

Revisiting the Thermochemistry of Chlorine Fluorides

Hernán R. Sánchez *

In this work, accurate calculations of standard enthalpies of formation of chlorine fluorides (ClF_n , $n = 1-7$; Cl_2F and Cl_3F_2) were performed through the isodesmic reactions scheme. It is argued that, for many chlorine fluorides, the gold standard method of quantum chemistry (CCSD(T)) is not capable to predict enthalpy values nearing chemical accuracy if atomization scheme is used. This is underpinned by a thorough analysis of total atomization energy results and the inspection of

multireference features of these compounds. Other thermodynamic quantities were also calculated at different temperatures. To complement the energetic description, elimination curves were studied through density functional theory as a computationally affordable alternative to highly correlated wave function-based methods. © 2017 Wiley Periodicals, Inc.

DOI: 10.1002/jcc.24838

Introduction

Chlorine fluorides are very reactive species with high potential uses as oxidizers. In these compounds, the chlorine atom has a formal oxidation state ranging from +I to +VII, allowing a wide coordination numbers variety. Most of these species, if not all,^[1,2] show hypervalent character, that is, they do not satisfy the traditional theories of Lewis and Langmuir. Currently there are limited experimental thermochemical data available about these species. Conversely, many theoretical studies have been carried out for years.^[1-11] Accurate prediction of thermochemical properties is crucial for the understanding of the rich chemistry of this class of compounds. Some chlorine fluorides present extreme reactivity, a solid understanding of these compounds is essential when considering the hazards and difficulties involved in their experimental manipulation.

Today, highly accurate molecular calculations are commonly considered almost synonymous of those performed with the so called “gold-standard” method in quantum chemistry, that is, coupled cluster singles and doubles approach^[12,13] with perturbational triples contribution (CCSD(T)),^[14,15] using very large basis sets. This is so because this method reaches energy values within chemical accuracy for most modest sized molecules (see e.g., Ref. [16]) in which the dynamical type correlation dominates. Going beyond this level of theory is neither affordable nor necessary in most cases. A lot of cheaper composite methods to approximate its values have been developed and used widely.

Among the nine molecules studied, experimental values are available for only three of them. This difficult the comparison between different theoretical estimations. In recent works the formation enthalpies of some of the above mentioned compounds have been calculated, using both: CCSD(T) with near complete basis set (CBS) values,^[8,11] and or composite methods.^[6,9,10] In the early work the results for molecules with experimental values show very large errors. Even in the recent works, the error for the largest of them is still too high.^[9-11] This discrepancy at the CCSD(T) level of theory should arise from an important contribution to the energy from the higher

excitations not accounted in the calculations. It should be noted that, when higher excitations contribute significantly to the molecular energy, there are not good error compensation in atomization reactions if the former are neglected. Due to seemingly similar chemical environments, it can be suspected that this behavior take place in other compounds of the series.

The main goal of this contribution is to suggest more reliable values for the formation enthalpies of these species. To that end, unlike previous works, the isodesmic reaction scheme^[17] is employed in pursuit of large systematic error compensation. The results obtained represent a very clear improvement for chlorine pentafluoride. To reinforce the idea that the improvement extends to most compounds of the series, the A_2 and %TAE[T] diagnostics for static correlation were performed because they correlate well with higher excitations.^[18,19] As they suggested severe to pathological multireference character and, multireference effects tends to increase the importance of large excitations,^[19] orbital occupancies of a multiconfigurational treatment were also inspected.

The Cl_2F and Cl_3F_2 were added to the ClF_n ($n = 1-7$) series to include species with Cl–Cl bonds that could arise in some reaction mechanisms involving fluorine chlorides.^[20]

The article is structured as follows: In methods section many methods used in this work for the calculation of enthalpies of formation are described. The the ClF_2 case subsection is devoted to the accurate calculation of the small ClF_2 molecule, which is also useful for use in other isodesmic reactions. In results and discussion section, the results are presented and it is argued that their anomalous discordance suggest the need of avoiding the atomization scheme in conjunction with the

H. R. Sánchez

Departamento de Química (Universidad Nacional de La Plata), Instituto de Física de Líquidos y Sistemas Biológicos (IFLysIB), Universidad Nacional de La Plata – CONICET, Calle 59 no. 789, La Plata, 1900, Argentina E-mail: hernan.sanchez@quimica.unlp.edu.ar

Contract grant sponsor: National Scientific and Technical Research Council (CONICET)

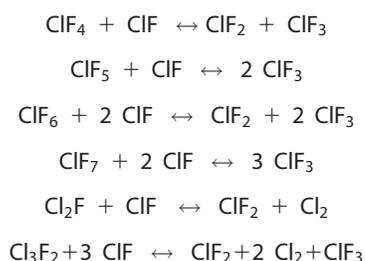
© 2017 Wiley Periodicals, Inc.

composite methods used. In multiconfigurational character subsection, results of standard diagnostics of multiconfigurational character are shown and an inspection of orbital occupancies is performed. The ClF_3 and the very difficult ClF_7 cases are analyzed in the ClF_3 and ClF_7 cases subsection. A summary of the values recommended in this contribution can be found in recommended values subsection, while in comparison with previous results subsection the values of this work are compared with previous results. In standard thermodynamic functions subsection calculated values for standard thermodynamic magnitudes as functions of temperature are presented. The difficulties in retrieving correlation energy of fluoride chlorides give raise to uncommon failures in the description of some potential energy elimination curves, it is briefly depicted in potential energy curves subsection. Finally, in density functional theory calculations subsection many density functionals have been tried as low cost alternatives to post-Hartree-Fock methods for nonequilibrium geometries.

Methods

The most used method for calculating standard enthalpies of formation is based on total atomization energies (TAE), and it is described, for example, in Nicolaides's work.^[21] Within this approach, accurate values for differences of energies are necessary for retrieving accurate enthalpy values. This method does not require further information from other molecules, and the required atomic heat of formation is well known for many chemical elements. One disadvantage is that the error compensation which occurs in the atomization reaction is not good enough to reach chemical accuracy for some reactions, even for the gold standard method. Instead, isodesmic reaction scheme,^[22] when feasible, provides highly improved systematic error compensation, including those related to basis set extension and poor treatment of correlation energy. However, it requires the usage of accurate experimental or calculated data from molecules included in the isodesmic reaction.

The following isodesmic and isogyric reactions were used in this work for the calculation of the enthalpies of formation of the first compound to the left in each reaction



The absence of reactions for ClF , ClF_2 is due to their enthalpies are the most accurately known among these compounds, and will be used to make predictions about the other species. If the atomization scheme is used, the electronic structure methods employed in this work return more disperse values for ClF_5 than for ClF_3 . To clearly illustrate the advantages of the isodesmic approach, as a first instance, the standard enthalpy

of formation of the ClF_5 molecule was calculated by using this approach. In the ClF_3 and ClF_7 cases section, it is argued that a better approach is to estimate the ClF_3 enthalpy by means of the ClF_5 value.

The accepted values of standard enthalpies of formation, at 298.15 K, for the isodesmic procedure are: -13.308 ± 0.014 kcal·mol⁻¹ for ClF .^[23,24] For ClF_2 and ClF_3 they are -9.7 and -39.6 kcal·mol⁻¹, respectively. The later values come from this work and are extensively discussed in the following sections.

It has been noted^[8] that basis set requirements increase going from ClF to ClF_3 , when CCSD(T) is used, and that accurate atomization calculations need at least aug-cc-pV(5 + d)Z^[25] basis sets quality combined with basis sets extrapolation schemes. Heavier species seem to be even more demanding. In this work, it was necessary to use cheaper methods, which at the same time is interesting because they include different empirical corrections, although many of these correction cancels out in the isodesmic cases.

In this work, a variety of composited methods were used: (CBS-QB3,^[26,27] G3MP2B3,^[28] G3B3,^[28] and G4^[29]) for isodesmic reactions scheme. For comparative purposes, the density functional theory (DFT)^[30,31] was also used at this stage, with the widely used M06-2X functional^[32] and Pople's 6-311 + G(3df) basis set.^[33-35]

Formation enthalpy was also calculated for the above methods via total atomization scheme. Experimental atomic values at 0 K, and their thermal corrections to enthalpy were taken from Ref. [36]. Atomic spin-orbit corrections were taken from Ref. [29]. Within this calculation scheme, two bond additivity correction (BAC) procedures, BAC-G3MP2B3^[37] and BAC-G3B3^[37] were included too. They lose many of their advantages in the framework of isodesmic reaction procedures because of term cancellation, which is the reason why they were omitted before.

The ClF_2 case

Since the ClF_2 radical is included in four isodesmic reactions, its formation enthalpy is particularly important here. Due to lack of experimental values, very high level of theory is needed to estimate the value for this radical. Fortunately, this species has few enough valence electrons to be able to perform high level frozen-core calculations on it. W1U^[38] and W1BD^[38] methods were used here and both returned formation enthalpies of -10.8 kcal·mol⁻¹. Ricca^[8] obtained a value of -9.0 kcal·mol⁻¹ for this property.

