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Heats of Formation of Simple Perfluorinated Carbon Compounds

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The heats of formation of CF_3, its cation and anion, CF_4, C_2F_4, and :$CFCF_3$ have been calculated at high levels of ab initio molecular orbital theory. Geometries and frequencies were determined, in general, with second-order perturbation theory. Total energies based on coupled cluster calculations with perturbative triples were determined with basis sets up through augmented quadruple-ζ in quality and were subsequently extrapolated to the complete one-particle basis set limit, so as to further reduce the basis set truncation error. Due to its importance as a standard, CF_4 was studied with even larger basis sets. Additional improvements in the atomization energy were achieved by applying corrections due to core/valence correlation, scalar relativistic, and atomic spin−orbit effects. Zero-point energies were based on the experimental fundamentals, when available, and harmonic frequencies obtained from MP2/cc-pVTZ calculations. Missing frequencies for :$CFCF_3$ were calculated at the MP2/DZP level. The calculated heats of formation (kcal/mol) are as follows: $\Delta H_f(CF_4) = -221.8 \pm 1.1$ vs -221.6 ± 0.3 (expt); $\Delta H_f(CF_3) = -111.9 \pm 1.0$ vs -111.7 ± 1.0 (expt); $\Delta H_f(CF_3^+) = 98.0 \pm 1.2$ vs 99.8 ± 2.8 (expt); $\Delta H_f(CF_3^-) = -151.9 \pm 0.7$ vs -154.9 ± 1.0 (expt); $\Delta H_f(C_2F_4) = -159.8 \pm 1.5$ vs -156.6 ± 0.7 (expt); and $\Delta H_f(:CFCF_3) = -122.6 \pm 1.5$, all at 0 K. These values are used to calculate a variety of bond energies and molecular energetics.

Introduction

Fluorocarbons play an important role in a wide range of technological materials including refrigerants, etching materials, and polymers such as poly(tetrafluoroethylene). Obtaining reliable heats of formation of fluorine-containing compounds has been hampered by the difficulties of handling molecular fluorine and HF and the lack of, until recently, reliable heats of formation of standards such as NaF.[1−3] This type of thermodynamic information is needed for process development, environmental impact studies, and in-use behavior models. For example, there is significant interest in the decomposition of fluorinated materials at higher temperatures because of their use as insulation materials in a range of electrical systems and in large refrigeration systems. The heats of formation of simple model compounds are needed as the base upon which to build group additivity methods and as test cases for new methods for predicting heats of formation. Important model fluorinated compounds include CF_4 as the prototypical perfluoroalkane and C_2F_4 as the prototypical perfluoroalkene. Important model species for decomposition include :CF_2, CF_3, and its ions, CF_3^- and CF_3^+, and :$CFCF_3$.

The heat of formation of CF_4 is often used as a standard and, consequently, has been the subject of experimental studies.[1] The situation for C_2F_4 is similar. We have recently revised the heat of formation of :CF_2 based on detailed theoretical *ab initio* molecular orbital calculations.[4] A revision in the heat of formation of CF_3 to -111.4 ± 0.9 kcal/mol at 298 K (-110.7 ± 0.9 kcal/mol at 0 K) has been suggested based on photoionization measurements.[5] This has led to a revision of the heat of formation of CF_3^+ to 97.4 ± 0.9 kcal/mol. These values can be compared to the JANAF values[1] of -111.7 ± 1.0 kcal/mol at 0 K for CF_3 and 99.8 ± 2.8 kcal/mol at 0 K for CF_3^+. The heat of formation for CF_3^- can be derived from measurements of the acidity or electron affinity of CF_3 but these measurements have much larger error bars.[6]

For perfluorocarbons, approaches such as Gaussian-1 (G1)[7] and Gaussian-2 (G2)[8] have had trouble predicting the atomization energies reliably. For example, the G2 value[9] for $\Delta H_f(CF_4)$ at 0 K is −227.2 kcal/mol as compared to the JANAF value of -221.6 ± 0.3 kcal/mol, an error of 5.6 kcal/mol. Similarly, the G2 value for $\Delta H_f(C_2F_4)$ at 0 K is −164.8 kcal/mol, compared to the experimental value of -156.6 ± 0.7 kcal/mol, an error of 8.2 kcal/mol. It is useful to note that the G2 values are more negative (higher atomization energy) than the experimental ones.

In a series of recent papers, we have begun calibrating a composite theoretical approach that is intended to reliably predict a variety of thermodynamic quantities, including heats of formation, without recourse to empirical parameters.[4,10−15] As described below, our approach starts with existing, reliable thermodynamic values (from either experiment or theory). Missing pieces of information are then computed by using high-level ab initio electronic structure methods. In the present work we turn our attention to accurately determining the heats of formation of neutral CF_3, its cation and anion, CF_4, C_2F_4, and :$CFCF_3$.

Approach

For chemical systems that can be qualitatively described by a single configuration wave function, such as the molecules examined in the present study, we use coupled cluster theory with single and double excitations and a perturbative correction for the triples (CCSD(T)).[16] Initial energetics are obtained within the frozen core (FC) approximation in which the carbon and fluorine 1s inner shell electrons are excluded from the correlation treatment. When combined with large basis sets, CCSD(T)(FC) is capable of recovering a significant fraction of the valence

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correlation energy. With current hardware and software, basis sets such as the correlation consistent augmented quadruple-ζ set[17] are at the limit of what is computationally feasible for molecules composed of no more than 6 second- or third-row elements and an equal number of hydrogens. Nonetheless, even with such large basis sets the errors in thermodynamic properties can still be unacceptably large.[14,15] Attacking the residual basis set truncation error via brute force techniques is usually not practical. Fortunately, the convergence of the total energies derived from the correlation consistent basis sets is sufficiently uniform to warrant some type of extrapolation to the complete basis set (CBS) limit, as will be described.

