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Heats of Formation for CF_n ($n = 1-4$), CF_n^+ ($n = 1-4$), and CF_n^- ($n = 1-3$)

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Accurate heats of formation are computed for CF_n ($n = 1-4$), CF_n^+ ($n = 1-4$), and CF_n^- ($n = 1-3$). The geometries and vibrational frequencies are determined at the B3LYP level of theory. The energetics are determined at the CCSD(T) level of theory. Basis set limit values are obtained by extrapolation. In those cases where the CCSD(T) calculations become prohibitively large, the basis set extrapolation is performed at the MP2 level. The temperature dependence of the heat of formation, heat capacity, and entropy are computed for the temperature range 300−4000 K and fit to a polynomial.

I. Introduction

The CF_n species, and their ions, are involved in semiconductor processes as plasma etching reagents. To optimize such fabrication processes, accurate thermochemical data on the reacting species are required. Of these species, the CF_4 heat of formation[1−3] is the best known, with a maximum uncertainty of 0.4 kcal/mol. Recently, Asher and Ruscic[4] remeasured, by photoionization mass spectrometry, the CF^+ and CF_3^+ fragment ion yield curves and reported a CF_3 heat of formation of -111.4 ± 0.9 kcal/mol and a CF_3^+ heat of formation of 97.4 ± 0.9 kcal/mol. From data on C_2F_4, they deduced a CF heat of formation of 62.5 ± 1.1 kcal/mol. While for CF_4 the agreement between the available experimental heats of formation is very good, for CF and CF_2, the experimental values can differ by as much as 5 kcal/mol. For the corresponding cations, the differences are even larger, and for the anions, only a few experimental values are reported. The Lias et al.[3] recommended value for the CF_3^- heat of formation is -154.88 ± 2.4 kcal/mol, while for CF^-, no value is reported due to a large uncertainty associated with the experimental electron affinity (EA) of CF measured by Thynne and MacNeil.[5]

Xie and Schaefer[6] computed the EA of CF, and they estimated the true adiabatic EA to be 0.45 ± 0.05 eV. The adiabatic EA of CF_2 has been measured by Lineberger and co-workers,[7] and they reported a value of 0.179 ± 0.005 eV. While the EA of CF and CF_2 have been established to within 0.05 eV or better, the uncertainty associated with the EA of CF_3 is at least 0.1 eV. The recommended value by Lias et al.[3] for the EA of CF_3 is 1.84 ± 0.16 eV, while Schaefer and co-workers[8] computed a value of 1.78 ± 0.1 eV.

Given the uncertainty in the heats of formation and electron affinities, it is useful to study these species using higher levels of theory. We use the coupled cluster singles and doubles approach,[9] including a perturbational estimate of the triple excitations,[10] CCSD(T), in conjunction with extrapolation to the complete basis set (CBS) limit. Unfortunately, it is not straightforward to apply this level of theory to systems such as CF_3 and CF_4, and for these systems, we estimate the CCSD(T) CBS values[11] using the ratio of the CCSD(T) and MP2[12] results, in the largest basis set where both calculations were possible, and the MP2 CBS limit value.

TABLE 1: Geometries of CF_n ($n = 1-4$), CF_n^+ ($n = 1-4$), and CF_n^- ($n = 1-3$) Computed at the B3LYP/6-311+G(2df) Level of Theory

	r (C−F)	∠(FCF)
CF $^2\Pi$ ($C_{\infty v}$)	1.275	
CF_2 $^1A_1$ (C_{2v})	1.303	104.79
CF_3 $^2A_1$ (C_{3v})	1.320	111.40
CF_4 $^1A_1$ (T_d)	1.325	109.47
CF^+ $^1\Sigma^+$ ($C_{\infty v}$)	1.155	
CF_2^+ $^2A_1$ (C_{2v})	1.218	124.73
CF_3^+ $^1A_1'$ (D_{3h})	1.235	120.00
CF_4^+ $^2A'$ (C_s)	2.529 (F_2)	89.99 ($F_2C_1F_3$)
	1.236 (F_3)	91.62 ($F_2C_1F_4$)
	1.236 (F_4)	119.97 ($F_3C_1F_4$)
	1.236 (F_5)	119.96 (F_4 C_1F_5)
CF^- $^3\Sigma^-$ ($C_{\infty v}$)	1.434	
CF_2^- $^2B_1$ (C_{2v})	1.443	100.50
CF_3^- $^1A_1$ (C_{3v})	1.432	99.90

