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Heats of Formation of CF_2, FCO, and CF_2O

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The heat of formation of CF_2O has been calculated at high levels of ab initio molecular orbital theory. The best values were obtained by extrapolating CCSD(T) energies obtained from the correlation consistent basis sets, up through augmented quadruple-ζ, to the complete basis set limit. Core/valence corrections were obtained from basis sets designed to recover such effects. Zero-point energies were taken from experiment, and missing values were calculated at the MP2/cc-pVTZ level and scaled to approximate experimental values. The calculated $\Delta H_f°$ values are CF $= -58.2 \pm 0.5$ kcal/mol, $CF_2 = -46.6 \pm 0.7$ kcal/mol, FCO $= -44.1 \pm 0.5$ kcal/mol, and $CF_2O = -145.2 \pm 0.8$ kcal/mol.

Introduction

Accurate heats of formation of simple compounds are essential building blocks for group additivity methods used for deriving heats of formation for larger systems. They also serve as convenient benchmarks for assessing the accuracy of new computational methods.[1] Compared with compounds formed from other second-period elements, fewer reliable heats of formation are available for fluorine compounds because of the practical difficulties associated with handling fluorine and the scarcity of reliable heats of formation for standards such as NaF, although a few have recently become available.[2,3] One such fluorinated compound which plays a role in atmospheric chemistry, flame suppression, and in the chemical industry is carbonyl fluoride, CF_2O. The heat of formation of this compound has proven to be a difficult quantity to measure. Standard tables[1,4] give experimental values that differ from high-level ab initio calculations by as much as 8 kcal/mol.[5,6] A recent photoionization study[7] reported a value for $\Delta H_f°(CF_2O)$ that fell somewhere between the available theoretical values in the literature and the earlier experimental data. We note that the study of Montgomery et al.[5] gave four different estimates for $\Delta H_f°(CF_2O)$. One was based on atomization energies ($\sum D_e$) obtained from the Gaussian-2 procedure. The second estimate resulted from complete basis set (CBS) quadratic configuration interaction (QCI) calculations based on atomic-pair natural orbitals (APNO).[8,9] Finally, the last two were based on an isodesmic reaction energy with these two methods. A final heat of formation was obtained by essentially averaging the various values.

The present study is part of a long-term project focused on the development of accurate methods for predicting a variety of thermodynamic quantities, including heats of formation, without recourse to empirical parameters. Such parameters might unnecessarily restrict the scope of the methodology to chemical systems similar to those used to derive the parameters. The current approach to computing reaction energies combines existing, reliable energies (from either experiment or theory) with newly calculated values obtained from levels of theory that have been demonstrated to yield high accuracy for well-characterized systems.[10−14] Primary energetics are obtained from highly correlated methods, such as multireference configuration interaction (MR-CI) and coupled-cluster theory with single and double excitations and a perturbative estimate of the effect of triple excitations (CCSD(T)).[15] One-particle basis sets are chosen from the correlation consistent[16] sequence of Gaussian basis sets, which facilitate effective extrapolations to the complete basis-set limit. MR−CI and CCSD(T) are capable of recovering a large fraction (>98%) of the empirical valence correlation energy for first- and second-period elements. Energetic corrections due to core/valence correlation are also applied. While these are small in an absolute sense, they are still significant in terms of the 1 kcal/mol or better accuracy we are trying to achieve. The evidence to date suggests that CCSD(T) is capable of predicting most atomization energies of compounds composed of H−Ar to better than 1 kcal/mol accuracy.[13]

Our approach differs from the Gaussian-1 (G1)[17] and Gaussian-2 (G2)[18] procedures, which attempt to compute energetics with an accuracy comparable to a quadratic configuration-interaction calculation performed with a 6-311+G(2df,p) basis set. Both of the Gaussian-*x* methods make assumptions about the additivity of basis-set and correlation corrections. They also include a “higher-order” empirical correction to minimize the error with respect to a body of reliable experimental atomization energies. The only empirical scaling that enters into our approach is in the treatment of the theoretical zero-point vibrational energies (ZPEs), when reliable experimental values are not available. A practical disadvantage of the present approach, compared to G1 and G2, is the significant increase in computer time required. As a consequence, current hardware limits the range of applicability of the procedures in this work to chemical systems with fewer than six second- and third-period atoms. Several time-saving approximations that can be exploited without severely impacting the accuracy of the energetics will be discussed.