The following unrestricted calculation procedure was carried out in this work. The partial contributions to total atomization energy are indicated in brackets. The optimized equilibrium geometry was found at the CCSD(T)/aug-cc-pV(Q + d)Z^[25] level of theory. Hartree-Fock's limit energy was approximated by using the exponential two point scheme with X dependent alpha as described for Halkier et al.,^[39] with the aug-cc-pVXZ basis sets (X = 5, 6) (-18.22 kcal·mol⁻¹). Also the Karton-Martin extrapolation scheme^[40] was tried but negligible differences were found for the purpose. The valence correlation energy was calculated at both CCSD(T)/aug-cc-pV(Q + 2df)Z

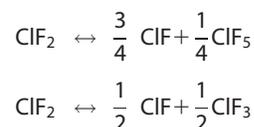
Table 1. Standard formation enthalpies at 298.15 K, in kcal·mol⁻¹, via total atomization energy approach and isodesmic reaction scheme.

Method	ClF	ClF ₂	ClF ₃	ClF ₄	ClF ₅	ClF ₆	ClF ₇	Cl ₂ F	Cl ₃ F ₂
Atomization approach									
M06-2X	-12.6	-6.0	-29.6	-22.1	-44.1	-27.1	33.9	13.4	24.4
G3MP2B3	-11.6	-8.8	-33.2	-24.2	-45.5	-29.3	26.5	13.5	23.9
G3B3	-11.9	-9.3	-34.9	-26.4	-48.7	-34.8	22.1	13.7	22.5
CBS-QB3	-13.6	-12.0	-36.3	-31.1	-49.8	-40.7	20.5	9.6	16.4
G4	-13.4	-12.6	-38.6	-31.8	-54.6	-41.4	16.2	11.8	18.9
BAC-G3MP2B3	-12.6	-11.2	-38.2	-31.7	-56.9	-44.1	8.1	10.3	16.6
BAC-G3B3	-13.4	-11.8	-39.2	-32.2	-56.9	-44.7	10.6	10.7	18.8
Isodesmic reactions approach									
M06-2X				-31.1	-55.3	-43.3	17.4	10.1	16.1
G3MP2B3				-29.8	-56.6	-39.5	10.7	13.6	20.2
G3B3				-30.2	-56.8	-42.0	10.6	12.8	16.4
CBS-QB3				-32.3	-56.6	-45.4	10.2	13.4	18.3
G4				-30.0	-56.6	-40.7	13.0	12.9	19.3

and CCSD(T)/aug-cc-pV(5 + 2df)Z levels of theory, and a complete basis set extrapolation was done following Helgaker's et al. method^[41,42] (95.91 kcal·mol⁻¹). The vibrational zero point energy was taken from the previous W1s calculations (-1.90 kcal·mol⁻¹). Core correlation and relativistic effects were computed as the difference between values from CCSD(T)/aug-cc-pCVTZ-DK^[43] with all electrons correlated plus Douglas-Kroll-Hess second-order scalar relativistic method^[44-47] and the frozen core nonrelativistic one (0.03 kcal·mol⁻¹). Spin-orbit corrections were carried out for atomic energies, and values were taken from Ref. [29] (-1.61 kcal·mol⁻¹). The molecular thermal correction to standard enthalpy of ClF₂ was provided by the W1s calculations (2.93 kcal·mol⁻¹). This procedure gives -8.9 kcal·mol⁻¹ for the standard enthalpy of formation of ClF₂. This value is almost equal to the one reported by Ricca. The big difference between it and those of W1s methods is noticeable being that the authors of those methods reported mean absolute error of 0.30 kcal·mol⁻¹ for them. All the computational calculations above have been carried out with the Gaussian 09 software package.^[48]

The effect of higher excitations was accounted as the energy difference between unrestricted valence-only calculations of CCSDT(2)_Q^[49] and CCSD(T), using the cc-pVDZ^[50,51] basis set. Such small basis set has been found useful for predicting energetic contribution due to high excitations.^[52,53] The CCSDT(2)_Q method is one of the best approximations to the CCSDTQ method.^[54] It includes the exact calculation of the CCSDT part, and a final noniterative T₄ correction based in perturbation theory. For the implementation used, this last step operational cost scales as O(n⁹) (n being a measure of the system size). Calculations were carried out with NWChem 6.1.^[55] The additive correction factor is found to be as large as -1.8 kcal·mol⁻¹. Then, the calculated value for the standard formation enthalpy at 298.15 K of ClF₂ is -10.7 kcal·mol⁻¹. Coincidence with W1s value seems to be fortuitous. Although the Cl₂F has the same number of valence electrons, its basis set is slightly larger, and this prevented the CCSDT(2)_Q calculations to be made.

The heat of formation of ClF₂ was also obtained via the isodesmic reaction approach. The two non isogyric reactions below were used for the purpose.



The heat of formation value used for ClF₅ is -57.2 ± 1.4 kcal·mol⁻¹ and was obtained through meta-analysis, please refer to the ClF₃ and ClF₇ cases section for details. The theoretical reaction enthalpy was computed as the difference between the corresponding heats of formation. For ClF₂ the above value -8.9 kcal·mol⁻¹ was used. The values for the remaining species were taken from Ref. [11]. Naturally, they were computed at a similar level of theory. The standard formation enthalpies at 298.15 K obtained for the first and second reactions above are -9.72 and -9.65 kcal·mol⁻¹.

Results and Discussion

The two values obtained for ClF₂ by using isodesmic reactions differ in a negligible amount and their arithmetic mean is -9.7 kcal·mol⁻¹. This value seems to be more reliable than the one calculated within the atomization energy approach for two reasons. First, because the latter uses the small cc-pVDZ basis set for this compound, which is very demanding in this respect.^[8] Second, because the effect of the experimental uncertainties of ClF₃ and ClF₅ is largely reduced due to their stoichiometric coefficients in the isodesmic reactions. Then, in this work, the final recommended value for the standard enthalpy of formation of ClF₂ is -9.7 kcal·mol⁻¹.

The composite methods used in the present contribution have been applied successfully in the accurate calculation of standard enthalpies of formation through atomization scheme. The mean absolute errors (MAE) in the heat of formation for G3MP2B3, G3B3, and CBS-QB3 are 1.13, 0.93, and 1.08 kcal·mol⁻¹ in the G2/97 test set,^[27,28] respectively. The G4 method presents a MAE of 0.80 kcal·mol⁻¹ for the heats of formation included in the G3/05 test set.^[29] Excluding the hydrogen containing molecules, the G3MP2B3, G3B3, and G4 values increase to 1.99, 1.65, and 1.13 kcal·mol⁻¹.^[28,29] The BAC-G3MP2B3 and BAC-G3B3 methods gave MAEs of 0.96 and

Table 2. Reaction enthalpies at 298.15 K, in kcal·mol⁻¹, for the used isodesmic reactions.

Method	ClF ₄	ClF ₅	ClF ₆	ClF ₇	Cl ₂ F	Cl ₃ F ₂
M06-2X	-4.9	-10.6	-19.0	-109.6	-6.5	-25.5
G3MP2B3	-6.2	-9.3	-22.8	-102.9	-10.0	-29.6
G3B3	-5.8	-9.1	-20.3	-102.8	-9.2	-25.8
CBS-QB3	-3.7	-9.3	-16.9	-102.4	-9.8	-27.7
G4	-6.0	-9.3	-21.6	-105.2	-9.3	-28.7

0.91 kcal·mol⁻¹. All this values correspond to the atomization scheme.

Some of them were used before for chlorine fluorides^[9,10] without good success, at least, for the last members of the series. The corresponding values were calculated and can be found in Table 1. Table 2 contains the calculated reaction enthalpies for the isodesmic reactions.

The fact that the mean of the absolute difference between the heats of formation, obtained with two methods for each molecule, far exceed those expected for the employed methods, implies abnormal behavior of at least one method. This is aggravated because there is a clear correlation between the errors of different methods. For example, in the Supporting Information of Ref. [37] there is a list of heat of formation of 46 compounds for which the BAC-G2 method has deviations higher than 1 kcal·mol⁻¹. For them, the MAE of G3MP2B3 and BAC-G3B3 is 2.4 and 1.9 kcal·mol⁻¹, while the MAE of the difference of errors of the methods is 1.2 kcal·mol⁻¹ with a Pearson's coefficient of 0.84, the largest difference in absolute value found is 4.3 kcal·mol⁻¹. For the molecules studied here the MAE of the difference of errors of the methods is 7.7 kcal·mol⁻¹, while the largest difference in absolute value is 15.9 kcal·mol⁻¹.

