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Heats of Formation for C_nF_m, $C_nF_m^+$, CHF_m, and CHF_m^+

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Heats of formation for C_nF_m, $C_nF_m^+$, CHF_m, and CHF_m^+ compounds are computed at the G3MP2 level. Calibration calculations are presented for C_2F_2, C_2F, CHF, and CHF_2. The results of these calibration calculations, in conjunction with the results of previous high-level calculations, show that the G3MP2 approach is accurate to ±2 kcal/mol for these systems. The trends in bond energies are discussed.

1. Introduction

Fluorocarbon plasmas, which contain both neutrals and ions, are used in the etching of silicon and silica. In addition to being the etching agent, the fluorocarbons are the feedstock for the formation of the protective polymer overlayer. Thus to fully model the etching requires accurate thermochemical data for both the neutrals and the cations. The data in the commonly used compilations[1,2] are incomplete. While there has been more recent work, as discussed by Ruscic et al.,[3] the newer results do not always lead to an improved, more consistent set of data. While there have been computational studies[4−6] for some of these systems, our goal is to generate a complete set of thermochemical data of equivalent accuracy.

In this manuscript we report the heats of formation of CF_n and CF_n^+, for $n = 1-4$, CHF_n and CHF_n^+, for $n = 1-3$, C_2F_n and $C_2F_n^+$, for $n = 1-6$, and C_3F_n and $C_3F_n^+$, for $n = 1-8$. We use the recently developed G3MP2 approach.[7] Highly accurate studies[6] support the use of the G3MP2 approach for these fluorine-containing compounds. Since some of the largest errors in the earlier Gn methods occur for halogen-containing molecules, additional highly accurate calculations are performed to calibrate the G3MP2 approach.

2. Methods

The G3MP2 calculations are performed as presented by Pople and co-workers[7] and by using Gaussian 98.[8]

The calibration calculations follow our previous work.[6] Namely, the geometries are determined at the B3LYP/6-31+G(2df) level[9−11] and the zero-point energies computed using the B3LYP/6-31+G* approach. The atomization energies are computed using the restricted coupled cluster singles and doubles approach[12,13] including the effect of connected triples determined using perturbation theory,[14,15] RCCSD(T). In the valence RCCSD(T) calculations, the H 1s electron and the C and F 2s and 2p electrons are correlated. In most calculations, the H and C basis sets are the correlation consistent valence polarized (cc-pV) sets developed by Dunning co-workers,[16−19] while the F basis sets are the augmented (aug) cc-pV basis sets.[18,19] In some cases, the aug-cc-pV sets are also used for H and C. The double-ζ (DZ), triple-ζ (TZ), quadruple-ζ (QZ), and quintuple-ζ (5Z) sets are used. To improve the accuracy of the CCSD(T) results, we extrapolate to the complete basis set (CBS) limit. We use the two-point (n^{-4}), three-point ($n^{-4} + n^{-6}$) and variable α ($n^{-\alpha}$) schemes described by Martin[20] and the two-point n^{-3} scheme described by Helgaker et al.[21] We denote these schemes as n4, n4n6, α, and n3, respectively.

The core-valence (CV) effect is computed at the RCCSD(T) level, as the difference between the treatment correlating only the valence electrons and the treatment in which the 1s electrons are also correlated. These calculations are performed using the CV basis set, which is derived from the C and F aug-cc-pV sets. We use the CV(tz), CV(qz), and CV(5z) sets described previously.[22] The aug-cc-pV H sets are used in conjunction with the CV sets.

The atomic spin−orbit effects are computed using the tabulation of Moore.[23] The scalar relativistic effects are computed as the differences between the results obtained using the nonrelativistic and the Douglas Kroll (DK) approaches.[24] More specifically, the systems are studied at the modified coupled pair functional[25] (MCPF) level of theory using the H and C cc-pVTZ and F aug-cc-pVTZ sets. Note that the contraction coefficients used in the molecular DK calculations are taken from DK atomic Hartree−Fock (HF) calculations.

The B3LYP calculations are performed using Gaussian 98,[8] the CCSD(T) calculations are performed using Molpro,[26] and the MCPF calculations are performed using Molecule-Sweden.[27] The DK integrals are computed using a modified version of the program written by Hess.