Methods

Geometries and harmonic frequencies were obtained at the frozen core, second-order Møller−Plesset (MP2) level of perturbation theory[19] with the cc-pVTZ basis, since this level of theory is economical enough to apply to relatively large systems. In previous work,[20] the use of MP2 geometries, as

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opposed to more expensive CCSD(T) geometries, proved to have a minimal effect on the computed energetics. To further test the impact of MP2/cc-pVTZ geometries, we have carried out a limited number of CCSD(T) optimizations in the present work. Calculated harmonic frequencies were used to augment the available experimental values. CCSD(T) calculations, at either the MP2/cc-pVTZ or optimal CCSD(T) geometries, were performed with the correlation consistent basis sets (cc-pVxZ for x = D, T, Q corresponding to the double, triple, and quadruple-ζ levels). This collection of basis sets was shown to be a good compromise set based on earlier calculations. As a further test of basis-set convergence, selected calculations were also performed with the diffuse-function-augmented sequence aug-cc-pVxZ, x = D, T, Q.[16] Only the spherical components (5d, 7f, and 9g) of the Cartesian basis functions were used.

Calculations were performed with the Gaussian-94[21] and MOLPRO-96[22] programs on Silicon Graphics PowerChallenge compute servers and Cray vector supercomputers. Unless otherwise noted, the 1s inner-shell electrons of the carbon, oxygen, and fluorine atoms were treated as frozen cores, i.e., they were excluded from the correlation treatment.

There are currently three widely used CCSD(T) approaches for handling open-shell systems. One approach begins with restricted open-shell Hartree−Fock (ROHF) orbitals and maintains the spin restriction throughout the coupled cluster calculation. We will denote this approach as RCCSD(T). A second approach also uses ROHF orbitals but relaxes the spin constraint in the coupled-cluster portion of the calculation. Energies obtained from this hybrid procedure are denoted R/UCCSD(T).[23] A third choice is to base the CCSD(T) calculation on unrestricted Hartree−Fock (UHF) orbitals, leading to what we will refer to as UCCSD(T). It should be noted that although R/UCCSD(T) uses ROHF orbitals, it does allow a limited amount of spin relaxation in the coupled-cluster calculation. Atomic energies for C (^{3}P), O(^{3}P), and F(^{2}P) are listed in Table A1 (Appendix). With the aug-cc-pVQZ basis set, the UCCSD(T) − RCCSD(T) differences amount to 0.17 (C), 0.26 (O), and 0.15 (F) kcal/mol and the R/UCCSD(T) − UCCSD(T) differences are much smaller. While these differences in energy are small on a per-atom basis, they are nonetheless significant when attempting to compute the atomization energy of polyatomic species with an accuracy of ∼1 kcal/mol. Benchmark full configuration-interaction calculations of some representative atomization energies, carried out with basis sets of sufficient quality, would be helpful in judging which of the three CCSD(T) approaches for open-shell systems yields the most accurate results. In the present work, we will report results from both R/UCCSD(T) and UCCSD(T) calculations.

To estimate properties at the CBS limit, we used a variety of two- and three-parameter functional forms. The first was an exponential of the form

$$F(x) = A_{\mathrm{CBS}} + B\exp(-Cx) \tag{1}$$

where, in general, A_{CBS}, B, and C are determined by a nonlinear least-squares fit and x = 2, 3, 4 for the DZ, TZ, and QZ basis sets.[24] Values estimated by this procedure will be denoted CBS(DTQ/e^{-x}) or denoted CBS(aDTQ/e^{-x}) if the augmented sets are used. We also used a mixed exponential/Gaussian function

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

which was first proposed by Peterson et al.[25] Results based on eq 2 will be denoted CBS(aDTQ/mix). An alternative expression based on the asymptotic limit of the MP2 two-electron cusp[26] is given by

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

where l_{max} is the maximum l value for the basis set (l = 0, 1, 2, ... for s, p, d, etc.).[27] In the present work, we used eq 3 to fit results from TZ and QZ basis sets, ignoring the DZ values since their inclusion in the fitting procedure produces noticeably poorer CBS estimates. These results are denoted throughout the text as CBS(TQ/l_{max}).