II. Methods

Geometries are optimized using density functional theory (DFT), in conjunction with the hybrid[13] B3LYP[14] approach. We first use the 6-31G* basis set[15] to optimize all the structures, but the lack of diffuse functions leads to bond lengths that are somewhat too long for the anions. Our final geometries are computed using the 6-311+G(2df) basis set,[15] and all the results are reported using these structures. The zero-point energy is computed as one-half the sum of the B3LYP/6-31G* harmonic frequencies, which are not scaled.

For open-shell molecules, energetics are computed using the restricted coupled cluster singles and doubles approach,[9,16] including the effect of connected triples determined using perturbation theory,[10,17] RCCSD(T). In these RCCSD(T) calculations, only the valence electrons (the C 2s and 2p and F 2s and 2p) are correlated. We use the augmented correlation consistent polarized valence (aug-cc-pV) sets developed by Dunning and co-workers,[18−20] namely the triple-ζ (TZ), quadruple-ζ (QZ), and quintuple-ζ (5Z) sets, as they appear to extrapolate consistently for all the extrapolation schemes.

To improve the accuracy of the results, several extrapolation techniques are used. We use the two-point (n^{-3}) scheme described by Helgaker et al.[21] We also use the two-point (n^{-4}), three-point ($n^{-4} + n^{-6}$), and variable α ($n^{-\alpha}$) schemes described by Martin.[22] Unfortunately, it is not possible to perform the RCCSD(T) calculations in the aug-cc-pVQZ and aug-cc-pV5Z basis sets for the largest systems; therefore, MP2 calculations

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TABLE 2: Extrapolated Dissociation Energies (in kcal/mol)

basis set	n^{-3} TZ,QZ	n^{-3} QZ,5Z	n^{-4} TZ,QZ	n^{-4} QZ,5Z	$n^{-4} + n^{-6}$ TZ,QZ,5Z	variable α[a] TZ,QZ,5Z
C−F	132.83	132.37	132.45	132.21	132.13	132.09 (4.790)
C$^+$−F	182.75	182.17	182.32	182.00	181.89	181.85 (4.932)
C−F$^-$	62.78	62.56	62.63	62.50	62.45	62.44 (5.082)
CF−F	126.61	126.20	126.32	126.09	126.01	125.98 (5.048)
CF$^+$ −F	72.50	72.08	72.25	71.99	71.90	71.88 (5.386)
CF$^-$−F	119.45	119.05	119.17	118.94	118.86	118.83 (5.068)

[a] The α values are reported in parentheses.

are performed using the correlation consistent sets to help in the extrapolation of the RCCSD(T) results to the basis set limit. Core−valence (CV) calculations are performed by adding the C 1s and F 1s electrons to the correlation treatment. Three core-valence basis sets are developed and are denoted CV(tz), CV(qz), and CV(5z). They are derived from the corresponding aug-cc-pV sets by contracting the first five (CV(tz)), six (CV(qz)), and seven (CV(5z)) s primitives to one function, for both C and F. For all three basis sets, the rest of the s functions and all of the p functions are uncontracted. Three even-tempered tight d and two even-tempered tight f functions are added to both C and F, for all three basis sets. A β value of 2.5 is used for the d functions and a value of 3.0 is used for the f functions. The α values are the tightest existing exponents. The CV effect is computed as the difference between correlating only valence electrons and correlating the valence plus inner-shell electrons, with both calculations performed using the CV basis sets and corrected for BSSE. The RCCSD(T) are performed using Molpro 96,[23] while all other calculations are performed using Gaussian94.[24]

The effect of spin−orbit coupling on the dissociation energy is computed using experiment. For CF, the spin−orbit effect is taken as half the splitting between the $^2\Pi$ sublevels given in Huber and Herzberg.[25] For all the other systems, the spin−orbit effect is obtained by using the accurately known spin−orbit splittings in the atoms[26] and we use the difference between the lowest m_j component and the m_j weighted average energy.