3. Results and Discussion

In Table 1 we compare the core-valence contribution to the atomization energy of CF, CF^+, CH, and CHF. These species are sufficiently small that it is possible to use the CV(5z) basis set. The agreement among the three basis sets and the agreement with and without including the basis set superposition error (BSSE) is very good. On the basis of these calculations we compute the CV contribution using the CV(tz) set and do not include the BSSE correction. This approximation dramatically reduces the cost of the calculations while introducing only a small error in the core-valence contribution to the atomization energy.

In Tables 2 and 3 we summarize our results for C_2F_2, C_2F, CHF, and CHF_2. Also given are the previously published[6] CF_4 and C_2F_4 results. We first note that the trends in the atomization energies using the different extrapolation methods are similar for all of the molecules considered. These results show that the 5Z basis set must be used to obtain accurate results, and once the 5Z results are included in the extrapolation, the n4n6{T,Q,5}Z, α{T,Q,5}Z, n3{Q,5}Z, and n4{Q,5}Z approaches are in reasonable agreement. Since the n4n6 results give the best agreement with experiment for CF_4, this approach is used

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TABLE 1: Core-Valence Contribution to the Atomization Energy, in kcal/mol, as a Function of Basis Set and with and without a Correction for the Basis Set Superposition Error (BSSE)

	CV no BSSE			CV with BSSE		
	CV(tz)	CV(qz)	CV(5z)	CV(tz)	CV(qz)	CV(5z)
CF	0.352	0.342	0.330	0.329	0.321	0.321
CF^+	0.722	0.710	0.699	0.688	0.684	0.687
CH	0.152	0.146	0.140	0.140	0.136	0.135
CHF	0.466	0.451	0.433	0.443	0.425	0.420

TABLE 2: Computed Atomization Energies and Heats of Formation[a] for CF_4, C_2F_4, and C_2F_2, in kcal/mol

	CF_4	C_2F_4	C_2F_2
CCSD(T) DZ	440.203	537.247	341.992
CCSD(T) TZ	466.715	571.706	370.922
CCSD(T) QZ	474.205	581.990	379.141
CCSD(T) 5Z	476.265	584.915	381.438
CCSD(T) n3{D,T}Z	477.879	586.215	383.103
CCSD(T) n3{T,Q}Z	479.671	589.494	385.138
CCSD(T) n3{Q,5}Z	478.426	587.983	383.847
CCSD(T) n4{D,T}Z	476.045	583.832	381.103
CCSD(T) n4{T,Q}Z	478.528	587.925	383.885
CCSD(T) n4{Q,5}Z	477.938	587.290	383.303
CCSD(T) n4n6{D,T,Q}Z	479.057	588.797	384.477
CCSD(T) n4n6{T,Q,5}Z	477.730	587.066	383.097
CCSD(T) α{D,T,Q}Z	480.175	590.889	385.746
CCSD(T) α{T,Q,5}Z	477.610	586.919	382.972
MCPF TZ	455.293	556.622	360.059
MCPF TZ(DK)	454.408	555.526	359.317
scalar rel contribution	−0.884	−1.096	−0.742
CCSD(T)/CV	468.403	575.186	374.490
CCSD(T)-1s/CV	469.563	577.872	377.499
ΔCV	1.161	2.687	3.008
spin−orbit contribution	−1.625	−1.710	−0.940
ZPE[b]	−10.83	−13.42	−8.184
atomization energy at 0 K[c]	465.55	573.53	376.240
atomization energy at 298 K	470.28	578.96	379.093
ΔH_{298}	−223.09	−160.48	1.433
ΔH_{298} G3MP2[d]	−223.04	−161.69	0.03

[a] The CF_4 and C_2F_4 values are taken from previous work.[6] [b] The ZPE values for CF_4 and C_2F_4 are taken from previous work,[6] while the ZPE for C_2F_2 is taken from the B3LYP/6-31+G* results. [c] The atomization energy is computed as CCSD(T) n4n6{T,Q,5}Z + ΔCV + spin orbit + ZPE + scalar relativistic. [d] The ΔH_{298} values are from Table 5 which are given for comparison.