Having estimated energies at the CCSD(T)(FC)/CBS level of theory, we then include a number of additional corrections to account for core/valence, atomic spin−orbit, and molecular scalar relativistic effects. Zero-point vibrational energies are also carefully considered. This composite approach has been shown to provide reliable atomization energies for a number of molecules, including small hydrocarbons and fluorinated compounds such as :CF_2 and CF_2O,[4] and is similar to the general approach used by Martin[18] and Bauschlicher and co-workers.[19,20]

The widely used G2 model chemistry differs from the present approach in the following ways: (1) G2 atomization energies are dependent on an empirical correction factor obtained by minimizing the atomization energy error with respect to a collection of experimental data; (2) G2 zero-point energies are obtained from scaled Hartree−Fock frequencies rather than from large basis set, correlated calculations; and (3) with the exception of Gaussian-3 (G3),[21] core/valence and atomic spin−orbit effects are not explicitly included. In contrast, we attempt to explicitly account for all contributions to $\sum D_0$ known to contribute ∼1 kcal/mol or more to molecules composed of elements from the first three periods. While G3 is the first of the Gaussian-x models to include core/valence and atomic spin−orbit effects (other than implicitly via the “higher order correction”), it still neglects scalar relativistic effects, which can be as large as 2.4 kcal/mol for the class of molecules we intend to study.[14,15] A disadvantage of our more computationally demanding approach, compared to G2 and G3, is that the size of the chemical systems to which it can be applied is, consequently, more limited. Nonetheless, Feller and Peterson[14,15] used essentially the same method on a group of 73 molecules, many of which were taken from the G2 and G2/97 test sets, and reported a mean absolute deviation with respect to experiment of 0.7−0.8 kcal/mol. The only difference between the procedure followed by Feller and Peterson and the present study is the use of CCSD(T) geometries in the former.

Geometries and harmonic frequencies were obtained from frozen core, second-order Møller−Plesset (MP2) level of perturbation theory[22] with the cc-pVTZ basis.[17] This level of theory is economical enough to apply to relatively large systems and provides reasonable geometries. In our previous work,[4,10] the use of MP2 geometries, as opposed to the much more expensive CCSD(T) geometries, proved to have a minimal effect on the computed energetics. The calculated harmonic frequencies were used to augment the available experimental values,[23−26] unless otherwise noted. CCSD(T)(FC) calculations were performed at the MP2/cc-pVTZ geometries with the correlation consistent basis sets (cc-pVxZ for x = D,T,Q corresponding to the double, triple, and quadruple-ζ levels) as well as the diffuse function augmented sets, denoted aug-cc-pVxZ,[17] where possible. This sequence of basis sets has been extensively demonstrated to provide reliable thermochemical properties, with rare exceptions. Only the spherical components (5-d, 7-f, and 9-g) of the Cartesian basis functions were used. All calculations were performed with the Gaussian-94[27] and MOLPRO-96/97[28] programs on Silicon Graphics PowerChallenge compute servers and Cray vector supercomputers.

Core/valence corrections to the dissociation energy were obtained from fully correlated CCSD(T) calculations with the cc-pCVTZ or cc-pCVQZ basis sets[17] at either the MP2/cc-pVTZ or CCSD(T)/aug-cc-pVTZ geometries. Experience has shown that the cc-pCVTZ basis set recovers ∼75% or more of the effect seen with the larger cc-pCVQZ basis.[17g]

There are currently three widely used CCSD(T) approaches for handling open shell systems.[29] We have chosen to base the CCSD(T) atomic calculations on unrestricted Hartree−Fock (UHF) orbitals with spin unrestricted CCSD(T), denoted as UCCSD(T). For the open shell CF_3 molecule, the SCF calculations were done with ROHF orbitals, but the spin constraint was relaxed in the coupled cluster portion of the calculation. Energies obtained from this hybrid procedure are denoted R/UCCSD(T). For calculating $\sum D_e$ for CF_3, we also used the R/UCCSD(T) procedure for the atomic energies for internal consistency.

In order to estimate energies at the CBS limit, we used a mixed exponential/Gaussian function of the form:

$$E(x) = A_{\mathrm{CBS}} + B\exp[-(x-1)] + C\exp[-(x-1)^2] \quad (1)$$

where x = 2 (DZ), 3 (TZ) etc., which was first proposed by Peterson et al.[30] As a crude estimate of the uncertainty in the CBS extrapolation, we adopted the spread in the CBS estimates obtained from the mixed expression and two alternative functional forms, a simple exponential:[31]

$$E(x) = A_{\mathrm{CBS}} + B\exp(-Cx) \quad (2)$$

and an expansion in $1/l_{\max}$:

$$E(x) = A_{\mathrm{CBS}} + B/(l_{\max} + 1)^4 \quad (3)$$

where $l_{\max}$ is the maximum l value for the basis set (l = 0, 1, 2, ... for s, p, d, etc.).[32,33] Note that for second- and third-row elements, x (eqs 1 and 2) = $l_{\max}$ (eq 3), when the correlation consistent basis sets are used. In the study of Feller and Peterson,[14,15] the mixed expression produced the smallest mean absolute deviation with respect to experiment by a small measure. However, when used with the very highest level basis sets and including all corrections, eqs 1−3 produced similar agreement with experiment in the mean. The CBS extrapolated atomic energies are given in the Appendix (Table 12).