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. We include the effect of electronic excitation for the atoms using the data from Moore[26] and the two sublevels of the CF $^2\Pi$ state. These results are fit in two temperature ranges, 300−1000 K and 1000−4000 K using the Chemkin[27] fitting program and following their constrained three-step procedure.

III. Results and Discussion

The geometries of CF$_n$ (n = 1−4), CF$_n^+$ (n = 1−4), and CF$_n^-$ (n = 1−3) are reported in Table 1. Before discussing the computed bond energies, we compare extrapolated dissociation energies, obtained by different extrapolation schemes, and we report them in Table 2. All the extrapolation schemes give consistent results, which confirms that the aug-cc-pV basis sets are of systematic quality. The two-point Martin (n^{-4}) TZ,QZ results tend to be slightly larger than the three-point Martin and variable α results, but the agreement is good. The two-point Helgaker (n^{-3}) TZ,QZ results are in less good agreement with the three-point Martin and variable α results.

TABLE 3: Computed Bond Energies (in kcal/mol), without Zero-Point Energies[a]

	method	ATZ	AQZ	A5Z	CBS[b]	α[c]
C−F	CCSD(T)	128.57	131.03	131.69	132.11	4.790
CF−F	CCSD(T)	123.41	125.26	125.72	126.00	5.048
CF$_2$−F	CCSD(T)	84.61			(85.95)	
	MP2	93.53	94.75	94.94	95.00	6.888
CF$_3$−F	CCSD(T)	130.96			(132.98)	
	MP2	137.53	139.14	139.49	139.65	5.686
C$^+$−F	CCSD(T)	177.91	180.71	181.42	181.87	4.932
CF$^+$−F	CCSD(T)	69.71	71.32	71.69	71.89	5.386
CF$_2^+$−F	CCSD(T)	139.72	141.51		(142.16)	
	MP2	146.63	148.46	148.90	149.15	5.211
CF$_3^+$−F	CCSD(T)	4.23			(3.99)	
	MP2	3.38	3.27		3.19[d]	
C−F$^-$	CCSD(T)	61.05	62.05	62.30	62.45	5.082
CF$^-$−F	CCSD(T)	116.33	118.13	118.58	118.85	5.068
CF$_2^-$−F	CCSD(T)	121.85			(124.02)	
	MP2	129.28	130.79	131.24	131.58	4.278

[a] The CCSD(T) values in parentheses are estimated using the MP2 CBS results. [b] Average of the three-point Martin ($n^{-4} + n^{-6}$) and variable α extrapolated values. [c] The α value is obtained by variable α extrapolation. [d] Computed using the ATZ and AQZ values in conjunction with the two-point Martin (n^{-4}) extrapolation.

TABLE 4: Computed Bond Energies (in kcal/mol) Corrected for Core−Valence Effects, Spin−Orbit Effects, Zero-Point Energy, and Thermal Effects

	D_e CBS[a]	CV	SO	ZPE	thermal	D_{298}
C−F	132.11	0.32	−0.36	−1.88	1.04	131.23
CF−F	126.00	0.11	−0.39	−2.48	1.16	124.40
CF$_2$−F	85.95	0.55	−0.39	−3.26	1.27	84.12
CF$_3$−F	132.98	0.11	−0.39	−3.12	1.25	130.83
C$^+$−F	181.87	0.69	−0.39	−2.55	1.07	180.69
CF$^+$−F	71.89	0.67	−0.39	−2.71	1.16	70.62
CF$_2^+$−F	142.16	0.35	−0.39	−3.82	1.36	139.66
CF$_3^+$−F	3.99	0.03	−0.39	−0.42	0.29	3.50
C−F$^-$	62.45	0.24	−0.09	−1.14	0.92	62.39
CF$^-$−F	118.85	0.11	−0.39	−1.84	1.05	117.78
CF$_2^-$−F	124.02	0.06	−0.39	−2.78	1.23	122.14

[a] Taken from Table 3.