As said before, the isodesmic scheme was employed to provide better theoretical estimates. Table 1 contains a summary of the results. At a glance, the difference among the values for each molecule has declined dramatically as it was expected, which implies that large error compensations have taken place. Among the molecules studied within the isodesmic reactions approach, ClF₅ is the only molecule with available experimental values, they are around -57.2 kcal·mol⁻¹ as

discussed in the ClF₃ and ClF₇ cases section. The current best calculation for this molecule was performed at the CCSD(T)/CBS level of theory using atomization scheme, giving -54.5 kcal·mol⁻¹.^[11] It is noteworthy that every value from the current work for ClF₅, obtained through isodesmic reactions approach, exceeds the accuracy of that result.

It is worth examining individual contributions to energy for both, total atomization and isodesmic reactions. It helps to illustrate the robustness in respect of basis set incompleteness. Some members of the ClF_n series were considered for that purpose. The restricted open-shell version of the CCSD(T) method^[15] (ROHF-CCSD(T)) was used. In Table 3, three contributions to their nonrelativistic electronic energy were included. Each of them contains the values computed by using the cc-pV(D + d)Z basis set.^[25] In a second row, the difference between cc-pV(T + d)Z^[25] and cc-pV(D + d)Z results ($\Delta(3\zeta, \text{CBS})$) are listed. The difference between the best considered approximation to CBS and cc-pV(T + d)Z values ($\Delta(3\zeta, \text{CBS})$) can be found in third place.

The Hartree-Fock contributions (SCF) were obtained by using the density fitting algorithm.^[56] The corresponding complete basis set approximations were performed with the Halkier's extrapolation method^[39] ($\alpha=1.94$) using the cc-pV(Q + d)Z and cc-pV(5 + d)Z^[25] basis sets. Auxiliary basis sets used are those from Ref. [56]. The CBS contributions to valence correlation energy were estimated as follows. In the case of CCSD by adding, to the CCSD/cc-pV(T + d)Z component, the correlation energy difference between frozen core resolution of identity MP2 calculations using cc-pV(5 + d)Z and cc-pV(T + d)Z basis sets.^[57,58] Although more accurate extrapolation schemes were proposed,^[59] this one is simple and exceeds what is required here. The perturbative triples were extrapolated using the Helgaker's method. The calculations were carried out using the PSI4 program.^[60]

The isodesmic reaction used for ClF₃ is discussed in the ClF₃ and ClF₇ cases section. For ClF₂ the first proposed reaction was chosen, The use of the second reaction would lead to very similar results. The advantages of the isodesmic reaction approach are clear from the second and thirds rows of each contribution. It can be greater or smaller depending on the

Table 3. Contributions to TAE and isodesmic reaction energy (IRE) in kcal·mol⁻¹.

		ClF ₂		ClF ₃		ClF ₄		ClF ₆		ClF ₇	
		TAE	IRE	TAE	IRE	TAE	IRE	TAE	IRE	TAE	IRE
SCF	cc-pV(D+d)Z	-36.6	-16.7	-39.8	4.9	-85.3	-4.0	-148.0	-22.1	-237.5	-108.4
	$\Delta(2\zeta, 3\zeta)$	14.2	-2.7	25.6	0.1	30.6	-1.0	42.2	-6.8	50.1	-10.3
	$\Delta(3\zeta, \text{CBS})$	6.5	-1.4	11.9	-0.1	14.3	-0.4	19.8	-2.9	23.6	-4.5
CCSD	cc-pV(D+d)Z	73.1	33.3	100.9	-2.5	140.0	2.2	213.7	11.1	250.1	19.7
	$\Delta(2\zeta, 3\zeta)$	3.7	1.5	6.7	0.4	8.3	-0.1	12.6	-0.4	13.7	-2.3
	$\Delta(3\zeta, \text{CBS})$	7.2	-0.1	11.2	0.6	13.8	-0.6	20.0	-1.7	5.8	-2.0
(T)	cc-pV(D+d)Z	7.9	1.3	10.0	-0.3	15.3	0.3	24.1	2.1	28.4	4.2
	$\Delta(2\zeta, 3\zeta)$	3.4	0.3	4.7	0.0	6.6	0.0	9.9	0.3	11.0	0.1
	$\Delta(3\zeta, \text{CBS})$	1.4	0.1	2.0	0.0	2.8	0.0	4.2	0.1	4.6	0.0
CCSD(T)	cc-pV(D+d)Z	44.4	-12.1	71.1	2.1	70.0	-1.5	89.8	-8.9	40.9	-84.4
	$\Delta(2\zeta, 3\zeta)$	21.4	-0.9	37.1	0.5	45.5	-1.0	64.7	-6.9	74.7	-12.6
	$\Delta(3\zeta, \text{CBS})$	15.1	-1.3	25.1	0.5	30.8	-1.0	44.0	-4.5	33.9	-6.5

Please, refer to the main text for details.

molecule and the isodesmic reaction chosen. For example, the total atomization energy increases in $37.1 \text{ kcal}\cdot\text{mol}^{-1}$ going from cc-pV(D + d)Z to cc-pV(T + d)Z basis sets for ClF_3 , but only $0.5 \text{ kcal}\cdot\text{mol}^{-1}$ for its isodesmic reaction, while for ClF_7 the corresponding values are $74.7 \text{ kcal}\cdot\text{mol}^{-1}$ and $-12.6 \text{ kcal}\cdot\text{mol}^{-1}$.

Multiconfigurational character

For practical purposes, the correlation energy is artificially and loosely divided in two contributions, dynamical correlation and static or nondynamical correlation. This distinction is rather arbitrary, physically speaking both arises from Coulomb interactions and from a mathematical perspective both can be obtained with linear combinations of Slater determinants.^[61] However, this distinction can be useful to guide a theoretical treatment.

There are many diagnostic methods to quantify the importance of nondynamical correlation.^[18] In this work the widely used T_1 diagnostic method^[62] was tried, together with the %TAEe[T]^[19] method and the new $A_{25\%}$ [PBE] and $A_{25\%}$ [BLYP]^[18] tests. The DFT calculations were carried out with Orca 2.9.1 software,^[63] with the def2-QZVPP^[64] basis set which assure near CBS values, using B3LYP/def2TZVPP^[64–68] equilibrium geometries. Test results are presented in Table 4

It was suggested that $T_1 > 0.02$ probably indicates multireference behavior.^[62] It is not necessary true for open shell systems.^[69] This test turns to be useless for predicting the multireference character of these species, as values below 0.02 for closed shell species do not imply single reference character.^[70] Conversely, $A_{25\%}$ [BLYP] and $A_{25\%}$ [PBE] tests provide useful results. According to the authors^[18] “ A_k values around or above 1 appear to indicate severe-to-pathological static correlation. Values around 0.5 appear to indicate moderate-to-severe nondynamical correlation. Values near 0.3 appear to indicate moderate nondynamical correlation. Near 0.15: mild. Below about 0.10: correlation is primarily dynamic in character.” According to this and Table 4, the A_λ diagnostic suggests that the molecules would present severe to pathological static correlation.

For the triatomic species ClF_2 and Cl_2F , %TAEe[T]^[19] diagnostic values were calculated with the G09 program using the aug-cc-pV(5 + d)Z basis set, giving 14.5% and 17.3%, respectively. It was necessary to use smaller basis sets for larger compounds, they were calculated by extrapolation using the values from cc-pV(D + d)Z and cc-pV(T + d)Z basis set in conjunction with the Helgaker's extrapolation method. The PSI4 program^[60] was used for that purpose. It was obtained 13.5, 18.3, 15.9, 21.0, 29.9, and 22.2% for ClF_3 , ClF_4 , ClF_5 , ClF_6 , ClF_7 , and Cl_3F_2 , respectively. According to the authors of the test “below 2% indicates systems dominated by dynamical correlation; 2–5% mild nondynamical correlation; 5–10% moderate nondynamical correlation; and in excess of 10% severe nondynamical correlation.”^[19] Therefore, the %TAEe[T] suggests severe nondynamical correlation for the studied compounds.

Unfortunately, anomalous large basis set dependence is found in the value of %TAEe[T] for ClF_7 . The raw cc-pV(D + d)Z

Table 4. Results of nondynamical correlation diagnostics.