TABLE 1: CH ($^2\Pi$) UCCSD(T) Results[a]

basis set	energy (E_h)	R_e (Å)	ω_e (cm^{-1})	D_e
aug-cc-pVDZ	−38.387315	1.1400	2815.6	77.30
aug-cc-pVTZ	−38.412817	1.1219	2843.7	82.30
aug-cc-pVQZ	−38.419623	1.1202	2853.2	83.33
CBS(aDTQ/e^{-x})	−38.4221[c]	1.1199	2858.1	83.5
CBS(aTQ/l_{max})	−38.4235			83.9
CBS(aDTQ/mix)	−38.4233			83.8
CBS(aDTQ/e^{-x})/CVQZ				83.7
CBS(TQ/l_{max})/CVQZ				84.1
CBS(aDTQ/mix)/CVQZ				84.0
exp.[b]		1.1199	2858.5	(83.9)

[a] D_e (kcal/mol) was computed with respect to UCCSD(T) atoms. For comparison purposes, Peterson and Dunning, ref 14 reported a frozen-core RCCSD(T) CBS (exp) value for D_e of 83. 6 kcal/mol. Adding their core/valence correction of 0.13 kcal/mol yields a final RCCSD(T) value of 83.7 kcal/mol. [b] Huber and Herberg, ref 28. D_e includes a 0.04 kcal/mol spin−orbit correction to make the experimental value more directly comparable to the present theoretical values. [c] Feller and Peterson, ref 13.

CBS dissociation energies can be obtained by subtracting the individually extrapolated CBS atomic energies from the extrapolated energy of the molecule or by directly extrapolating the D_e values. Differences are typically small (≤0.1 kcal/mol). In this work, we have adopted the former approach.

Unless otherwise noted, core/valence corrections to the dissociation energy were obtained from fully correlated CCSD(T) calculations with the cc-pCVTZ basis set[16] at the optimized MP2 geometries. Selected comparisons were made with core/valence corrections determined at the optimal CCSD(T)/aug-cc-pVTZ geometry using the larger cc-pCVQZ basis set. In previous work, these two approaches to estimating the core/valence correction differed by ∼20% or less.

Results

CH, CH$_2$, CH$_4$, HCO, and CH$_2$O. To calibrate our approach, we have calculated the heats of formation of some simple compounds containing C, H, and O using total atomization energies. These include CH ($^2\Pi$), CH$_2$ (^{3}B$_1$), CH$_4$ (^{1}A$_1$), CH$_2$O (^{1}A$_1$), and HCO(^{2}A′). The first three of these have been studied previously by Peterson and Dunning[14] using the RCCSD(T) method and the cc-pVxZ sequence of basis sets. They reported a core/valence CBS D_e for CH of 83.7 kcal/mol. Although the atomization energies for CH$_2$ and CH$_4$ were not given by Peterson and Dunning, it is possible to compute these numbers from the total energies provided in their tables or by adding the appropriate entries in their Table 1.

Table 1 contains the results of the present UCCSD(T) calculations on CH. Bond lengths and harmonic frequencies are in good agreement with the values listed by Huber and Herzberg.[28] The spread in D_e among the three CBS extrapolations is only 0.4 kcal/mol (83.7−84.1). If we combine the CBS(aDTQ/mix)/CVQZ value of 84.00 kcal/mol with a −0.04 kcal/

TABLE 2: CH_2 ($^3B_1$) UCCSD(T) Results

				harmonic normal modes			
basis set	energy (E_h)	R_{CH}	∠HCH	a_1	a_1	b_2	$\sum D_e$
aug-cc-pVDZ	−39.046049	1.0943	133.1	1104.6	3114.4	3342.2	178.72
aug-cc-pVTZ	−39.080081	1.0791	133.6	1090.6	3134.4	3359.2	187.38
aug-cc-pVQZ	−39.088071	1.0775	133.7	1097.8	3157.9	3384.0	189.07
CBS(aDTQ/e^{-x})	−39.0908[c]	1.0772	133.7				189.4
CBS(aTQ/l_{max})	−39.0927						190.1
CBS(aDTQ/mix)	−39.0923						189.9
CBS(aDTQ/e^{-x})/CVQZ							190.1
CBS(TQ/l_{max})/CVQZ							190.8
CBS(aDTQ/mix)/CVQZ							190.7
exp.[b]		1.0748	133.8	1080.	3090.	3220.	(190.2)

[a] $\sum D_e$ (kcal/mol) was computed with respect to UCCSD(T) atoms. Bond lengths are in angstroms, and angles are in degrees. Frequencies are in cm^{-1}. The experimental frequencies correspond to harmonic frequencies. [b] Jensen et al., ref 30. $\sum D_e$ includes a 0.08 kcal/mol spin−orbit correction to make the experimental value more directly comparable to the present theoretical values. [c] Feller and Peterson, ref 13.