The computed and extrapolated bond energies are reported in Table 3. The CBS values for CF$_3$ and CF$_4$ are estimated using the ratio of the CCSD(T) and MP2 results, in the largest basis set where both calculations were possible, and the MP2 CBS limit value. To justify the validity of this approach we focus on the CF$_2$ system, for which a CCSD(T) CBS value of 126.0 kcal/mol has been obtained. The estimated CBS value obtained using the CCSD(T) TZ, MP2 TZ, and MP2 CBS values is 125.95 kcal/mol. The excellent agreement between the two values supports the validity of the approach mentioned above for large systems. The CCSD(T) extrapolated results obtained by the three-point ($n^{-4} + n^{-6}$) scheme are in very good agreement with the results obtained by the variable α ($n^{-\alpha}$) scheme, and the reported CBS value is the average between the two extrapolated results. The α values are higher than the recommended value of 4.5,[28] but the good agreement between the different extrapolation results is an indication that the extrapolations are reliable. For all the systems, except for CF$_4^+$, the bond energies increase when the basis set size increases. The very small CF$_4^+$ bond energy has a larger uncertainty, but it clearly indicates that CF$_4^+$ is not sufficiently stable to be involved in the etching process.

TABLE 5: Heats of Formation (in kcal/mol) at 298 K

	PW[a]	Melius[30]	JANAF[1]	Lias[3]	other
CF_4	[−223.04]	[−223.26][b]	−223.04 ± 0.3	−223.4 ± 0.1	−223.00 ± 0.1[c]
CF_3	−111.18	−112.79	−112.40 ± 1.0	−110 ± 1.0	−111.71 ± 2.0[d], −111.4 ± 0.9[e]
CF_2	−46.03	−48.59	−43.50 ± 1.5	−49 ± 3.0	−44.60 ± 1.5[f]
CF	59.40	56.48	60.99 ± 1.9	61.0 ± 2.0	57.48 ± 2.4[g], 62.5 ± 1.1[e]
C	171.66		171.29 ± 0.1	171.3	
C^+	[432.47]		432.47	431.0	
CF^+	270.75		274.71 ± 1.2	271.1	
CF_2^+	219.10		225.09 ± 3.0	214	
CF_3^+	98.41		100.62 ± 2.8	95.4	97.4 ± 0.9[e]
F^-	[−60.97]		−60.97		
CF^-	47.93				
CF_2^-	−50.88				
CF_3^-	−154.05			−154.88 ± 2.4	

[a] Present work. The values in square brackets are taken from JANAF[1] as is the F heat of formation (18.97 at 298 K). [b] The BAC parameters for C−F bonds are based on calibration with CF_4. [c] Reference 2. [d] Reference 29. [e] Reference 4. [f] Reference 31. [g] Reference 32.

The extrapolated D_e values (D_e CBS) are corrected for CV effects, spin−orbit effects, zero-point energy, and thermal effects to obtain the bond energies at 298 K (D_{298}) reported in Table 4.

The CV effect decreases going from the smallest systems, CF, CF^+, and CF^-, to the largest ones, until rehybridization occurs. At this point, the CV effect either increases or remains constant. After the rehybridization has occurred, the CV effect continue to decrease.

For the neutrals, the largest C−F bond energy is for CF. The bond energy decreases slightly going from CF to CF_2 due to some repulsion between the fluorine atoms. For CF_3, the bond energy drops significantly due to the rehybridization required to form three C−F bonds. The bond energies for CF and CF_4 are very similar, as CF_4 has a tetrahedral geometry reducing the repulsion between the fluorine atoms. The distance between the fluorine atoms is 2.064 Å, for CF_2, while for CF_4, it is 2.164 Å.

For the cations, the drop in the bond energy occurs for CF_2^+ because the rehybridization occurs when the second fluorine atom is added. The bond energy increases for CF_3^+ as for CF_4. The CF_4^+ system is very weakly bound and consists of CF_3^+ + F with the "extra" fluorine atom at a distance of 2.53 Å from the carbon atom.

For the anions, there is no drop in bond energy since three unpaired electrons are available on the carbon atom to form three C−F bonds. The bond energy increases going from CF^- to CF_3^-. For CF^-, the bond energy is considerably smaller than for CF_2^- and CF_3^-. The loss in exchange energy is the largest when adding the first fluorine atom and it reduces the CF^- bond energy.