	T_1	$A_{25\%}$ [BLYP]	$A_{25\%}$ [PBE]
ClF	0.011	0.62	0.62
ClF ₂	0.043	1.04	1.02
ClF ₃	0.017	0.89	0.88
ClF ₄	0.029	1.10	1.07
ClF ₅	0.017	1.00	0.96
ClF ₆	0.020	1.15	1.10
ClF ₇	0.015	1.56	1.41
Cl ₂ F	0.040	1.01	0.98
Cl ₃ F ₂	0.034	1.17	1.11

and cc-pV(T + d)Z values obtained are 69.3% and 34.0%. This is remarkable, because authors of %TAEe[T] diagnostic found very little basis set dependence in the 140 molecules that they tested. Their double zeta values are generally within 1% of the basis set limit values, and they found that for pathologically multireference cases the deviation may reach up to 2%. Although they used little larger basis sets, these differences must be due to the ClF_7 behavior. The value obtained through extrapolation (29.9%) is assumed to be close to the basis set limit. Taking advantage of the fast convergence of (T) contribution to atomization energy,^[71] by using cc-pV(D,T)Z basis set extrapolation with Helgaker's method^[41] and the energy values reported by Dixon,^[11] a crude estimation of the %TAEe[T] was done, resulting in $\approx 30\%$. This coincidence supports the reliability of the previous value.

Results of the test should not be surprising nor conclusive. The %TAEe[T] test is founded on the approximate linear relationship between %TAEe[T] and the percentage in which superior excitations contribute to the total atomization energies. The results of the %TAEe[T] diagnostic suggest that, for the molecules studied, an uncommon large percentage of the TAE may correspond to the higher excitations. As A_λ is also approximately proportional to %TAEe[T],^[18] its results allows to draw similar conclusions. Both diagnostic are only indirectly connected with static correlation, however, their results are very useful here in that they support the suspicions about similar tendencies on the behavior of species without experimental values.

It is interesting to explore the particular reasons for this behavior because, as said before, it is expected that the importance of higher excitations increase in multireference systems. A more direct approach is to inspect the orbital occupancies of a multiconfigurational self-consistent field calculation. It was done for the four closed shell species. A stability analysis performed with Gaussian 09 did not reveal instabilities. Complete Active Space SCF (CASSCF) calculations^[72–77] were performed employing ORCA using natural orbitals^[78] coming from previous MP2/def2-TZVP^[79,80] calculations. To correlate the entire valence space is prohibitively expensive except for ClF. Smaller spaces were explored, in Figure 1 orbital occupancies were plotted for the active spaces considered. Calculations using other active spaces were performed, they are not qualitatively different for the purpose, so details are omitted to conserve space.

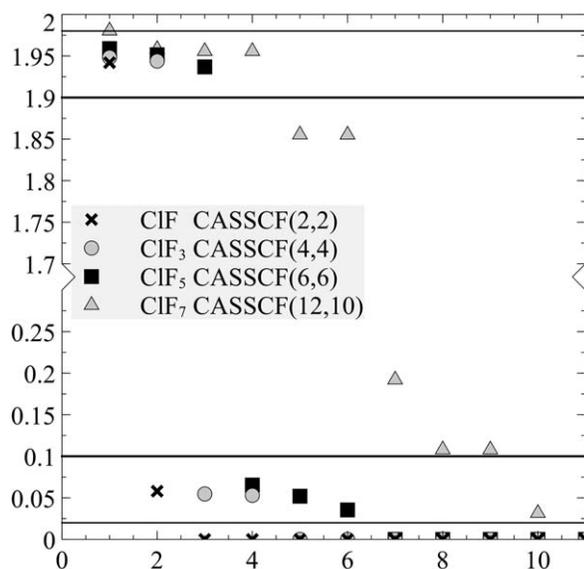


Figure 1. Occupancy of orbital n versus n , starting from $n = 1$ for the first (lowest energy) orbital from the active space.

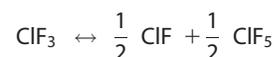
The active spaces were sought trying to avoid the inclusion of orbitals with close to empty (≤ 0.02) or full (≥ 1.98) occupancies. The orbitals of ClF_7 with occupancies between 0.1 and 1.9 indicate that this specie has considerable multiconfigurational character.^[81] The remaining active orbitals can be considered borderline cases.^[82] This suggests that the use of methodologies with good error compensation becomes more important. The methods that add dynamical correlation on top of a multiconfigurational calculation are prohibitively expensive for these cases, in particular if one takes into consideration that the dynamical contribution does not seem to be small.^[4] Because of this, it is convenient to estimate the values using a good single reference method in an error compensating scheme like the ones used in this work.

The ClF_3 and ClF_7 cases

A special situation arises in the case of ClF_7 molecule, where the largest differences between the values of the methods arise to $25.8 \text{ kcal}\cdot\text{mol}^{-1}$ and $7.2 \text{ kcal}\cdot\text{mol}^{-1}$, for the atomization and isodesmic reaction schemes, respectively. BAC procedures, especially BAC-G3B3, showed high accuracy for the three closed shell experimentally characterized species. At first glance, BAC procedures should also be reliable for ClF_7 if there are similar chemical environments for F—Cl bonds in all these molecules. Although Mulliken atomic charges^[83] and Mayer Bond orders^[84] have reasonable similarities in ClF_3 , ClF_5 , and ClF_7 , according to orbital occupancies diagnostic it is not the case. The approximated mean energies per mol of F—Cl bonds of the closed shell series are -13.3 , -13.1 , -11.4 , and $2 \text{ kcal}\cdot\text{mol}^{-1}$ so the good performance BAC methods in principle cannot be extrapolated to ClF_7 .

The error in the heat of formation predicted by using an isodesmic reaction is due to the errors in the calculated heat of reaction and due to the experimental errors. The former can be greatly reduced if good error compensation takes place.

The similarity between the ClF_n ($n = 1,3,5$) suggest that there is a very good error compensation in the isodesmic reaction used for ClF_5 . If such is the case, it is convenient to use this reaction for estimate the formation enthalpy of ClF_3 because the coefficients for experimental values of ClF and ClF_5 are divided by two, decreasing the effect of experimental uncertainty. Notice that the error in the isodesmic reaction energy is divided by the same factor.



By performing the corresponding calculation is seen that all the composite methods differ from each other in less than $0.2 \text{ kcal}\cdot\text{mol}^{-1}$ for the reaction energy. These results motivated the calculation of this reaction energy using the values calculated at CCSD(T)/aug-cc-pV(5+d)Z level of theory reported in Ref. [11], which is more robust and it is expected to bring better error compensation. It gives a value that only differs in $0.1 \text{ kcal}\cdot\text{mol}^{-1}$ from the composite methods used in this work. This coincidence among methods strongly suggests that the reaction energy was obtained very accurately.

The experimental ClF_5 value with lower uncertainty is $-56.9 \pm 1.7 \text{ kcal}\cdot\text{mol}^{-1}$.^[85] This implies that in absence of errors due to the calculation of the reaction energy, the calculated heat of formation of ClF_3 has less uncertainty than the experimental one ($-39.3 \pm 1.2 \text{ kcal}\cdot\text{mol}^{-1}$).^[85]

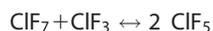
Other experimental values for the ClF_5 molecule are available^[11]: $-59.9 \pm 3.9 \text{ kcal}\cdot\text{mol}^{-1}$, $-57.2 \pm 4.2 \text{ kcal}\cdot\text{mol}^{-1}$, $-56 \pm 4.5 \text{ kcal}\cdot\text{mol}^{-1}$. To choose only one value to be employed in the isodesmic scheme calculation without discarding information, the minimum-variance unbiased estimator of the mean ($\tilde{\theta}$) was taken. It is obtained, under the assumption that the observations are unbiased, by taking a linear combination of the means $\{\theta_i\}$ weighted by the inverse of the associated variances. The estimated variance ($\sigma^2(\tilde{\theta})$) is obtained as the inverse of the sum of the inverse of the variances $\{\sigma_i^2\}$. As the true variances are unknown they were equated to those estimated in the experiments. That is, for the experimental available values $\{(\theta_i, \sigma_i)\}$, the estimations are computed as^[86]

$$\tilde{\theta} = \frac{\sum_i \sigma_i^{-2} \theta_i}{\sum_i \sigma_i^{-2}} \quad \sigma^2(\tilde{\theta}) = \frac{1}{\sum_i \sigma_i^{-2}}$$

This procedure gives $-57.2 \pm 1.4 \text{ kcal}\cdot\text{mol}^{-1}$ for the reference enthalpy of formation of ClF_5 . Then, neglecting the error for the reaction enthalpy, the estimated formation enthalpy at 298.15 K of ClF_3 is $-39.75 \pm 0.7 \text{ kcal}\cdot\text{mol}^{-1}$. As this result is completely independent of the experimental value of this molecule ($-39.3 \pm 1.2 \text{ kcal}\cdot\text{mol}^{-1}$), they may be combined through the procedure above to get the final value of $-39.6 \pm 0.6 \text{ kcal}\cdot\text{mol}^{-1}$.

The use CCSD(T)/aug-cc-pV(5+d)Z in the isodesmic reaction scheme together with the accepted values above gives $16.6 \text{ kcal}\cdot\text{mol}^{-1}$ for the standard reaction enthalpy of ClF_7 at

298.15 K. Another isodesmic and isogyric reaction was also tested to check consistency:



The corresponding value is $17.2 \text{ kcal}\cdot\text{mol}^{-1}$.