Our atomic calculations do not correspond to the lowest energy spin multiplet, but instead to an average of the multiplets associated with, for example, the ^3P state of carbon. If an accuracy of 1 kcal/mol or better is desired, atomization energies must be corrected for this effect. Thus, we apply atomic spin−orbit corrections based on the excitation energies of Moore.[34] The actual corrections are 0.08 kcal/mol (C) and 0.385 kcal/mol (F), leading to a *decrease* in the total atomization energy.

A final correction to account for scalar relativistic effects is also applied. Ideally, this correction should be obtained from fully relativistic, four-component wave functions, but at present such calculations are too time-consuming to consider using them on polyatomic molecules with a dozen or so atoms. In lieu of this, we evaluate the scalar relativistic correction using configuration interaction wave functions with single and double excitations (CISD/cc-pVTZ). Specifically, the scalar relativistic energy lowering is defined to be the sum of the expectation values of the one-electron Darwin and mass-velocity terms in

TABLE 1: C_2H_4 ($^1A_1$) CCSD(T)(FC) Results[a]

basis set	energy (E_h)	r_{CC} (Å)	r_{CH} (Å)	CCH (deg)	$\sum D_e$ (kcal/mol)
aug-cc-pVDZ	−78.369667	1.355	1.097	121.4	528.7
aug-cc-pVTZ	−78.443764	1.338	1.084	121.5	552.7
aug-cc-pVQZ	−78.463592	1.335	1.083	121.4	558.5
aug-cc-pV5Z	−78.469314	1.335	1.082	121.4	560.1
CBS(aDTQ/e^{-x})	−78.4709				560.3
CBS(aTQ/l_{max})	−78.4751				561.9
CBS(aDTQ/mix)	−78.4744				561.6
CBS(aTQ5/e^{-x})	−78.4716				560.7
CBS(aTQ5/l_{max})	−78.4740				561.5
CBS(aTQ5/mix)	−78.4726				561.0
expt[b]		1.339	1.087	121.3	

[a] Results taken from Feller and Peterson, ref 15. [b] $\sum D_e$ was computed with respect to UCCSD(T)(FC) atoms. [c] Experimental geometry was taken from Harmony et al., ref 35.

the Breit−Pauli Hamiltonian.[35] Tests show this approach to be capable of reproducing scalar relativistic corrections obtained from more accurate methods to within about 0.1 kcal/mol.

By combining our computed $\sum D_0$ values with the known[1] heats of formation at 0 K for the elements: $\Delta H_f^0(C) = 169.98 \pm 0.1$ kcal/mol, $\Delta H_f^0(H) = 51.63$ kcal/mol, and $\Delta H_f^0(F) = 18.47 \pm 0.07$ kcal/mol, we can derive ΔH_f^0 values for the molecules under study. The uncertainties in our theoretical approach are probably large enough that the uncertainties in the experimental heats of formation of carbon and fluorine are of no consequence. Nonetheless, as pointed out by Feller and Peterson,[15] theory is rapidly approaching the point where the scarcity of highly accurate experimental heats of formation may hinder the calibration of newer methods.

Results and Discussion

A measure of the potential accuracy of our approach can be obtained by considering the calculation of the heat of formation of C_2H_4. CCSD(T)(FC) total energies and optimized geometries, taken from the work of Feller and Peterson,[14,15] are listed in Table 1. Agreement with experiment for the three geometric parameters (r_{CC}, r_{CH}, and $\angle$CCH) is good.[36] The CCSD(T)(FC)/CBS estimates of $\sum D_e$, based on aug-cc-pV5Z energies, span a relatively narrow range of 0.8 kcal/mol. When combined with a zero-point energy of 31.7 kcal/mol, based on CCSD(T)/aug-cc-pVDZ harmonic frequencies, all three CBS values of $\sum D_0$ underestimate the experimental result[1] by amounts ranging from 0.3 to 1.1 kcal/mol.. Alternatively, if we substituted the experimental ZPE (31.5 kcal/mol)[37] or a theoretical value that includes anharmonic corrections (31.4 kcal/mol)[38] for the CCSD(T) value, the agreement with $\sum D_0$(expt) would improve by several tenths of a kcal/mol, bringing all estimates to within 1 kcal/mol. (Note that use of $0.5\sum\nu_i$ from the experimental anharmonic frequencies[23] gives ZPE = 30.9 kcal/mol, too low by 0.5 kcal/mol, in accord with the observations of Grev et al.[39]) By combining the CBS/(aVTQ5/mix) value of $\sum D_e$ with a core/valence correction of 2.3 kcal/mol (see Table 2), a scalar relativistic plus spin−orbit correction of −0.5 kcal/mol and the experimental ZPE, we arrive at $\sum D_0 = 531.3 \pm 0.6$ kcal/mol. The uncertainty is one-half the spread in the CBS values among the three extrapolation formulas plus twice the 0.1 kcal/mol uncertainty in the heat of formation of the C atom. From the known heats of formation of carbon and hydrogen, we obtain $\Delta H_f^0(C_2H_4, \text{theory}) = 15.2 \pm 0.6$ kcal/mol, as compared to the 14.6 ± 0.1 kcal/mol 0 K value listed in the JANAF Tables[1] (see Table 3).

The optimized CF_4 geometry and harmonic frequencies are given in Table 4. The geometry at the MP2/cc-pVTZ level is in excellent agreement with experiment[40] as are the calculated frequencies with the largest deviation being 31 cm^{-1} for the t_2 stretch.[23] The details for calculating the atomization energy of CF_4 are given in Tables 2, 5, and 6. The core-valence correction is 1.3 kcal/mol and the sum of the spin−orbit and scalar relativistic terms is −2.9 kcal/mol. The value of $\sum D_e$ without the corrections at the CBS(aDTQ/mix) level is 478.3 kcal/mol. We take the average of the calculated and experimental ($0.5\sum\nu_i$) zero-point energies as our best estimate of the zero-point energy. This gives $\sum D_0^0 = 465.7$ kcal/mol which converts to $\Delta H_f^0(CF_4) = -221.8 \pm 1.1$ kcal/mol with the uncertainty taken from the extrapolation error as described above and the errors in the heat of formation of the elements. This can be compared to the experimental JANAF value[1] of −221.6 ± 0.3 kcal/mol.