TABLE 3: CH_4 ($^1A_1$) CCSD(T) Results

			harmonic normal modes				
basis set	energy (E_h)	R_{CH}	t_2	e	a_1	t_2	$\sum D_e$
aug-cc-pVDZ	−40.395820	1.1026	1319.3	1534.9	3016.6	3144.4	397.60
aug-cc-pVTZ	−40.440930	1.0899					414.04
aug-cc-pVQZ	−40.451729	1.0882					417.33
CBS(aDTQ/e^{-x})	−40.4551[c]	1.0879					418.0
CBS(aTQ/l_{max})	−40.4580						419.3
CBS(aDTQ/mix)	−40.4575						419.1
CBS(aDTQ/e^{-x})/CVQZ							419.2
CBS(TQ/l_{max})/CVQZ							420.6
CBS(aDTQ/mix)/CVQZ							420.2
exp.[b]		1.0858	1367.4	1582.7	3025.5	3156.8	(420.3)

[a] $\sum D_e$ (kcal/mol) was computed with respect to UCCSD(T) atoms. Bond lengths are in angstroms. Frequencies are in cm^{-1}. The experimental frequencies correspond to harmonic frequencies. [b] R_{CH} and vibrational frequencies are from D. L. Gray and A. G. Robiette, ref 31. For comparison purposes, the CCSD(T)/cc-pVQZ harmonic frequencies reported by Lee et al., ref 35, are 1345.3, 1570.4, 3036.2, and 3157.1 cm^{-1}. [c] Feller and Peterson, ref 13.

mol correction for spin−orbit effects in carbon, we arrive at our best estimate of D_e (83.92 kcal/mol). Our carbon-atom calculations correspond to an average of the ^3P spin multiplets. The spin−orbit correction accounts for this effect in the atomic energies and for the molecular spin−orbit splitting between the $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ states of CH. Atomic spin−orbit corrections were obtained from the excitation energies of Moore.[29]

The experimental zero-point energy is 4.04 kcal/mol, which yields a value of $D_0° = 79.9$ kcal/mol, compared to the experimental value of 79.9 ± 0.1 kcal/mol.[28] By using the known heats of formation at 0 K for the elements,[1] $\Delta H_f°(H) = 51.63$ kcal/mol and $\Delta H_f°(C) = 169.98 \pm 0.1$ kcal/mol, we calculate $\Delta H_f°(CH) = 141.7 \pm 0.3$ kcal/mol. The error limit is taken as one-half the spread in the CBS extrapolation methods plus the error in $\Delta H_f(C)$. This can be compared to the JANAF[1] value of 141.2 ± 4.2 kcal/mol, showing excellent agreement.

UCCSD(T) results for $CH_2(^3B_1)$ are listed in Table 2. As was the case for CH, the predicted bond lengths and harmonic frequencies are in good agreement with the experimental values reported by Jensen et al.[30] The calculated atomization energy, $\sum D_e$, is 190.6 kcal/mol, including core correlation and a 0.08 kcal/mol spin−orbit correction, very close to the 190.2 kcal/mol of Peterson and Dunning.[14] Experimental force fields[33] predict a zero-point energy of 10.55 kcal/mol. Thus, our final CCSD(T) value for $D_0°$ is 180.1 kcal/mol, compared to the experimental value of 179.9 ± 0.7 kcal/mol, and $\Delta H_f°(CH_2) = 93.1 \pm 0.4$ kcal/mol. The corresponding JANAF value is 92.2 ± 1.0 kcal/mol, in reasonable agreement with the values derived from the atomization energies, although we prefer our calculated value of 93.1 kcal/mol.

Table 3 contains the results of CCSD(T) calculations on CH_4 ($^1A_1$). The experimental bond length was taken from Gray and Robiette.[31] The CCSD(T) CBS(aDTQ/mix)/CVQZ value for $\sum D_e(CH_4)$, after subtracting the spin−orbit correction, is 420.22 kcal/mol. This can be compared to a value of 419.6 kcal/mol obtained by Peterson and Dunning[14] using the exponential extrapolation or our value of 419.3 kcal/mol using the same extrapolation procedure. The zero-point energy (ZPE), obtained as $^1/_2\sum\nu_i$, where ν_i are the experimental fundamental frequencies,[32] is 27.09 kcal/mol. This yields $\sum D_0°(CH_4) = 393.1$ kcal/mol and $\Delta H_f°(CH_4) = -16.6 \pm 0.7$ kcal/mol, whereas the experimental value is -16.0 ± 0.1 kcal/mol. Use of the somewhat larger ZPE (27.71 kcal/mol) proposed by Grev et al.[33] leads to $\Delta H_f°(CH_4) = -16.0 \pm 0.7$ kcal/mol, identical to the experimental value for ΔH. Martin[34] quotes a similar ZPE value of 27.6 kcal/mol, obtained from the ab initio quartic force field of Lee et al.[35] We note here that the zero-point energy for CH_4 is probably the most difficult to calculate from $^1/_2\sum\nu_i$ due to the presence of large anharmonic corrections associated with the hydrogens.