Recommended values

Some compounds (ClF_2 , ClF_3 , ClF_5 , and ClF_7) have received a special treatment as discussed above. For the others the best we can do is contemplate the strengths and weaknesses of the methods qualitatively and make a conscious guess. As said before, best estimates must come mostly from isodesmic calculations (or experiments when available), specially from those using G4 model chemistry. Notice, that as the values of the methods are not truly independent of each other, the minimum-variance unbiased estimator of the mean cannot be used for this purpose. Best estimates of this work are summarized in Table 5, corresponding values for homolytic elimination of a fluorine atom were also tabulated when they are available from suggested heat of formation.

Reliability is very case-dependent. The ClF value is very well established both empirically^[23] and theoretically.^[19] It should be expected that the ClF_2 predicted value is to be very accurate, probably with an error significantly lower than about $1 \text{ kcal}\cdot\text{mol}^{-1}$. As these composite methods have not been exhaustively tested on radicals, the values of ClF_4 , ClF_6 , Cl_2F , and Cl_3F_2 should be considered less reliable and errors of about $2 \text{ kcal}\cdot\text{mol}^{-1}$ should not be surprising. For the ClF_5 molecule the estimated uncertainty is about $1 \text{ kcal}\cdot\text{mol}^{-1}$, as the underlying assumptions of the statistical treatment cannot be proved, but it is in good accordance with the experimental value of chlorine trifluoride. The value for ClF_3 gives us more confidence and makes us expect an error lower than about $1 \text{ kcal}\cdot\text{mol}^{-1}$. For the difficult ClF_7 case we must be more conservative and estimate an error range not smaller than $2 \text{ kcal}\cdot\text{mol}^{-1}$.

Comparison with previous results

As far as is known in this work there are only two other works (Refs. [8,11]) that employed equal or higher level of theory on some of the compounds in question. In one of them,^[11] authors concluded that the closed shell compounds here are monodeterminantal cases because the results of the T_1 test, and they estimate error bars of $\pm 1.5 \text{ kcal}\cdot\text{mol}^{-1}$ for their computed heats of formation, calculated via total atomization scheme. In that work, formation enthalpies were calculated with two methods which are very similar to each other. For the one that uses larger basis sets, they got the values $-13.1 \text{ kcal}\cdot\text{mol}^{-1}$, $-38.3 \text{ kcal}\cdot\text{mol}^{-1}$, $-54.5 \text{ kcal}\cdot\text{mol}^{-1}$, and $20.7 \text{ kcal}\cdot\text{mol}^{-1}$, for ClF, ClF_3 , ClF_5 , and ClF_7 , respectively.

Recommended values in the present work have some discrepancies with those mentioned above, especially for the ClF_7 case, for which a value around $17 \text{ kcal}\cdot\text{mol}^{-1}$ is suggested (see Table 5). That is, values differ in almost $4 \text{ kcal}\cdot\text{mol}^{-1}$.

For ClF_3 , the raw value from this work is $-39.75 \pm 0.7 \text{ kcal}\cdot\text{mol}^{-1}$. Again, this is lower than the corresponding result

Table 5. Estimates for values of standard formation enthalpy, and for the enthalpy change for the homolytic elimination of a fluorine/chlorine atom, at 298.15 K in units of $\text{kcal}\cdot\text{mol}^{-1}$.

Molecule	$\Delta_f H(298.15\text{K})$	$\Delta_{dis} H(298.15\text{K})$
ClF	-13.3	61.3
ClF_2	-9.7	15.4
ClF_3	-39.6	48.9
ClF_4	-30.0	9.4
ClF_5	-57.2	46.2
ClF_6	-40.7	2.5
ClF_7	17.0	-38.7
Cl_2F	11.9	6.1/2.8
Cl_3F_2	19.3	-

from Ref. [11]: $-38.3 \text{ kcal}\cdot\text{mol}^{-1}$. It is convenient to sound a note of caution: The experimental value $-38.0 \pm 0.7 \text{ kcal}\cdot\text{mol}^{-1}$ from NIST-JANAF^[87] should not be used for comparisons. This value was criticized by Ricca in favor of the Gurvich's one ($-39.3 \pm 1.2 \text{ kcal}\cdot\text{mol}^{-1}$,^[85]). The latter was then adopted by NIST's "Computational Chemistry Comparison and Benchmark Database."^[88] It is interesting to note that the value $-38.0 \pm 0.7 \text{ kcal}\cdot\text{mol}^{-1}$ was obtained indirectly by using the enthalpy of the thermal decomposition reaction of ClF_3 , giving ClF and F_2 as products, and using a value of $-12.0 \pm 0.1 \text{ kcal}\cdot\text{mol}^{-1}$ ^[87] for the standard enthalpy of formation of ClF. Again, this value was criticized by Ricca in favor of the newer Gurvich's one, that is, $-13.3 \pm 0.1 \text{ kcal}\cdot\text{mol}^{-1}$. The latter coincides with the Active Thermochemical Tables^[23] $-13.308 \pm 0.014 \text{ kcal}\cdot\text{mol}^{-1}$. The highest level calculation performed on the ClF molecule is that by Karton,^[19] which gives an atomization value that, once converted to standard formation enthalpy at 0 K, is at $0.1 \text{ kcal}\cdot\text{mol}^{-1}$ from the experimental value reported in the Ref. [23]. If the newer and more reliable value of ClF molecule is used, the old NIST-JANAF value for ClF_3 will result in coincidence with the Gurvich's value.

If values of this work are compared to those from Ref. [11], there is a clear tendency to get lower values as molecular mass increases. Differences may lie in two factors: in this series of compounds basis set requirements increase with the number of fluorine atoms, as has been claimed before for ClF, ClF_2 , and ClF_3 ^[8] and shown in Table 3; and the error of their result seems to increase with the number of Cl—F bonds.

Large differences as in the ClF_7 are reasonable for multireference cases. We can see it by Figure 2 where the contribution (in percentages) of excitations higher than (T) to the atomization energy is plotted versus the corresponding contribution of perturbative triples excitations, for the results published in Ref. [19]. The atomization energy for this molecule is around $150\text{--}160 \text{ kcal}\cdot\text{mol}^{-1}$, and its %TAEe[T] $\approx 30\%$, so employing Figure 2 an error of about $4 \text{ kcal}\cdot\text{mol}^{-1}$ for the CCSD(T) method is fairly plausible. This issue was discussed in detail in a recent review by Karton,^[89] who pointed out that for molecules with %TAEe[T] $\geq 10\%$, the magnitude of the post-CCSD(T) contribution can exceed the $3.0 \text{ kcal}\cdot\text{mol}^{-1}$. We must bear in mind that the latter number was obtained for a subset of relatively small molecules, on which very high level of theory calculations were performed.

The before mentioned review shows that %TAEe[T] diagnostic can serve as an upper bound for the $T_4 + T_5$ contribution to the TAE. It is very interesting to note that it is possible to have

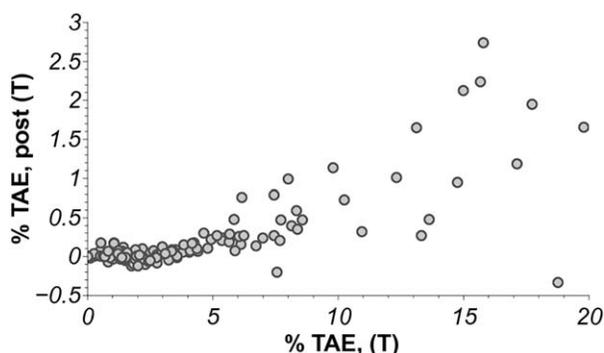


Figure 2. Percentage in which above (T) excitations contributes to the total atomization energy versus the corresponding percentage for (T).

a good idea of the magnitude of the error bounds of the post-(T) excitations to the formation enthalpy when the %TAEe[T] values are not too large. That is to say, for CCSD(T)/CBS calculations when mild static correlation is present (%TAEe[T] < 4%), a good estimate of the error bounds in heats of formation calculated via atomization reactions is given by $\approx 0.3\%$ of the total atomization energy.