For CF_4, we were able to use a larger basis set, the aug-cc-pV5Z set which includes up through h functions. The bond energies are shown in Table 7. We investigated different types of extrapolations. For example, if the CBS(aTQ5/mix) level is used, $\sum D_e = 476.9$ kcal/mol, 1.4 kcal/mol below the CBS(aDTQ/mix) result. Use of the aug-cc-pVDZ result in the extrapolation (CBS(aDTQ5/mix)) gives $\sum D_e = 477.6$ kcal/mol, only 0.6 kcal/mol below the CBS(aDTQ/mix) result. The use of the additional term in our fit leads to an improvement in our extrapolated results and this makes it less dependent on the exact nature of the functional form that we have used. It is useful to note that the best actual calculated energy for $\sum D_e$ of 475.9 kcal/mol at the aug-cc-pV5Z level is only 1.7 kcal/mol below our best extrapolated result at the CBS(aDTQ5/mix) level, an average error of only 0.4−0.5 kcal/mol per C−F bond. Use of $\sum D_e$ at the CBS(aDTQ5/mix) level gives $\sum D_0^0 = 465.0$ kcal/mol and $\Delta H_f^0(CF_4) = -221.1 \pm 0.9$ kcal/mol. This value is just outside the lower range of the JANAF value given above, but the JANAF value is within our error limits. This result demonstrates together with our previous work that there is no difficulty in calculating the heat of formation of fluorocarbon systems. The results that we have obtained suggest that the difficulty in calculating $\Delta H_f^0(CF_4)$ at the G1/G2 levels is due in part to the fact that the results are effectively “extrapolated” from basis sets that are too small which leads to an overestimate of the $\sum D_e$. We also updated our previous values[4] as shown in Table 5 where we now include the effect of scalar relativity on the energies of CF and CF_2.

The geometry and frequency parameters for CF_3 are given in Table 3. The experimental geometry of CF_3 is not known, but based on the results for CF_4 and $:CF_2$, the calculated geometry should be quite accurate. The molecule is nonplanar with a near-tetrahedral bond angle and the barrier to inversion is quite high.[41] The calculated frequencies are in good agreement with experiment[24] with the largest errors being 30−40 cm^{-1} for the stretches. We were unable to calculate the energy of CF_3 with the aug-cc-pVQZ basis set due to computer limitations. We estimated this value as follows. We compared the energy difference between the cc-pVTZ and aug-cc-pVTZ for CF_3^+, CF_3, and CF_4 and found that the differences in energy for CF_3 were essentially the average of the differences for CF_3^+ and CF_4. In order to estimate the energy for CF_3 at the aug-cc-pVQZ basis set level, we averaged the difference in the cc-pVQZ and aug-cc-pVQZ energies for CF_3^+ and CF_4 and added the average to the cc-pVQZ for CF_3. The core-valence correction is 1.0 kcal/mol and the sum of the spin−orbit and scalar relativistic effects is −1.8 kcal/mol giving $\sum D_e = 345.0$ kcal/mol. Again, taking the average of the calculated and experimental zero-point energies, we obtain $\sum D_0^0 = 337.3$ kcal/mol. This yields $\Delta H_f^0(CF_3) = -111.9 \pm 1.0$ kcal/mol with the uncertainty

TABLE 2: Summary of Energy Contributions (in kcal/mol) to $\sum D_0$

molecule	basis[a]	CBS $\sum D_e$	ZPE[b] MP2	ZPE[b] CCSD(T)	ZPE[b] expt[c]	ΔE_{CV}[d]	ΔE_{SR}[e]	atomic SO[f]	$\sum D_0$[g]
C_2H_4	aV5Z	561.0	32.3	31.7	31.5	2.3	−0.3	−0.2	531.3
CF	aV5Z	132.2	1.9	1.7	1.9	0.4	−0.3	−0.5	129.9
CF_2	aV5Z	258.1	4.5	4.1	4.3	0.6	−0.6	−0.9	252.9
CF_3	aVQZ	345.7[h]	7.8		7.6	1.1	−0.5	−1.2	337.4
CF_3^+	aVQZ	137.6	9.5			1.0	−0.5	−1.2	127.4
CF_3^-	aVQZ	384.3	6.0			0.8	−0.5	−1.2	377.3
CF_4	aV5Z	478.3	10.9	10.5	10.7	1.3	−1.5	−1.6	465.7
C_2F_4	aVQZ	587.9	13.5[i]	13.2	13.3	2.3	−1.5	−1.7	573.8

[a] Largest basis set used in the CBS(mix) extrapolation. [b] Zero-point vibrational energy corrections, defined as $0.5\sum\omega_i$. The MP2 and CCSD(T) values were obtained with the cc-pVTZ and aug-cc-pVDZ basis sets, respectively. For the sake of comparison, ZPE(CF) = 1.9 kcal/mol (CCSD(T)/aug-cc-pVQZ) and ZPE(CF_2) = 4.3 kcal/mol (CCSD(T)/aug-cc-pVTZ). [c] Experimental ZPEs are taken from: C_2H_4, Harmony et al., ref 36; CF, Huber and Herzberg, ref 25; CF_2, Murray et al., ref 26; CF_3, Jacox, ref 24; CF_4 and C_2F_4, Shimanouchi, ref 23. [d] Core valence corrections based on CCSD(T)/cc-pCVQZ calculations. A positive sign indicates that the contribution increases the atomization energy. [e] Scalar relativistic correction. A negative sign indicates a decrease in the atomization energy. [f] Atomic spin−orbit correction. [g] ZPEs were taken from: C_2H_4 = expt, CF = expt, CF_2 = expt, CF_3 = 0.5(MP2 + expt), CF_3^+ and CF_3^- = MP2, CF_4, and C_2F_4 = 0.5(CCSD(T) + expt). [h] $\sum D_e$ (kcal/mol) was computed with respect to R/UCCSD(T) atoms except for CF_3 (see text). [i] MP2/DZP.