The bond energies at 298 K (D_{298}) are used, in conjunction with the experimental heat of formation (at 298 K) of CF_4 (−223.04 kcal/mol),[1] of F (18.97 kcal/mol),[1] of C^+ (432.47 kcal/mol),[1] and of F^- (−60.97 kcal/mol),[1] to compute the heats of formation reported in Table 5. Our CF_3 value of −111.18 kcal/mol is in very good agreement with the recent value of −111.4 ± 0.9 kcal/mol measured by Asher and Ruscic[4] and is close to the value of −111.71 ± 2.0 kcal/mol reported by McMillen and Golden.[29] The JANAF value of −112.40 ± 1.0 kcal/mol and Melius and co-workers[30] value of −112.79 kcal/mol appear to be slightly overestimated. Our CF_2 value of −46.03 kcal/mol is within the error bar of the value of −44.60 ± 1.5 kcal/mol by Rodgers[31] and the value of −49 ± 3.0 kcal/mol by Lias.[3] Melius[30] value of −48.59 kcal/mol is close to the Lias[3] value and larger than most of the values. The JANAF value of −43.50 ± 1.5 kcal/mol appears to be too small. Our CF value of 59.40 kcal/mol is within the error bars of all the experimental values,[1,3,32] except for the Asher and Ruscic[4] value of 62.5 ± 1.1 kcal/mol, which seems to be overestimated. On the other hand, Melius[30] value of 56.48 kcal/mol appears to be too small. Our heat of formation of C is in very good agreement with the JANAF value and confirms that our atomization energy of CF_4 is accurate. Because we expect similar accuracies for all bonds in the neutrals, this observation supports the general accuracy of our heats of formation. For the cations, the experimental error bars are larger than for the neutrals, and the experimental values can differ by as much as 10 kcal/mol. Our CF^+ value of 270.75 kcal/mol is close to the Lias value, while for CF_2^+ our value of 219.10 kcal/mol is between the JANAF and the Lias values. For CF_3^+, our value of 98.41 kcal/mol is in good agreement with the value of 97.4 ± 0.9 kcal/mol obtained by Asher and Ruscic.[4] For the anions, few experimental data are available due to large uncertainties in the experimental EAs. Our CF_3^- value of −154.05 kcal/mol is in good agreement with the Lias recommended value of −154.88 ± 2.4 kcal/mol.

TABLE 6: Adiabatic Electron Affinities (in eV)

	present work	Schaefer	expt
CF_3	1.83	1.78 ± 0.10[a]	1.84 ± 0.16[b]
CF_2	0.15		0.179 ± 0.005[c]
CF	0.43	0.45 ± 0.05[d]	

[a] Reference 8. [b] Reference 3. [c] Reference 7. [d] Reference 6.

In Table 6, we summarize our computed EA values along with the computed values by Schaefer and co-workers and with experiment. Our CF_3 EA is in very good agreement with the recommended value by Lias and is within the error bar of Schaefer's value. For CF_2, our value is 0.029 eV smaller than experiment, but the agreement is still good. Our CF EA is in very good agreement with Schaefer's result.

We use our computed heats of formation at 298 K and the B3LYP geometries and frequencies to evaluate the heat capacity, entropy, and heat of formation from 300 to 4000 K. The parameters obtained from the resulting fits can be found on the web.[33]

IV. Conclusions

The bond energies of CF_n (n = 1−4), CF_n^+ (n = 1−4), and CF_n^- (n = 1−3) are computed using the CCSD(T) results, which have been extrapolated to the complete basis set limit. High accuracy is achieved by taking into account core−valence correlation effects, spin−orbit effects, zero-point energy, and thermal effects. The resulting bond energies at 298 K are used, in conjunction with the accurately known heats of formation of CF_4, F, C^+, and F^-, to obtain the heats of formation of all the remaining systems. The temperature dependence of the heat of formation, heat capacity, and entropy are computed and fit to the standard 14 coefficients,[27] which are available on the web.[33]

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