TABLE 3: Computed Atomization Energies and Heats of Formation for C_2F, CHF, and CHF_2, in kcal/mol

	C_2F	CHF[a]	CHF_2
CCSD(T) DZ	224.857	195.048	301.673
CCSD(T) TZ	244.241	207.901	320.094
CCSD(T) QZ	250.042	210.990	325.301
CCSD(T) 5Z	251.744	211.811	326.812
CCSD(T) n3{D,T}Z	252.402	213.313	327.851
CCSD(T) n3{T,Q}Z	254.275[b]	213.244	329.101
CCSD(T) n3{Q,5}Z	253.529	212.673	328.397
CCSD(T) n4{D,T}Z	251.062	212.425	326.577
CCSD(T) n4{T,Q}Z	253.390[b]	212.773	328.306
CCSD(T) n4{Q,5}Z	253.126	212.478	328.039
CCSD(T) n4n6{D,T,Q}Z	253.886	212.847	328.675
CCSD(T) n4n6{T,Q,5}Z	253.032	212.374	327.944
CCSD(T) α{D,T,Q}Z	255.083	212.954	329.455
CCSD(T) α{T,Q,5}Z	252.964	212.322	327.878
MCPF TZ	239.739	203.597	314.419
MCPF TZ(DK)	239.380	203.370	313.900
scalar rel contribution	−0.359	−0.227	−0.519
CCSD(T)/CV	247.266[c]	208.476	321.817
CCSD(T)-1s/CV	248.937	208.943	322.894
ΔCV	1.671	0.443	1.078
spin−orbit contribution	−0.555	−0.470	−0.855
ZPE(B3LYP)	−4.641	−7.760	−12.062
atomization energy at 0 K[d]	249.148	204.384	315.586
atomization energy at 298 K	251.229	206.601	319.201
ΔH_{298}	110.322	35.789	−57.884
ΔH_{298} G3MP2[e]	108.95	34.52	−58.51

[a] The aug-cc-pV sets are used on all three atoms. [b] Using the aug-cc-pV basis set on C as well as F yields 254.40 and 253.61 kcal/mol for the CCSD(T) n3{T,Q}Z and CCSD(T) n4{T,Q}Z approaches, respectively. [c] The CCSD(T)/CV, CCSD(T)-1s/CV, and ΔCV values for the CV(qz) basis set are 250.735, 252.375, and 1.640 kcal/mol, respectively. [d] The atomization energy is computed as CCSD(T) n4n6{T,Q,5}Z + ΔCV + spin orbit + ZPE + scalar relativistic. [e] The ΔH_{298} values are from Table 5, which are given for comparison.

TABLE 4: Scalar Relativistic Contribution to the Heat of Formation for CF, CF_2, CF^+, and CF_2^+, kcal/mol

	CF	CF_2	CF^+	CF_2^+
scalar rel	−0.168	−0.335	−0.115	−0.413
AE_{298}	131.05	254.87	180.46	250.09
ΔH_{298}[a]	59.21	−45.63	270.98	220.32
ΔH_{298} G3MP2	57.41	−47.08	271.26	220.53

[a] The previous values[22] corrected for scalar relativistic effects.

to determine our CCSD(T) CBS values. This is corrected for scalar relativistic, core-valence, and spin−orbit effects, as well as for the zero-point energy (ZPE). The correction from 0 to 298 K is made using the rigid rotor/harmonic oscillator approximation. The same procedure, excluding the scalar relativistic contribution to the atomization energy, was previously[22] used for CF, CF_2, CF^+, and CF_2^+. Therefore, in this work, we compute the scalar relativistic effects and add them to the previous atomization energies; this is summarized in Table 4.

In Tables 2−4, the accurate atomization energies are converted to heats of formation using the well-known heats of formation[2] for H, C, and F. The G3MP2 values are also given in Tables 2−4, and the G3MP2 values agree with the high-level calculations to better than 2 kcal/mol. The G3MP2 atomization energies are slightly larger than those found in the higher level calculations. We should note that Ruscic et al.[3] found that the G3 heats of formation for some carbon−halogen systems were about 1 kcal/mol more negative than experiment. Thus both the G3 and G3MP2 approaches appear to yield an atomization energy that is slightly too large.

The calibration calculations support the use of the G3MP2 approach for these systems. The G3MP2 atomization energies at 0 K and heats of formation, at both 0 and 298 K, are given in Table 5. Also included in Table 5 are the results of Gurvich et al.[1] In general, we report the G3MP2 results only for the most stable isomer; for a few systems we also report the results for more than one state or isomer in Table 5. For C_2, there are two low-lying states, and the G3MP2 approach correctly predicts a $^1\Sigma_g^+$ ground state. The $^3\Pi_u$ state is computed to be 4.38 kcal/mol higher in energy, which is to be compared with the experimental value[28] of 1.74 kcal/mol. For C_2F_2 and C_2F_4, we also report results for the CCF_2 and $FCCF_3$ isomers (which are higher in energy than FCCF and F_2CCF_2, respectively), since these can be produced by the fragmentation of C_3F_n species. For C_3F_2 and $C_3F_2^+$, we consider the two possible structures, FCCCF and $CCCF_2$. For FCCCF, we also consider both the singlet and triplet states. The most stable form is the singlet state of $CCCF_2$. It is interesting to note, however, that $FCCCF^+$ is more stable than $CCCF_2^+$. Starting from C_3F_8, two isomers of C_3F_7 can be formed by removing a F atom attached to the terminal or the central C. We consider both forms of C_3F_7, and for the neutral, we find that it is favorable to remove the F on