With the help of the results published in Ref. [19], it is simple to get the errors of the estimated TAE at 0K for F_2 and Cl_2 at the CCSD(T)/CBS level of theory. By using the corresponding multiplicative factors (due to stoichiometry) they can be added to the formation enthalpies calculated in the Ref. [11], to get the formation enthalpies calculated through the formation reactions. This procedure implies to discard the negligible differences due to errors in thermal corrections and gives $-13.6 \text{ kcal}\cdot\text{mol}^{-1}$, $-39.6 \text{ kcal}\cdot\text{mol}^{-1}$, $-56.5 \text{ kcal}\cdot\text{mol}^{-1}$, and $17.9 \text{ kcal}\cdot\text{mol}^{-1}$ for ClF , ClF_3 , ClF_5 , and ClF_7 , respectively. It can be seen that the values for ClF_3 , ClF_5 , and ClF_7 are now closer to those recommended in the present work. In fact for the ClF_3 molecule the values are exactly the same. The tendency to obtain lower values, in the present work, as the fluorine atoms number increases can still be seen, and it can be argued that this is due to the better error compensations that take place in isodesmic reactions. The ClF value predicted by this procedure is lower than the experimental one in $0.3 \text{ kcal}\cdot\text{mol}^{-1}$, this is expected due to the relatively large contribution to energy of “post (T) excitations” in the difluorine molecule. According to the values reported in Ref. [19] the post (T) contribution to the formation reaction is $0.25 \text{ kcal}\cdot\text{mol}^{-1}$. The comments in the current paragraph support the main hypothesis and the recommended values from the present work.

Standard thermodynamic functions

Standard heat capacities at constant pressure and standard entropies were calculated based on statistical thermodynamics at temperatures between 200 K and 800 K. The B3LYP/6-311 + G(3d2f) level of theory was used for the calculation of rotational and vibrational constants. All usual approximation were used, that is, separation of movements contributions, ideal gas law behavior, replacement of summation over the discrete levels by integration over continuous levels when feasible, neglect of degeneracies of nuclear spins, and so forth. Thermal changes in enthalpy were also computed and reported as the

difference between its value at the temperature T and the one corresponding at 298.15 K. The results are presented in Table 6.

Calculated $S_m^\circ(T)$ and $C_{p,m}^\circ(T)$ values are in reasonable accordance with the experimental ones and with those reported in Ref. 10. The last ones, obtained at HF/6-31G(d) level of theory, were recalculated in this work and some noticeable differences were found for many cases. The new values, at 298.15 K, agree exactly with those reported in the thermo-chemistry analysis provided by the Gaussian 09 software. To analyze the importance of the basis set effect, the calculations were also performed using the larger basis set 6-311 + G(3d2f). Results do not differ significantly from those obtained with 6-31G(d). The detailed values are available in the Supporting Information.

For completeness, to be able to work at any temperature in the range 200–800 K, three well known functions were fitted to interpolate the tabulated results. By abuse of language they all are often referred as “NASA Polynomials” and they are defined by the equations

$$H_m^\circ(T)/(RT) := \sum_{i=1}^5 i^{-1} a_i T^{i-1} + a_6 T^{-1}$$

$$C_{p,m}^\circ(T)/R := \sum_{i=1}^5 b_i T^{i-1}$$

$$S_m^\circ(T)/R := c_1 \ln(T) + \sum_{i=2}^5 c_i T^{i-1} + c_6$$

Table 6. Standard molar entropies ($S_m^\circ(T)$ in $\text{JK}^{-1}\text{mol}^{-1}$) and standard molar heat capacities at constant pressure ($C_{p,m}^\circ(T)$ in $\text{JK}^{-1}\text{mol}^{-1}$), difference between molar standard enthalpy at temperature T and molar standard enthalpy at 298.15 K ($H_m^\circ(T^*)$ in $\text{kJ}\cdot\text{mol}^{-1}$).

Specie	Property	200 K	298.15 K	400 K	500 K	600 K	700 K	800 K
ClF	$H_m^\circ(T^*)$	-3.0	0.0	3.3	6.8	10.3	13.8	17.4
	$C_{p,m}^\circ(T)$	30.1	32.0	33.6	34.6	35.4	35.8	36.2
	$S_m^\circ(T)$	205.4	217.7	227.4	235.0	241.4	246.8	251.7
ClF ₂	$H_m^\circ(T^*)$	-4.7	0.0	5.3	10.7	16.2	21.8	27.5
	$C_{p,m}^\circ(T)$	45.1	50.3	53.2	54.8	55.8	56.4	56.8
	$S_m^\circ(T)$	247.1	266.2	281.4	293.4	303.5	312.2	319.7
ClF ₃	$H_m^\circ(T^*)$	-5.9	0.0	7.0	14.3	21.9	29.7	37.6
	$C_{p,m}^\circ(T)$	54.0	64.8	71.3	74.9	77.2	78.7	79.6
	$S_m^\circ(T)$	265.4	289.2	309.2	325.6	339.5	351.5	362.0
ClF ₄	$H_m^\circ(T^*)$	-7.8	0.0	9.2	18.9	28.9	39.1	49.4
	$C_{p,m}^\circ(T)$	70.9	85.9	94.1	98.6	101.3	103.0	104.1
	$S_m^\circ(T)$	286.7	318.1	344.6	366.1	384.3	400.1	413.9
ClF ₅	$H_m^\circ(T^*)$	-8.7	0.0	10.7	22.2	34.2	46.5	59.1
	$C_{p,m}^\circ(T)$	76.9	98.4	110.8	117.7	122.0	124.7	126.5
	$S_m^\circ(T)$	289.5	324.6	355.5	381.0	402.9	421.9	438.7
ClF ₆	$H_m^\circ(T^*)$	-11.4	0.0	13.5	27.6	42.2	57.1	72.2
	$C_{p,m}^\circ(T)$	103.7	125.5	137.4	144.0	147.9	150.4	152.1
	$S_m^\circ(T)$	319.4	365.4	404.1	435.5	462.1	485.1	505.3
ClF ₇	$H_m^\circ(T^*)$	-11.6	0.0	14.4	30.0	46.4	63.2	80.4
	$C_{p,m}^\circ(T)$	100.9	131.9	150.1	160.3	166.5	170.6	173.3
	$S_m^\circ(T)$	317.9	364.5	406.1	440.8	470.6	496.6	519.5
Cl ₂ F	$H_m^\circ(T^*)$	-5.1	0.0	5.6	11.2	16.8	22.5	28.3
	$C_{p,m}^\circ(T)$	49.5	53.5	55.4	56.3	56.9	57.2	57.4
	$S_m^\circ(T)$	261.1	281.8	297.8	310.3	320.6	329.4	337.0
Cl ₃ F ₂	$H_m^\circ(T^*)$	-8.8	0.0	9.9	20.0	30.4	40.8	51.4
	$C_{p,m}^\circ(T)$	84.1	94.5	99.7	102.4	104.1	105.1	105.8
	$S_m^\circ(T)$	323.5	359.3	387.8	410.4	429.2	445.4	459.4

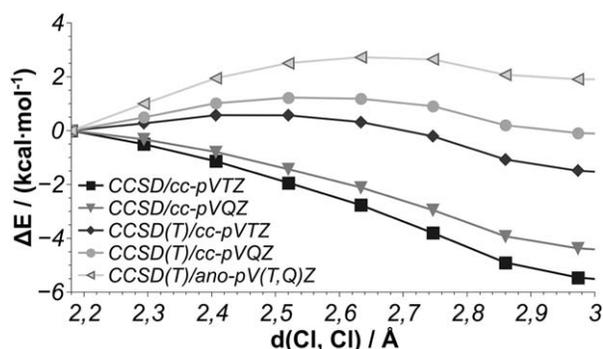


Figure 3. Energy elimination curves of a chlorine atom from Cl_2F for CCSD/cc-pVTZ, CCSD/cc-pVQZ, CCSD(T)/cc-pVTZ, CCSD(T)/cc-pVQZ and CCSD(T)/ano-pV(T,Q)Z^[90] methods. Geometries were optimized at B3LYP/def2-TZVPP level of theory.

The obtained coefficients can be found in the Supporting Information. Note that they are reported mostly due to common practice, and that simpler interpolation schemes should suffice.

Potential energy curves

Correct description of potential energy surfaces (PES) is essential for many chemistry applications, especially for kinetics studies where accurate description of energy curves are usually needed. Some uncommon behaviors were found in the description of the energy elimination curves from chlorine fluorides, throughout the use of mono reference wave function-based methods. It can be illustrated with the peculiar situation that arises around the equilibrium geometry of the Cl_2F radical, in which triples excitations are needed into the coupled clusters framework to do not predict a dissociative geometry. It is shown in Figure 3 where elimination curves at B3LYP/def2-TZVPP geometries are plotted, and negative slope indicate dissociative behavior. Here, coupled cluster calculations were performed using the unrestricted approach.

Density functional theory calculations

Due to the difficulties in retrieving correlation energy in chlorine fluorides, it is not expected that low correlated *ab initio* single reference methods retrieve reliable energy values. BAC procedures performed reasonably well, especially for closed shell cases, but they are parametrized for equilibrium geometries so results are uncertain in other cases. Far from equilibrium geometries, the importance of correlation energy grows. As noted before, very extended basis sets are required when dealing with these species using *ab initio* single reference methods. This is due almost exclusively to correlation part because, as it is well known, the convergence of this part is slower than that of the Hartree–Fock method.^[39] In brief, for predicting reasonable elimination curves using single reference *ab initio* methods, very large basis sets and highly correlated methods are necessary, which is very computationally demanding.