TABLE 3: Comparison of Calculated and Experimental Heats of Formation (in kcal/mol)[a]

system	ΔH_f^0(calc)	ΔH_f^0(expt)
$C_2H_4(^1A_g)$	15.2 ± 0.6	14.58 ± 0.07
$CF(^2\Pi)$	58.6 ± 0.3	60.1 ± 2
$CF_2(^1A_1)$	−46.0 ± 0.3	−43.6 ± 1.5, −44.3 ± 1,[c] −49.0 ± 3[d]
$CF_3(^2A_1)$	−111.9 ± 1.0	−111.7 ± 1.0, −110.7 ± 0.9[b]
$CF_3^+(^1A_1')$	98.0 ± 1.2	99.8 ± 2.8, 98.1 ± 0.9[b]
$CF_3^-(^1A)$	−151.9 ± 0.7	−154.9
$CF_4(^1A_1)$	−221.8 ± 1.1 −221.1 ± 0.9[e]	−221.6 ± 0.3
$C_2F_4(^1A_g)$	−159.8 ± 1.5	−156.6 ± 0.7
$:CFCF_3(^1A)$	−122.6 ± 1.5	
$C(^3P)$		169.98 ± 0.1
$F(^2P)$		18.47 ± 0.07
$F^+(^3P)$		420.25 ± 0.07
$F^-(^1S)$		−59.91 ± 0.14

[a] Unless noted, all experimental heats of formation are from the JANAF Tables, ref 1. [b] Reference 5. [c] Berman, D. W.; Bomse, D. W.; Beauchamp, J. L. *Int. J. Mass Spectrom. Ion Phys.* **1981**, *39*, 263. [d] Lias, S. G.; Karpas, Z.; Liebman, J. F. *J. Am. Chem. Soc.* **1985**, *107*, 6080 [e] Calculated at the CBS(aDTQ5/mix) level.

calculated as described above. This is in excellent agreement with the JANAF value[1] of −111.7 ± 1.0 kcal/mol but is not in as good agreement with the newer value of −110.7 ± 0.9 kcal/mol based on photoionization measurements.[5] We thus suggest that the JANAF value is more reliable.

We also studied the ions derived by removing or adding an electron to CF_3 as these have been studied experimentally. Removal of an electron leads to substantial change in the geometry. The cation CF_3^+ is now isoelectronic to BF_3 with a planar D_{3h} structure and a much shorter bond length. The C−F bond decreases by 0.08 Å going from the neutral radical to the cation. The frequencies (Table 4) also dramatically change in going from the radical to the neutral with the splitting of the stretching frequencies becoming quite large. The degenerate stretching frequency is calculated to be 50 cm^{-1} larger than the observed band in an Ar matrix.[24,42] The corrections to the atomization energy due to core-valence, spin−orbit, and scalar relativistic effects (Table 2) are comparable to those in CF_3 giving $\sum D_e = 136.8$ kcal/mol. We note that we have actually calculated the energy of the following process and denote this as the "atomization energy" of CF_3^+:

$$e^- + CF_3^+ \rightarrow C(^3P) + 3F(^2P) \qquad (4)$$

We take the zero-point energy from the calculated values (Tables 2 and 4) to obtain $D_0^0 = 127.4$ kcal/mol which gives $\Delta H_f^0(CF_3^+) = 98.0 \pm 1.2$ kcal/mol at 0 K. This can be compared to the values of 99.8 ± 2.8 kcal/mol reported in the JANAF Tables[1] and 98.1 ± 0.9 based on the latest photoionization measurements.[5] The calculated ionization potential is 9.10 ± 0.02 eV which is quite close to the ionization potential obtained from the photoionization of C_2F_4 to produce CF_3 of $9.05_5 \pm 0.01_1$ eV.[5] Other workers obtain ionization potentials for CF_3 of 9.25 ± 0.04 eV based on direct photoionization[43] of CF_3 and 9.11 eV from the photodissociative ionization[44] of CF_3X compounds. Our value is closer to the latter one.

The addition of an electron to CF_3 also induces significant changes in the geometry. (Table 4) The C−F bonds become significantly longer by 0.11 Å as compared to the neutral and the molecule becomes more pyramidal with the FCF bond angle decreasing to below 100°. This is consistent with previously calculated values[45] of the geometry parameters. The core-valence correction is slightly smaller in CF_3^- than in CF_3 (Table 2). The value of $\sum D_e$ is 383.3 kcal/mol and $\sum D_0^0 = 377.3$ kcal/mol for reaction 5

$$CF_3^- \rightarrow C(^3P) + 3F(^2P) + e^- \qquad (5)$$

based on the calculated frequencies (Tables 2 and 4). This yields $\Delta H_f^0(CF_3^-) = -151.9 \pm 0.7$ kcal/mol at 0 K. The calculated electron affinity at 0 K is 1.77 ± 0.02 eV. These can be compared to the value of $\Delta H_f^0(CF_3^-) = -154.9 \pm 2.2$ kcal/mol reported in the NIST I on Tables[4,46] based on a thermodynamic cycle from acidity measurements, which gives an electron affinity of 1.86 ± 0.16 eV. Our calculated electron affinity is clearly within the experimental error limits. We prefer our lower value as compared to the estimated value based on the acidity cycle. The electron affinity from the acidity cycle is calculated from the experimental acidity obtained from equilibria and bracketing experiments, the ionization potential of H, and the CF_3−H bond dissociation energy. There are small sources of error in these values, all of which can lead to the difference in the calculated and experimental electron affinities.