TABLE 5: G3MP2 Atomization Energies and Heats of Formation, in kcal/mol

	AE(0)	ΔH(0)	ΔH(298)	ΔH(298) (Gurvich[1])
CF	131.82	56.63	57.41	58.3 ± 2.4
CF^+	179.11	269.01	271.26	
CF_2	254.13	−47.21	−47.08	−43.0 ± 2.4
CF_2^+	247.67	218.92	220.53	
CF_3	336.75	−111.36	−111.99	−112.8 ± 1.2
CF_3^+	384.53	100.53	101.28	
CF_4	465.52	−221.66	−223.04	−223.0 ± 0.18
CF_4^+	388.20	115.33	116.40	
CH	81.73	139.88	140.70	
CH^+	94.16	387.12	389.42	
CHF	205.64	34.44	34.52	25.2 ± 6.0
CHF^+	231.37	268.38	269.94	
CHF_2	316.25	−57.70	−58.51	−60.7 ± 3.6
CHF_2^+	372.45	145.77	146.38	
CHF_3	441.91	−164.89	−166.52	−166.5 ± 0.6
CHF_3^+	387.05	149.64	150.82	
C_2 $^1\Sigma_g^+$	148.73	191.23	192.81	198.4 ± 2.4
C_2 $^3\Pi_u$	144.35	195.61	197.18	
C_2^+ $^4\Sigma_g^-$	131.31	468.32	471.38	479.2 ± 2.4
C_2F	250.70	107.73	108.95	92.9 ± 12.0
C_2F^+	178.73	439.37	441.56	
FC_2F	377.32	−0.42	0.03	−34.6 ± 4.8
CCF_2	347.30	29.60	29.88	
FC_2F^+	376.92	259.65	261.70	
CCF_2^+	353.51	283.06	284.87	
C_2F_3	448.80	−53.43	−53.57	−54.5 ± 4.8
$C_2F_3^+$	473.38	181.66	183.16	
C_2F_4	574.73	−160.89	−161.69	−157.6 ± 0.6
$FCCF_3$	536.82	−122.98	−123.61	
$C_2F_4^+$	598.98	74.53	75.25	
$FCCF_3^+$	551.10	122.41	123.37	
C_2F_5	646.36	−214.05	−215.29	−214.1 ± 1.4
$C_2F_5^+$	688.69	3.29	3.58	
C_2F_6	771.20	−320.42	−322.34	−321.2 ± 1.0
$C_2F_6^+$	734.50	−24.05	−23.87	
C_3	319.51	190.43	192.60	200.8 ± 3.1
C_3^+	272.08	497.53	501.05	
C_3F	394.73	133.68	135.20	
C_3F^+	443.27	344.81	347.66	
C_3F_2 ($CCCF_2$)	516.13	30.75	31.44	
C_3F_2 (FCCCF ^1A)	492.53	54.35	55.19	
C_3F_2 (FCCCF ^3B)	481.43	65.45	66.44	
$C_3F_2^+$ (FCCCF)	539.34	267.21	269.66	
$C_3F_2^+$ ($CCCF_2$)	512.35	294.20	296.33	
C_3F_3 ($FC{=}C{=}CF_2$)	597.67	−32.32	−31.94	
$C_3F_3^+$ ($FC{=}C{=}CF_2$)	667.79	157.23	158.74	
C_3F_4 ($F_2C{=}C{=}CF_2$)	715.74	−131.92	−132.34	
$C_3F_4^+$ ($F_2C{=}C{=}CF_2$)	735.06	108.43	109.44	
C_3F_5 ($F_2C{=}(CF){=}CF_2$)	775.84	−173.55	−174.11	
$C_3F_5^+$ ($F_2C{=}(CF){=}CF_2$)	851.82	10.14	10.63	
C_3F_6 ($F_3C(CF){=}CF_2$)	895.36	−274.60	−276.04	
$C_3F_6^+$ ($F_3C(CF){=}CF_2$)	907.21	−26.78	−26.59	
C_3F_7 ($F_3C(CF)CF_3$)	959.85	−320.62	−322.41	
C_3F_7 ($F_2C(CF_2)CF_3$)	953.10	−313.87	−315.64	
$C_3F_7^+$ ($F_2C(CF_2)CF_3$)	997.85	−98.95	−99.19	
$C_3F_7^+$ ($F_3C(CF)CF_3$)	984.27	−85.37	−85.58	
C_3F_8 ($F_3C(CF_2)CF_3$)	1077.23	−419.53	−422.00	
$C_3F_8^+$ ($F_3C(CF_2)CF_3$)	1043.93	−126.56	−126.89	