DFT calculations do not suffer this basis sets drawback, and as they present some implicit coverage of multireference effects,^[91,92] it is interesting to test many functionals for these species. Nevertheless, it has been well tested that DFT results for multireference systems are normally poorer than those corresponding to systems with small static correlation.^[19,93]

Atomization energies for the chlorine fluorides were computed in this work, using B3LYP/def2-TZVPP geometries, and more than fifty different functionals with the def2-QZVPP basis set (see the Supporting Information for details). Formation enthalpy was calculated adding the difference between formation enthalpy and atomization electronic energy for the G4 method, to the atomization electronic energy obtained for the functionals.

Results of some of the best performers are listed in Table 7, see the Supporting Information for the complete list and references. The better performance of the M05 functional with the smaller 6–311 + G(3d2f) basis set, can be understood in terms of the similarities between this basis set and the one used for the parametrization of the functional.

Potential energy curves must be carefully analyzed for the functional in question. In this work the energy curves, for the elimination of an atom of fluorine/chlorine from chloride fluorides, were calculated. They include singlet and triplet states for the dissociation of closed shell species.

The functional chosen, belonging to the Minnesota 06 family, was the Truhlar's hybrid M06 functional, because it was the most accurate among of the hybrid functional used here. Double hybrid functionals were deliberately avoided because of its additional complexity, although it can be interesting to test the PWPB95 functional in future works. The omission of ClF_7 molecule is because the homolytic elimination of a fluorine atom is very unfavorable respect of the elimination of a F_2 molecule, so the latter is the natural elimination.

Geometry optimization and the single point calculation were performed with the def2-TZVP basis sets, except for the radicals Cl_2F and Cl_3F_2 for which the def2-SVP basis set was used during the geometry optimization step. The Orca software was chosen to perform the calculations, because its ability to use the chain-of-spheres algorithm^[94] that allows to save considerable computation time. The curves can be found in the Supporting Information. It is seen that the M06 method

Table 7. Mean absolute error (MAE), root mean square error (RMSE), mean signed error (MSE), and largest absolute error (LAE), accepted values are those from Table 5.

	MAE	RMSE	MSE	LAE
B3LYP	4.8	6.0	0.3	11.8
PBE0	4.5	5.5	−3.5	−10.5
PW6B95	4.2	4.9	−2.8	−9.2
RI-B2PLYP	2.9	3.3	0.0	−6.3
M05–2X	3.3	5.2	2.6	13.3
M06	2.8	3.1	−0.8	−4.7
RI-PWPB95	2.1	2.7	−0.4	−5.2
M05 ^[a]	3.2	3.8	−0.1	7.4

Values are in $\text{kcal}\cdot\text{mol}^{-1}$. [a] Geometry optimization and single point energy calculations using the 6–311 + G(3d2f) Pople's basis set.

behave qualitatively correct, so its usage is recommended as a low cost alternative for the matter.

Concluding Remarks

Good estimated values for formation enthalpies calculated via atomization scheme require to go beyond CCSD(T)/CBS for the heaviest members. Using isodesmic reaction scheme provides very high systematic error compensation which can even include noncalculated higher excitations. Based on this approach, new estimates for standard enthalpies of formation were suggested.

Bond additivity corrections work properly for most chlorine fluorides but they are only reliable for equilibrium geometries where they were parametrized. Composite methods which include low correlated *ab initio* calculations should be avoided or used with extreme caution for these cases.

In this work it was found that in rare cases the %TAEe[T] diagnostic may show large basis set dependence, because of this it is encouraged the use of A_k diagnostic method for casual users.

A general method was suggested for the prediction of error bounds on heats of formation calculated via atomization reactions with CCSD(T)/CBS method, for cases with as much as mild multireference character.

For the study of cases where energies corresponding to nonequilibrium geometries are needed, post-Hartree-Fock methods turn to be too expensive. DFT is suggested as a low cost alternative of simple application, through the hybrid M06 functional together with the def2-QZVPP basis sets.

Keywords: chlorine fluorides · static correlation · heats of formation

How to cite this article: H. R. Sánchez. *J. Comput. Chem.* **2017**, DOI: 10.1002/jcc.24838

 Additional Supporting Information may be found in the online version of this article.

- [1] L. Chen, D. Woon, T. Dunning, Jr., *J. Phys. Chem. A* **2009**, *113*, 12645.
- [2] L. Chen, D. E. Woon, T. H. Dunning, Jr., *J. Phys. Chem. A* **2013**, *117*, 4251.
- [3] O. Gropen, E. Wisløff-Nilssen, *Comput. Theory Chem.* **1982**, *88*, 243.
- [4] L. Pettersson, P. Siegbahn, O. Gropen, *Mol. Phys.* **1983**, *48*, 871.
- [5] V. Pershin, A. Boldyrev, *Comput. Theory Chem.* **1987**, *150*, 171.
- [6] P. Jasien, *Chem. Phys. Lett.* **1992**, *188*, 135.
- [7] T. J. Van Huis, J. Morrison Galbraith, H. F. Schaefer, *Mol. Phys.* **1996**, *89*, 607.
- [8] A. Ricca, *Chem. Phys. Lett.* **2000**, *323*, 498.
- [9] C. Law, S. Chien, W. Li, Y. Cheung, *J. Phys. Chem. A* **2002**, *106*, 11271.
- [10] H. Du, Y. Liu, F. Wang, J. Zhang, H. Liu, X. Gong, *Thermochim. Acta* **2011**, *523*, 79.
- [11] K. S. Thanthiriwatte, M. Vasiliu, D. A. Dixon, K. O. Christe, *Inorg. Chem.* **2012**, *51*, 10966.
- [12] R. Bartlett, *Annu. Rev. Phys. Chem.* **1981**, *32*, 359.
- [13] P. Knowles, C. Hampel, H. Werner, *J. Chem. Phys.* **1993**, *99*, 5219.
- [14] K. Raghavachari, G. Trucks, J. Pople, M. Head-Gordon, *Chem. Phys. Lett.* **1989**, *157*, 479.
- [15] J. Watts, J. Gauss, R. Bartlett, *J. Chem. Phys.* **1993**, *98*, 8718.
- [16] J. M. Martin, P. R. Taylor, *J. Chem. Phys.* **1997**, *106*, 8620.
- [17] S. E. Wheeler, *WIREs Comput. Mol. Sci.* **2012**, *2*, 204.
- [18] U. R. Fogueri, S. Kozuch, A. Karton, J. M. Martin, *Theor. Chem. Acc.* **2013**, *132*,
- [19] A. Karton, S. Daon, J. M. Martin, *Chem. Phys. Lett.* **2011**, *510*, 165.
- [20] E. San Román, H. Schumacher, *J. Photochem.* **1982**, *20*, 287.
- [21] A. Nicolaides, A. Rauk, M. N. Glukhovtsev, L. Radom, *J. Phys. Chem.* **1996**, *100*, 17460.
- [22] D. Bakowies, *J. Chem. Phys.* **2009**, *130*, 144113.
- [23] B. Ruscic, *Active thermochemical tables (atct) values based on ver. 1.118 of the thermochemical network*, **2015**. Available at: atct.anl.gov.
- [24] B. Ruscic, R. E. Pinzon, G. Von Laszewski, D. Kodeboyina, A. Burcat, D. Leahy, D. Montoy, A. F. Wagner, *J. Phys. Conf. Ser. (IOP Publishing)* **2005**, *16*, 561.
- [25] T. Dunning, Jr., K. Peterson, A. Wilson, *J. Chem. Phys.* **2001**, *114*, 9244.
- [26] J. Montgomery, Jr., M. Frisch, J. Ochterski, G. Petersson, *J. Chem. Phys.* **1999**, *110*, 2822.
- [27] J. Montgomery, Jr., M. Frisch, J. Ochterski, G. Petersson, *J. Chem. Phys.* **2000**, *112*, 6532.
- [28] A. Baboul, L. Curtiss, P. Redfern, K. Raghavachari, *J. Chem. Phys.* **1999**, *110*, 7650.
- [29] L. Curtiss, P. Redfern, K. Raghavachari, *J. Chem. Phys.* **2007**, *126*, 084108.
- [30] P. Hohenberg, W. Kohn, *Phys. Rev.* **1964**, *136*, B864.
- [31] W. Kohn, L. J. Sham, *Phys. Rev.* **1965**, *140*, A1133.
- [32] Y. Zhao, D. Truhlar, *Theor. Chem. Acc.* **2008**, *120*, 215.
- [33] A. McLean, G. Chandler, *Chem Phys.* **1980**, *72*, 5639.
- [34] T. Clark, J. Chandrasekhar, G. W. Spitznagel, P. V. R. Schleyer, *J. Comput. Chem.* **1983**, *4*, 294.
- [35] M. J. Frisch, J. A. Pople, J. S. Binkley, *J. Chem. Phys.* **1984**, *80*, 3265.
- [36] J. W. Ochterski, *Thermochemistry in Gaussian*; Gaussian, Inc.: Wallingford, CT, **2000**; pp 1–19.
- [37] B. Anantharaman, C. Melius, *J. Phys. Chem. A* **2005**, *109*, 1734.
- [38] E. Barnes, G. Petersson, J. Montgomery, Jr., M. Frisch, J. Martin, *J. Chem. Theory Comput.* **2009**, *5*, 2687.
- [39] A. Halkier, T. Helgaker, P. Jørgensen, W. Klopper, J. Olsen, *Chem. Phys. Lett.* **1999**, *302*, 437.
- [40] A. Karton, J. Martin, *Theor. Chem. Acc.* **2006**, *115*, 330.
- [41] T. Helgaker, W. Klopper, H. Koch, J. Noga, *J. Chem. Phys.* **1997**, *106*, 9639.
- [42] A. Halkier, T. Helgaker, P. Jørgensen, W. Klopper, H. Koch, J. Olsen, A. Wilson, *Chem. Phys. Lett.* **1998**, *286*, 243.
- [43] B. Prascher, D. Woon, K. Peterson, T. Dunning, A. Wilson, *Theor. Chem. Acc.* **2011**, *128*, 69.
- [44] M. Douglas, N. Kroll, *Ann. Phys.* **1974**, *82*, 89.
- [45] B. Hess, *Phys. Rev. A* **1985**, *32*, 756.
- [46] B. Hess, *Phys. Rev. A* **1986**, *33*, 3742.
- [47] G. Jansen, B. Heß, *Phys. Rev. A Gen. Phys.* **1989**, *39*, 6016.
- [48] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, M. J. J. A., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, *Gaussian 09 Revision A.1*; Gaussian Inc.: Wallingford, CT, **2009**.
- [49] S. Hirata, P.-D. Fan, A. A. Auer, M. Nooijen, P. Piecuch, *J. Chem. Phys.* **2004**, *121*, 12197.
- [50] T. H. Dunning, Jr., *J. Chem. Phys.* **1989**, *90*, 1007.
- [51] D. E. Woon, T. H. Dunning, Jr., *J. Chem. Phys.* **1993**, *98*, 1358.
- [52] Y. J. Bomble, J. Vázquez, M. Kállay, C. Michaux, P. G. Szalay, A. G. Császár, J. Gauss, J. F. Stanton, *J. Chem. Phys.* **2006**, *125*, 64108.
- [53] M. E. Harding, J. Vázquez, B. Ruscic, A. K. Wilson, J. Gauss, J. F. Stanton, *J. Chem. Phys.* **2008**, *128*, 114111.
- [54] R. J. Bartlett, M. Musiał, *Rev. Mod. Phys.* **2007**, *79*, 291.