The calculated geometry and frequencies for C_2F_4 are given in Table 8. The original calculations were done with a smaller polarized double-ζ basis set[47] at the MP2 level. The calculated values at the DZP/MP2 level differ somewhat more from the experimental values[48] than the differences noted above for CF_4. The C═C bond distance is 0.026 Å too long and the C−F bond distance is 0.008 Å too long. The calculated frequencies at the MP2/DZP level are in quite good agreement with the experi-

TABLE 4: Geometries and Frequencies for Compounds with One Carbon[a]

molecule	level	energy (E_h)	r_{CF} (Å)	∠FCF (°)	ω_1	ω_2	ω_3	ω_4
CF_4	MP2/VTZ	−436.966 070	1.3192	109.5	925 (a_1)	440 (e)	1312 (t_2)	640 (t_2)
	CCSD(T)/aVDZ		1.3368	109.5	876	417	1263	606
	CCSD(T)/aVTZ		1.3211	109.5				
	CCSD(T)/aVQZ		1.3180	109.5				
	CCSD(T)/aV5Z		1.317[b]	109.5				
expt[c]			1.319	109.5	909	435	1281	632
CF_3	MP2/VTZ	−337.142 822	1.3156	111.4	1122 (a)	717 (a)	1298 (e)	517 (e)
expt[d]					1089	701	1260	508 (Ne)
CF_3^+	MP2/VTZ	−336.822 226	1.2326	120.0	1072 (a_1')	825 (a_2'')	1717 (e′)	601 (e′)
							(1667)[e]	
CF_3^-	MP2/VTZ	−337.181 871	1.4292	99.7	1047 (a)	621 (a)	817 (e)	459 (e)

[a] Bond lengths are in angstroms. Frequencies are in cm^{-1}. The experimental frequencies correspond to anharmonic frequencies. [b] Estimated from an exponential fit of the aug-cc-pVDZ through aug-cc-pVQZ bond lengths. [c] r_{CF} from ref 36 and vibrational frequencies are from ref 23. [d] Vibrational frequencies are from ref 24. [e] Experimental vibrational frequency from ref 24.

TABLE 5: Total CCSD(T) Energies (in hartrees)

basis set	$CF_4(^1A_1)$	$CF_3(^2A_1)$[a]	$CF_3^+(^1A'_1)$	$CF_3^-(^1A)$	$C_2F_4(^1A_g$, DZP)	$C_2F_4(^1A_g$, pVTZ)	:$CFCF_3(^1A$, DZP)
cc-pVDZ	−436.560 181	−336.833 993	−336.521 153	−336.856 671	−474.472 203	−474.471 547	−474.414 320
cc-pVTZ	−437.001 103	−337.173 008	−336.850 234	−337.214 895	−474.947 762	−474.948 364	−474.887 790
cc-pVQZ	−437.139 704	−337.279 387	−336.951 530	−336.332 057	−475.096 616	−475.097 538	−475.036 053
aug-cc-pVDZ	−436.666 467[b]	−336.916 510	−336.583 041	−336.982 577	−474.588 509	−474.586 957	
aug-cc-pVTZ	−437.037 160[b]	−337.201 204	−336.870 779	−337.263 194	−474.986 970	−474.987 443	
aug-cc-pVQZ	−437.154 338[b]	−337.290 972[c]	−336.960 074	−337.352 770	−475.112 746	−475.113615	
aug-cc-pV5Z	−437.193 487[b]						

[a] R/UCCSD(T). [b] Evaluated at the optimal CCSD(T)(FC) geometry. R_{CF} = 1.337 Å (aVDZ), 1.321 Å (aVTZ), 1.318 Å (aVQZ), and 1.317 Å (est.) (aV5Z). [c] Estimated as described in the text.

TABLE 6: Extrapolated CCSD(T) Results for Fluorinated Compounds with One Carbon

basis set	CF_4 energy (E_h)	CF_4 $\sum D_e$[a]	CF_3 energy (E_h)	CF_3 $\sum D_e$[b]	CF_3^+ energy (E_h)	CF_3^+ $\sum D_e$[a]	CF_3^- energy (E_h)	CF_3^- $\sum D_e$[a]
CBS(DTQ/e^{-x})	−437.203 247	474.73	−337.328 03	342.67	−336.996 58	134.50	−337.389 00	380.74
CBS(TQ/l_{max})	−437.219 699	476.75	−337.340 78	344.29	−337.009 99	136.53	−337.399 68	381.06
CBS(DTQ/mix)	−437.218 129	476.50	−337.339 56	344.10	−337.008 61	136.23	−337.398 86	381.11
CBS(aDTQ/e^{-x})	−437.208 51	476.84	−337.332 31	344.53	−337.000 26	135.97	−337.394 77	383.53
CBS(aTQ/l_{max})	−437.221 96	478.55	−337.342 78	345.84	−337.011 61	137.84	−337.404 47	384.36
CBS(aDTQ/mix)	−437.220 67	478.29	−337.341 80	345.68	−337.010 47	137.58	−337.403 61	384.28

[a] $\sum D_e$ (kcal/mol) was computed with respect to UCCSD(T) atoms. [b] $\sum D_e$ (kcal/mol) was computed with respect to R/UCCSD(T) atoms.