the central carbon, while for the cation it is more favorable to remove the F on the terminal carbon atom.

The heats of formation of CF_4, CF_3, CF_3^+, C_2F_4, and $FCCF_3$ in Table 5 agree well with the high-level calculations of Dixon et al.[4] The largest difference is 2.5 kcal/mol for CF_3^+ and the second largest difference is 1.1 kcal/mol for C_2F_4. This is not surprising since their high-level computational approach is very similar to our high-level calibration calculations. Our results agree to within 2 kcal/mol with the results of Zachariah et al.[5] for CF, CF_2, CF_3, CF_4, CHF_2, CHF_3, C_2F, C_2F_3, C_2F_5, and C_2F_6. For CHF, C_2F_2, and C_2F_4, we differ by 3.0, 7.6, and 5.5 kcal/mol, respectively. For these three systems they assign error bars of ±3.9, ±6.5 and ±4.0 kcal/mol. Since the G3MP2 has an error bar of ±2 kcal/mol, even for these systems, the two methods agree to within their mutual uncertainties. Our high-level calibration calculations support our values over those of Zachariah et al.

The agreement between theory and the work of Gurvich et al.[1] is somewhat mixed. For the species with one carbon atom, theory and experiment are in good agreement for all systems except CF_2 (N.B. that the Gurvich et al. value for CHF is only an estimate). The high-level treatment for CF_2 (−45.6 kcal/mol) is at the lower limit of the experimental value (−43.0 ± 2.4 kcal/mol), suggesting that the G3MP2 value is about 2 kcal/mol too negative. That is, the true result probably lies between experiment and the G3MP2 value. The high-level calculations for CHF yield a slightly larger value than the G3MP2 approach (35.8 vs 34.5 kcal/mol). Thus we conclude that the estimate is even less accurate than the large error bar would imply.

For the systems with two carbon atoms, the agreement between theory and experiment is not as good as found for the single carbon systems. For C_2 the G3MP2 and Gurvich values differ by 6 kcal/mol. Using a more recent[29] experimental atomization energy yields a C_2 heat of formation at 298 K of 196.3 kcal/mol, which shows that the Gurvich value is a bit too large but that the G3MP2 value is too small by 3.5 kcal/mol. While the error at the G3MP2 level is larger than the desired 2 kcal/mol accuracy, C_2 is known to be a very difficult problem. We note however, that high-level calculations[30] yield an atomization energy of 144.6 kcal/mol, which is in good agreement with the experimental[29] atomization energy of 145.2 ± 0.5 kcal/mol. Lowering the Gurvich C_2^+ result by 2 kcal/mol to account for the newer C_2 atomization energy still leaves the G3MP2 value about 6 kcal/mol too small.

The agreement between theory and experiment is good for C_2F_3, C_2F_5, and C_2F_6. The agreement for C_2F_4 is reasonable, but previous work,[6] which is summarized in Table 2, strongly suggests that the G3MP2 value is closer to the true value than is experiment, despite the small error bars on the experimental result. The experimental value for C_2F is poorly known and the G3MP2 value is 16 kcal/mol larger than experiment. The calibration value is slightly larger than the G3MP2 value. The experimental C_2F_2 value is 35 kcal/mol more negative than the G3MP2 value. The calibration calculations show that the experimental value must be wrong for C_2F and C_2F_2.

Ruscic and co-workers have determined the heats of formation at 298 K for CF_3 (−111.3 ± 0.5[3] and −111.4 ± 0.9[31]), CHF_3 (−165.6 ± 0.5 kcal/mol [3]), and C_2F_6 (−321.3 ± 0.8 kcal/mol [3]). These values differ slightly from those by Gurvich and hence are consistent with our G3MP2 values. We should note that these authors believe that the experimental value of C_2F_4 is in error by up to 2.5 kcal/mol, which is consistent with our results.

