5^+ + e^-$ correspond to ionization from a stable neutral to a less stable cation, and thus, the IEs (in eV) of ClF (12.67), ClF_3 (12.58), and ClF_5 (12.84) have large values. The smaller IEs for ClF_2 (10.89), ClF_4 (11.12), and ClF_6 (10.70) are due to ionization from a less stable neutral to a more stable cation. Correspondingly, the electron detachment processes $ClF_2^- \rightarrow ClF_2 + e^-$, $ClF_4^- \rightarrow ClF_4 + e^-$, and $ClF_6^- \rightarrow ClF_6 + e^-$ involve the formation of a less stable species from a more stable one. Therefore, we would expect the EAs (in eV) for ClF_2 (4.78), ClF_4 (5.65), and ClF_6 (5.82) to be larger than those for ClF (2.07), ClF_3 (3.32), and ClF_5 (4.05), which correspond to detachment processes from a less stable anion to a more stable neutral. The alternating patterns for the IEs, EAs, and DEs of chlorine fluorides and their ions discussed here have also been observed for the corresponding data of sulfur fluorides, phosphorus fluorides, and their ions.[2,3]

Conclusion

We have applied the G3 and G3X methods to study the thermochemistry of chlorine fluorides ClF_n, as well as for their singly charged cations and anions. Specifically, we have obtained the ΔH_f values and the DEs of all of the species, and the IEs and EAs of all of the neutrals. When we compare the G3 and G3X ΔH_f results with the experimental data for ClF and ClF_3, it is found that G3X is more reliable method for this type for non-hydrogen systems. For the IEs or EAs of ClF_n, both the G3 and G3X method give similar results and these results are in good agreement with the available literature values. Based on the G3X results, a set of self-consistent experimental thermochemical data for ClF_n, ClF_n^+, and ClF_n^- is recommended. The experimental bond dissociation energies are only available for Cl−F, which is consistent with our G3X result. The fair to excellent agreement between the known experimental values and the G3X results lends support to our predictions for the missing experimental thermochemical data of chlorine fluorides. The general trends of the thermochemical data of the chlorine fluorides and their ions may be rationalized in terms of the electronic configurations of the species involved.

Acknowledgment. The authors are grateful to the Computer Services Centre of The Chinese University of Hong Kong for its allocation of computer time on the SGI Origin 2000 High-Performance Server. The work described in this paper was supported by a grant from the Research Grants Council of the Hong Kong Special Administrative Region (Project No. CUHK4275/00P).

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