TABLE 7: Calculated Total Bond Energies $\sum D_e$ for CF_4 ($^1A_1$) (in kcal/mol)

basis set	$\sum D_e$	total energies (au)
cc-pVDZ	432.67	
cc-pVTZ	463.66	
cc-pVQZ	471.96	
aug-cc-pVDZ	440.08	
aug-cc-pVTZ	466.88	
aug-cc-pVQZ	474.28	
aug-cc-pV5Z	475.92	
CBS(DTQ/e^{-x})	474.73	
CBS(TQ/l_{max})	476.75	
CBS(DTQ/mix)	476.50	
CBS(aDTQ/e^{-x})	476.84	
CBS(aTQ/l_{max})	478.55	
CBS(aDTQ/mix)	478.29	
CBS(aTQ5/e^{-x})	476.12	−437.212 30
CBS(aDTQ5/e^{-x})	476.45	−437.210 63
CBS(aQ5/l_{max})	477.26	−437.225 28
CBS(aTQ5/mix)	476.41	−437.215 69
CBS(aDTQ5/mix)	477.57	−437.218 33

TABLE 8: Calculated Geometries and Frequencies for C_2F_4[a]

method	energy (au)	R(C═C)	R(C−F)	∠FCF
MP2/DZP	−474.450 789	1.337	1.327	113.5
MP2/cc-pVTZ	−474.898 854	1.325	1.315	113.5
expt[b]		1.311	1.319	112.5

Frequencies

symmetry	CCSD(T)/aVDZ	MP2/DZP	expt[c]
a_g	1900	1922	1872
	764	789	778
	385	393	394
a_u	196	199	190
b_{1g}	1331	1372	1340
	543	549	551
b_{1u}	401	410	406
b_{2g}	479	483	508
b_{2u}	1320	1370	1337
	207	207	218
b_{3u}	1160	1201	1186
	536	547	558

[a] Bond lengths are in angstroms. Frequencies are in cm^{-1}. The experimental frequencies correspond to anharmonic frequencies. [b] Experimental geometry from ref 48. [c] Experimental vibrational frequencies from ref 23.

mental values. We reoptimized the geometry with the larger cc-pVTZ basis set and find that both bond distances are now in better agreement with experiment. However, the predicted C═C bond length is still 0.014 Å longer than experiment and the FCF bond angle is still larger by 1°. We do note that there is an uncertainty of 0.006 Å in the experimental C═C bond length. The total energies for C_2F_4 are given in Table 5 and the extrapolated energies are given in Table 9. The difference in the extrapolated energies with the two different geometries is 0.7 kcal/mol with the normal and augmented cc-pVxZ basis sets with the MP2/cc-pVTZ geometry having the lower energy. We use the $\sum D_e$ at the MP2/cc-pVTZ geometry and the other correction terms were calculated at the MP2/DZP geometry.

TABLE 9: C_2F_4 ($^1A_1$) and :$CFCF_3$ Extrapolated CCSD(T) Results[a]

basis set	C_2F_4(DZP) energy (E_h)	C_2F_4(DZP) $\sum D_e$	C_2F_4(pVTZ) energy (E_h)	C_2F_4(pVTZ) $\sum D_e$	:$CFCF_3$(DZP) energy (E_h)	:$CFCF_3$(DZP) $\sum D_e$
CBS(DTQ/e^{-x})	−475.164 44	582.88	−475.165 46	583.52	−475.103 65	544.74
CBS(TQ/l_{max})	−475.182 53	585.28	−475.183 64	585.98	−475.121 62	547.06
CBS(DTQ/mix)	−475.180 77	585.00	−475.181 87	585.69	−475.119 88	546.79
CBS(aDTQ/e^{-x})	−475.170 76	585.66	−475.171 65	586.22		
CBS(aTQ/l_{max})	−475.185 34	587.48	−475.186 44	588.17		
CBS(aDTQ/mix)	−475.183 97	587.26	−475.185 04	587.93		

[a] $\sum D_e$ (kcal/mol) was computed with respect to UCCSD(T) atoms. Labels in parentheses indicate the basis set at which the MP2 geometry optimization was done.

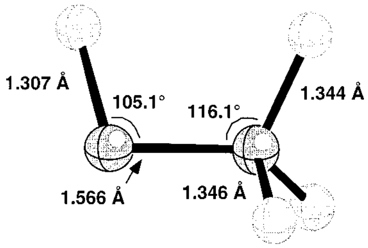

Figure 1. MP2/DZP optimized geometry of :$CFCF_3$.

TABLE 10: Frequencies (cm^{-1}) Calculated at the MP-2 Level for :$CFCF_3$

symmetry	MP2/DZP
a′	1355
	1267
	1253
	842
	696
	543
	408
	270
a″	1210
	534
	365
	18

TABLE 11: Reaction Energies Calculated from Heats of Formation (in kcal/mol)

reaction	calc	expt
$C_2H_4 \rightarrow 2$:CH_2	170.5	169.8
$CF_4 \rightarrow CF_3 + F$	128.4	128.4
$CF_3 \rightarrow CF_2 + F$	84.4	85.9
$CF_2 \rightarrow CF + F$	123.0	122.9
$CF \rightarrow C + F$	130.0	128.4
$C_2F_4 \rightarrow 2$:CF_2	67.8	68.0
:$CFCF_3 \rightarrow CF + CF_3$	69.2	
$CF_3^- \rightarrow CF_2 + F^-$	46.0	50.7
$CF_3^+ \rightarrow CF_2 + F^+$	278.6	276.2