The experimental data for C_3F_n is very limited. Lias et al.[32] give −426 ± 2 kcal/mol for C_3F_8, which is in good agreement with the G3MP2 value of −422.0 kcal/mol. Theory and experiment differ by 8 kcal/mol for C_3. On the basis of C_2, we would not be surprised to find that the error in the G3MP2 result for C_3 exceeds the desired value of ±2 kcal/mol.

The ionization potentials (IPs) of some of the systems studied have been measured very accurately. In Table 6 we compare our computed G3MP2 IPs with those for systems where experiment is believed to be accurate. Excluding CHF_3 and C_3F_8, the computed values are 0.1−0.15 eV larger than experiment.[31,32] An error of this magnitude is consistent with an uncertainty of about 2 kcal/mol in the G3MP2 energies, but suggests that the errors in the neutrals and ions go in opposite

TABLE 6: A Comparison of the G3MP2 Ionization Potentials (in eV) with Experiment for Selected Systems

molecule	G3MP2	Expt[a]	molecule	G3MP2	expt[a]
CF	9.21	9.11 ± 0.01	C_2F_4	10.21	10.12 ± 0.02
CF_2	11.54	11.42 ± 0.01	C_2F_2	11.28	11.18
CF_3	9.19	9.05 ± 0.01[b]	C_3F_6	10.75	10.60 ± 0.03
CHF_3	13.64	13.86	C_3F_8	12.70	13.38

[a] From Lias et al.,[32] unless otherwise noted. [b] From Asher and Ruscic.[31]

TABLE 7: Selected Bond Energies for CF_n and CHF_n, in kcal/mol

reaction	bond energy	neutral analog
$CF_4^+ \rightarrow CF_3^+ + F$	3.67	128.77
$CF_3^+ \rightarrow CF_2^+ + F$	136.87	82.62
$CF_2^+ \rightarrow CF^+ + F$	68.55	122.31
$CF^+ \rightarrow C^+ + F$	179.11	131.82
$CHF_3^+ \rightarrow CHF_2^+ + F$	14.60	125.66
$CHF_2^+ \rightarrow CHF^+ + F$	141.08	110.62
$CHF^+ \rightarrow CH^+ + F$	137.21	123.91
$CHF_3^+ \rightarrow CF_3^+ + H$	2.51	105.16
$CHF_2^+ \rightarrow CF_2^+ + H$	124.78	62.13
$CHF^+ \rightarrow CF^+ + H$	52.25	73.81
$CH^+ \rightarrow C^+ + H$	94.16	81.73

directions or that the experimental error bars are somewhat optimistic. The computed values for CHF_3 and C_3F_8 are smaller than experiment. We suspect this is due to experiment not obtaining the adiabatic IP. For the saturated systems such as CF_4, CHF_3, and C_3F_8, the cations are weakly bound charge-induced dipole complexes; thus, CF_4^+ is $CF_3^+\cdots F$, CHF_3^+ is $CHF_2^+\cdots F$, and $C_3F_8^+$ is $C_3F_5^+\cdots CF_3$. For this type of complex, it would be difficult to obtain the adiabatic IP because of a very small Franck−Condon factor, and therefore, we believe that the best estimate for the adiabatic IP of these systems is 0.1 eV smaller than our computed value. Finally we should note that $C_2F_6^+$ is a $CF_3^+\cdots CF_3$ complex, but it is somewhat more bound than the other saturated systems, because of resonance charge exchange, i.e., $CF_3^+\cdots CF_3 \leftrightarrow CF_3\cdots CF_3^+$.

In conclusion, the calibration calculations support the view that on average the G3MP2 approach is accurate to ±2 kcal/mol. The accurate experimental results, excluding C_2 and C_2F_4, also support this view. Highly accurate calculations[6] for C_2F_4 support the accuracy of the G3MP2 approach. Experiment suggests that the errors in the G3MP2 treatment of C_2 are larger than 2 kcal/mol. It is possible that the error in the G3MP2 treatment of C_3 also exceeds 2 kcal/mol. Thus, excluding C_2 and C_3, the G3MP2 approach should yield the most complete and accurate set of data for the C_nF_m, $C_nF_m^+$, CHF_m, and CHF_m^+ systems.