- [55] M. Valiev, E. J. Bylaska, N. Govind, K. Kowalski, T. P. Straatsma, H. J. J. Van Dam, D. Wang, J. Nieplocha, E. Apra, T. L. Windus, W. A. de Jong, *Comput. Phys. Commun.* **2010**, *181*, 1477.
- [56] F. Weigend, *Phys. Chem. Chem. Phys.* **2002**, *4*, 4285.
- [57] F. Weigend, A. Köhn, C. Hättig, *J. Chem. Phys.* **2002**, *116*, 3175.
- [58] C. Hättig, *Phys. Chem. Chem. Phys.* **2005**, *7*, 59.
- [59] P. R. Spackman, A. Karton, *AIP Adv.* **2015**, *5*, 057148.
- [60] J. M. Turney, A. C. Simmonett, R. M. Parrish, E. G. Hohenstein, F. A. Evangelista, J. T. Fermann, B. J. Mintz, L. A. Burns, J. J. Wilke, M. L. Abrams, N. J. Russ, M. L. Leininger, C. L. Janssen, E. T. Seidl, W. D. Allen, H. F. Schaefer, R. A. King, E. F. Valeev, C. D. Sherrill, T. D. Crawford, *WIREs Comput. Mol. Sci.* **2012**, *2*, 556.
- [61] D. P. Tew, W. Klopper, T. Helgaker, *J. Comput. Chem.* **2007**, *28*, 1307.
- [62] T. J. Lee, P. R. Taylor, *Int. J. Quantum Chem.* **1989**, *36*, 199.
- [63] F. Neese, *WIREs Comput. Mol. Sci.* **2012**, *2*, 73.
- [64] F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297.
- [65] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648.
- [66] C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785.
- [67] S. H. Vosko, L. Wilk, M. Nusair, *Can. J. Phys.* **1980**, *58*, 1200.
- [68] P. J. Stephens, F. J. Devlin, C. F. Chabalowski, M. J. Frisch, *J. Phys. Chem.* **1994**, *98*, 11623.
- [69] D. J. Henry, C. J. Parkinson, L. Radom, *J. Phys. Chem. A* **2002**, *106*, 7927.
- [70] W. Jiang, N. J. DeYonker, A. K. Wilson, *J. Chem. Theory Comput.* **2012**, *8*, 460.
- [71] D. S. Ranasinghe, G. A. Petersson, *J. Chem. Phys.* **2013**, *138*, 144104.
- [72] H. B. Schlegel, M. A. Robb, *Chem. Phys. Lett.* **1982**, *93*, 43.
- [73] F. Bernardi, A. Bottoni, J. J. W. McDouall, M. A. Robb, H. B. Schlegel, In *Faraday Symposia of the Chemical Society*, Vol. 19; Royal Society of Chemistry, **1984**; pp. 137–147. Available at: <http://dx.doi.org/10.1039/FS9841900137>
- [74] M. Frisch, I. N. Ragazos, M. A. Robb, H. B. Schlegel, *Chem. Phys. Lett.* **1992**, *189*, 524.
- [75] N. Yamamoto, T. Vreven, M. A. Robb, M. J. Frisch, H. B. Schlegel, *Chem. Phys. Lett.* **1996**, *250*, 373.
- [76] D. Hegarty, M. A. Robb, *Mol. Phys.* **1979**, *38*, 1795.
- [77] R. H. Eade, M. A. Robb, *Chem. Phys. Lett.* **1981**, *83*, 362.
- [78] P.-O. Löwdin, H. Shull, *Phys. Rev.* **1956**, *101*, 1730.
- [79] C. Möller, M. S. Plesset, *Phys. Rev.* **1934**, *46*, 618.
- [80] M. Head-Gordon, J. A. Pople, M. J. Frisch, *Chem. Phys. Lett.* **1988**, *153*, 503.
- [81] M. W. Schmidt, M. S. Gordon, *Annu. Rev. Phys. Chem.* **1998**, *49*, 233.
- [82] S. Keller, K. Boguslawski, T. Janowski, M. Reiher, P. Pulay, *J. Chem. Phys.* **2015**, *142*, 244104.
- [83] R. S. Mulliken, *J. Chem. Phys.* **1955**, *23*, 1833.
- [84] I. Mayer, *Chem. Phys. Lett.* **1983**, *97*, 270.
- [85] L. Gurvich, I. Veyts, C. Alcock, *Thermodynamic Properties of Individual Substances*; CRC Press: Hoboken, New Jersey, **1994**.
- [86] J. Hartung, G. Knapp, B. K. Sinha, *Statistical Meta-Analysis with Applications*, Vol. 738; Wiley: Hoboken, New Jersey, published simultaneously in Canada, **2008**.
- [87] M. W. Chase, *NIST-JANAF Thermochemical Tables, 4th ed.*; American Institute of Physics for the National Institute of Standards and Technology: Woodbury, N.Y.: Washington, D.C. **1998**.
- [88] R. D. Johnson, III, editor, *NIST Computational Chemistry Comparison and Benchmark Database, NIST Standard Reference Database Number 101, Release 17b*, **2015**. Available at: <http://cccbdb.nist.gov/>
- [89] A. Karton, *WIREs Comput. Mol. Sci.* **2016**, *6*, 292.
- [90] F. Neese, E. F. Valeev, *J. Chem. Theory Comput.* **2010**, *7*, 33.
- [91] D. Cremer, M. Filatov, V. Polo, E. Kraka, S. Shaik, *Int. J. Mol. Sci.* **2002**, *3*, 604.
- [92] V. Polo, E. Kraka, D. Cremer, *Theor. Chem. Acc.* **2002**, *107*, 291.
- [93] L. Goerigk, S. Grimme, *J. Chem. Theory Comput.* **2010**, *7*, 291.
- [94] F. Neese, F. Wennmohs, A. Hansen, U. Becker, *Chem. Phys.* **2009**, *356*, 98.

Received: 28 December 2016
Revised: 28 April 2017
Accepted: 3 May 2017
Published online on 00 Month 2017