The core-valence term is significant, 2.3 kcal/mol, and the scalar-relativistic and spin−orbit terms sum to −3.2 kcal/mol, more than canceling the core-valence effect. We take the zero-point energy to be the average of the experimental and calculated values to obtain $\sum D_0^0 = 573.7$ kcal/mol. The calculated value for $\Delta H_f^0(C_2F_4)$ is -159.8 ± 1.5 kcal/mol, significantly lower than the NIST-JANAF value of -156.6 ± 0.7 kcal/mol. This difference is far outside our error estimates. Based on the confidence that we have in our computational method due to the good agreement found for C_2H_4 and CF_4, we suggest that there may well be an error in the heat of formation of C_2F_4 and suggest that it is actually more stable relative to the standard state of the elements than previously thought. Even if we are slightly overestimating the dissociation energy for C_2F_4, we are still unlikely to be off by more than 1.5 kcal/mol. Taking the exponential extrapolation which usually underestimates $\sum D_e$, we obtain $\Delta H_f^0(C_2F_4) = -158.1$ kcal/mol, still larger than the experimental value.

We calculated the structure of :$CFCF_3$ at the MP2/DZP level. Based on previous calculations, the ground state is the singlet.[49] The structure is shown in Figure 1 and has an eclipsed structure with approximate C_s symmetry. The staggered structure formed by rotating the CF_3 group by 180° is a transition state, 0.41 kcal/mol higher in energy than the structure shown in the figure. The frequencies are given in Table 10. The energies for the carbene were calculated only with the correlation consistent basis sets without the extra shell of diffuse functions, as the lack of symmetry significantly increases the computational cost. For the cc-pVQZ calculation, we used the program NWChem[50] on an IBM -SP massively parallel computer because of its large size. The total energies are given in Table 5 and the extrapolated energies in Table 8. The carbene :$CFCF_3$ is an isomer of C_2F_4 so we did not calculate the relativistic or core-valence corrections to the atomization energy (the spin−orbit is the same). This is based on the assumption that these terms should approximately cancel for isomers. Thus we take the heat of formation for C_2F_4 and calculate ΔH_f^0(:$CFCF_3$) from it based on the isomerization energy including the difference in zero-point energies, where the zero-point energy for :$CFCF_3$ is 12.52 kcal/mol. The electronic isomerization energy is taken as the difference in the extrapolated atomization energies and is 38.21 kcal/mol at the CBS(DTQ/mix) level (the value with the exponential extrapolation differs by only 0.07 kcal/mol). The difference in zero-point energies is 0.97 kcal/mol giving an isomerization energy at 0 K of 37.24 kcal/mol. Using our calculated value for $\Delta H_f^0(C_2F_4)$ we obtain ΔH_f^0(:$CFCF_3$) $= -122.6 \pm 1.5$ kcal/mol (the uncertainty comes from the error in C_2F_4) whereas use of the experimental value for $\Delta H_f^0(C_2F_4)$ yields -119.4 ± 0.6 kcal/mol.

The calculated and experimental heats of formation can be used to calculate a variety of bond energies as shown in Table 11. For example, the C−F bond energies derived from CF_4 show an interesting series with three of the four C−F bond energies greater than 120 kcal/mol and only the C−F bond in CF_3 is weak, 84.4 kcal/mol. The smaller value for the C−F bond in CF_3 is most likely due to the stability of the singlet difluorocarbene. By using a singlet−triplet splitting of 46.0 kcal/mol,[49] one can estimate a value for the bond dissociation energy of CF_3 to form F + ^{3}:CF_2 of 130 kcal/mol. The double bond energy in C_2H_4 is significantly higher than a C−C bond energy (typically about 88 kcal/mol in a hydrocarbon, 89.7 kcal/mol[1,51] in C_2H_6 at 298 K) as expected, near 170 kcal/mol. The double bond energy in C_2F_4 is very low, 67.8 kcal/mol, and is significantly lower than a single C−C bond value of ∼95 kcal/mol found[52] in perfluorocarbon alkanes. In fact, the double bond energy is only 18 kcal/mol higher than the π bond energy of 49.6 kcal/mol calculated by Wang and Borden[53] and only 16 kcal/mol higher than the π bond energy reported by Wu and Rodgers.[54] The C−C bond energy in :$CFCF_3$ is also quite low,

TABLE 12: Total CCSD(T) Energies (hartrees) for Atoms

	C(u)[a]	F(u)[a]	C(ru)[b]	F(ru)[b]
CBS(DTQ/e^{-x})	−37.788 826	−99.664 471	−37.788 722	−99.664 405
CBS(TQ/l_{max})	−37.789 875	−99.667 514	−37.789 766	−99.667 446
CBS(DTQ/mix)	−37.789 740	−99.667 256	−37.789 632	−99.667 188
CBS(aDTQ/e^{-x})	−37.789 015	−99.664 850	−37.788 912	−99.664 784
CBS(aTQ/l_{max})	−37.789 789	−99.667 384	−37.789 682	−99.667 317
CBS(aDTQ/mix)	−37.789 706	−99.667 170	−37.789 594	−99.667 104
CBS(aTQ5/e^{-x})	−37.789 019	−99.664 850		
CBS(aQ5/l_{max})	−37.789 602	−99.668 778		
CBS(aTQ5/l_{max})	−37.789 536	−99.669 269		
CBS(aTQ5/mix)	−37.789 252	−99.666 758		

[a] UHF/UCCSD(T). [b] RHF/UCCSD(T).

69.2 kcal/mol, as compared to a normal C−C bond energy in a perfluorocarbon alkane. The fluoride affinity of :CF_2 can now be calculated quite accurately as 46.0 kcal/mol, and the F^+ detachment energy from CF_3^+ is very high, 278.6 kcal/mol, as compared to many inorganic systems.[55]

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Appendix

The CBS extrapolated atomic energies are given in Table 12.

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