Selected bond energies for CF_n, CF_n^+, CHF_n, and CHF_n^+ are reported in Table 7. While the first, second, and fourth C−F bonds in CF_n are similar, the third bond is weaker, because carbon must change hybridization to form three bonds. The trends for CF_n^+ are very different. CF^+ is much more strongly bound than CF, presumably due to F donation into empty C π orbitals. The second bond is much weaker since the C^+ has to hybridize to form a second bond. The third bond is strong, but not as strong as the first, probably because the electrostatic interaction for each bond is weaker since it is spread over three bonds. The fourth bond is weak, as C^+ only has three valence electrons. The results for CHF_n and CHF_n^+ are similar to those found for CF_n and CF_n^+. The only exception is for CH and CH^+, which have similar bond energies since hydrogen has no π lone pairs to donate to the carbon.

TABLE 8: Selected Bond Energies for C_2F_n, in kcal/mol

reaction	bond energy	neutral analog
$C_2F_6^+ \rightarrow C_2F_5^+ + F$	45.81	124.84
$C_2F_6^+ \rightarrow CF_3 + CF_3^+$	13.21	97.70
$C_2F_5^+ \rightarrow C_2F_4^+ + F$	89.71	71.63
$C_2F_5^+ \rightarrow CF_2 + CF_3^+$	50.03	55.48
$C_2F_4^+ \rightarrow C_2F_3^+ + F$	125.60	125.93
$C_2F_4^+ \rightarrow CF_2 + CF_2^+$	97.19	66.48
$C_2F_3^+ \rightarrow C_2F_2^+ + F$	96.46	71.47
$C_2F_3^+ \rightarrow CF_2 + CF^+$	40.14	62.85
$C_2F_2^+ \rightarrow C_2F^+ + F$	198.19	126.63
$C_2F_2^+ \rightarrow CF + CF^+$	65.99	113.68
$C_2F^+ \rightarrow C_2^+ + F$	47.42	101.97
$C_2F^+ \rightarrow C + CF^+$	−0.39	118.88

TABLE 9: Selected Bond Energies for C_3F_n, in kcal/mol

reaction	bond energy	neutral analog
$C_3F_8^+ \rightarrow C_3F_7^+(F_3C(CF)CF_3) + F$	59.66	117.38
$C_3F_8^+ \rightarrow C_3F_7^+(F_2C(CF_2)CF_3) + F$	46.08	124.13
$C_3F_8^+ \rightarrow C_2F_5^+ + CF_3$	18.49	94.11
$C_3F_8^+ \rightarrow C_2F_5 + CF_3^+$	13.03	
$C_3F_7^+(F_3C(CF)CF_3) \rightarrow C_3F_6^+ (F_3C(CF){=}CF_2) + F$	77.06	64.49
$C_3F_7^+(F_3C(CF)CF_3) \rightarrow CF_3^+ + FCCF_3$	62.92	86.28
$C_3F_7^+(F_3C(CF)CF_3) \rightarrow CF_3 + FCCF_3^+$	96.43	
$C_3F_7^+(F_2C(CF_2)CF_3) \rightarrow C_3F_6^+ + F$	90.64	57.74
$C_3F_7^+(F_2C(CF_2)CF_3) \rightarrow CF_3^+ + C_2F_4$	38.59	41.62
$C_3F_7^+(F_2C(CF_2)CF_3) \rightarrow CF_3 + C_2F_4^+$	62.12	
$C_3F_7^+(F_2C(CF_2)CF_3) \rightarrow CF_2^+ + C_2F_5$	103.82	52.61
$C_3F_7^+(F_2C(CF_2)CF_3) \rightarrow CF_2 + C_2F_5^+$	55.03	
$C_3F_6^+(F_3C(CF){=}CF_2) \rightarrow C_3F_5^+ (F_2C{=}(CF){=}CF_2) + F$	55.40	119.52
$C_3F_6^+(F_3C(CF){=}CF_2) \rightarrow CF_3^+ + C_2F_3$	73.88	109.81
$C_3F_6^+(F_3C(CF){=}CF_2) \rightarrow CF_3 + C_2F_3^+$	97.08	
$C_3F_6^+(F_3C(CF){=}CF_2) \rightarrow CF_2 + FCCF_3^+$	101.99	104.41
$C_3F_6^+(F_3C(CF){=}CF_2) \rightarrow CF_2^+ + FCCF_3$	122.73	
$C_3F_5^+(F_2C{=}C(CF){=}CF_2) \rightarrow C_3F_4^+(F_2C{=}C{=}CF_2) + F$	116.75	60.09
$C_3F_5^+(F_2C{=}C(CF){=}CF_2) \rightarrow CF_2^+ + C_2F_3$	155.35	72.92
$C_3F_5^+(F_2C{=}C(CF){=}CF_2) \rightarrow CF_2 + C_2F_3^+$	124.31	
$C_3F_4^+ \rightarrow C_3F_3^+ + F$	67.28	118.07
$C_3F_4^+ \rightarrow CF_2 + C_2F_2^+(CCF_2)$	127.43	114.31
$C_3F_4^+ \rightarrow CF_2^+ + C_2F_2(CCF_2)$	140.09	
$C_3F_3^+ \rightarrow FC_3F^+ + F$	128.45	81.54[a]
$C_3F_3^+ \rightarrow CF_2^+ + C_2F$	169.42	92.85
$C_3F_3^+ \rightarrow CF_2 + C_2F^+$	234.93	
$C_3F_3^+ \rightarrow CCF_2^+ + CF$	182.46	118.54
$C_3F_3^+ \rightarrow CCF_2 + CF^+$	141.37	
$FC_3F^+ \rightarrow C_3F^+ + F$	96.06	
$FC_3F^+ \rightarrow CF^+ + CCF$	135.48	
$FC_3F^+ \rightarrow CF + CCF^+$	134.22	
$C_3F_2 \rightarrow C_3F + F$		121.40
$C_3F_2 \rightarrow C + C_2F_2$		168.83
$C_3F_2 \rightarrow C_2 + CF_2$		113.28
$C_3F^+ \rightarrow C_3^+ + F$	171.19	75.21
$C_3F^+ \rightarrow CF^+ + C_2$	115.43	114.18
$C_3F^+ \rightarrow CF + C_2^+$	180.14	
$C_3F^+ \rightarrow C_2F^+ + C$	264.54	144.03
$C_3F^+ \rightarrow C_2F + C^+$	192.57	

[a] The neutral form is $CCCF_2$.

Selected bond energies for C_2F_n and $C_2F_n^+$ are reported in Table 8. One observation is that for $C_2F_n^+$ it is easier to break the C−C bond than a C−F bond. This is consistent with the appearance potentials[33] for C_2F_6, C_3F_6, and C_3F_8, which show a breaking of the C−C bonds before breaking of the C−F bonds. The breaking of the C−C bonds before the C−F bonds is even true for $C_2F_2^+$ and $C_2F_4^+$, which have C−C multiple bonding. For the neutrals, the C−C bonds are weaker than the C−F bonds, except for C_2F. To form multiple C−C bonds, CF_2 and CF must promote to the triplet and quartet states, respectively. This promotion energy is much larger for CF_2 and CF than the analogous promotion energies for CH_2 and CH, and therefore, the C−F bonds weaken the C−C π bonds. Thus it is far more favorable to break C−C multiple bonds in the C_xF_y systems than in the analogous C_xH_y systems.

Selected bond energies for C_3F_n and $C_3F_n^+$ are given in Table

9. For $C_3F_8^+$ and $C_3F_7^+$, breaking a C−C bond is easier than breaking a C−F bond. For the species with fewer F atoms, it tends to be easier to remove a F atom than to break a C−C bond; this is different from $C_2F_n^+$. For the neutrals, the species with an even number of F atoms tend to have stronger C−F bonds that C−C bonds, while those with an odd number of F atoms are open-shell systems, which would rather lose a F atom to become closed-shell than break a C−C bond.

The heat capacity, entropy, and temperature dependence of the heat of formation are computed for 300−4000 K using a rigid rotor/harmonic oscillator approximation. The scaled HF frequencies are used in these calculations. These results are fit in two temperature ranges, 300−1000 and 1000−4000 K using the Chemkin[34] fitting program and following their constrained three-step procedure. The parameters obtained from the resulting fits can be found on the Web.[35]

4. Conclusions

We have performed highly accurate calibration calculations for several species, which support the use of the G3MP2 approach. There is reasonable agreement between theory and experiment for most systems. The only obvious problems with the G3MP2 approach arise for C_2 and C_3, where the errors are about 4 and 6 kcal/mol, whereas the rest of the systems appear to be accurate to about ±2 kcal/mol. The heat capacity, entropy, and temperature dependence of the heat of formation are fit to 14 parameters that can be found on the Web.[35]

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