We also examined formaldehyde, H_2CO, the simplest carbonyl compound. The experimental geometry shown in Table 4 was taken from Duncan.[36] The CBS(aDTQ/mix)/CVQZ value for $\sum D_e$ is 374.6 kcal/mol, including a correction for spin−orbit effects. Note that the $\sum D_e$ values in Table 4 do not include a spin−orbit correction and that the "experimental" $\sum D_e$ has been adjusted so that it is more directly comparable to the theoretical results. The variance in the atomization energy due to the different ways of computing the atomic energies is only 0.16 kcal/mol. Taking the zero-point energy as $^1/_2\sum\nu_i$, where

TABLE 4: H_2CO ($^1A_1$) CCSD(T) Results

basis set	energy (E_h)	R_{CO}	R_{CH}	∠HCH	ZPE	$\sum D_e$
aug-cc-pVDZ	−114.245209	1.2226	1.1153	116.6	16.59	348.91
aug-cc-pVTZ	−114.342076	1.2111	1.1028	116.5		364.99
aug-cc-pVQZ	−114.372380	1.2078	1.1017	116.4		370.44
CBS(aDTQ/e^{-x})	−114.3862[c]	1.2065	1.1016	116.4		373.2
CBS(aTQ/l_{max})	−114.3899					373.6
CBS(aDTQ/mix)	−114.3895					373.6
CBS(aDTQ/e^{-x})/CVQZ						374.5
CBS(TQ/l_{max})/CVQZ						374.9
CBS(aDTQ/mix)/CVQZ						374.9
exp.[b]		1.2033	1.1005	116.2	16.53	(374.1)

[a] $\sum D_e$ (kcal/mol) was computed with respect to UCCSD(T) atoms. Bond lengths are in angstroms and angles are in degrees. The ZPE is in kcal/mol. [b] R_{CH}, R_{CH} and ∠HCH are from J. L. Duncan, ref 36. The experimental ZPE is from Clabo et al., ref 37. $\sum D_e$ includes a 0.30 kcal/mol spin−orbit correction to make the experimental value more directly comparable to the present theoretical values. [c] Feller and Peterson, ref 13.

TABLE 5: HCO ($^2A'$) UCCSD(T) Results

				harmonic normal modes			
basis set	energy (E_h)	R_{CO}/R_{CH}	∠HCH	a_1	a_1	b_2	$\sum D_e$
aug-cc-pVDZ	−113.600070	1.1940 1.1354	124.2	1097.1	1847.9	2676.2	257.41
aug-cc-pVTZ	−113.692517	1.1830 1.1202	124.5	1109.4	1881.6	2703.6	271.03
aug-cc-pVQZ	−113.721047	1.1787 1.1195	124.5				275.45
CBS(aDTQ/e^{-x})	−113.7338[c]	1.1759 1.1194	124.5				277.6
CBS(aTQ/l_{max})	−113.7375						278.0
CBS(aDTQ/mix)	−113.7371						277.9
CBS(aDTQ/e^{-x})/CVQZ							278.8
CBS(TQ/l_{max})/CVQZ							279.2
CBS(aDTQ/mix)/CVQZ							279.1
exp.[b]		1.175 1.125	125.0	1080.8	1868.2	2434.5	(278.8)

[a] $\sum D_e$ (kcal/mol) was computed with respect to UCCSD(T) atoms. Bond lengths are in angstroms, and angles are in degrees. Frequencies are in cm^{-1}. [b] R_{CO}, R_{CH}, and ∠HCO are from J. M. Brown and D. A. Ramsay, ref 37. The experimental frequencies are ν_i values reported by Sappey and Crosley, ref 38. The experimental ZPE is from Clabo et al., ref 36. $\sum D_e$ includes a 0.30 kcal/mol spin−orbit correction to make the experimental value more directly comparable to the present theoretical values. [c] Feller and Peterson, ref 13.

ν_i are the experimental fundamental frequencies,[32] we obtain ZPE = 16.13 kcal/mol. As seen in Table 4, if we use the CCSD(T)/aug-cc-pVDZ frequencies, we obtain ZPE = 16.59 kcal/mol, which is nearly identical to the estimated experimental ZPE (16.53) reported by Clabo et al.[37] The overestimation of the exerimental ZPE resulting from the use of $^1/_2\sum\nu_i$ was noted by Grev et al.[33] If we adopt 16.13 kcal/mol as the ZPE, we obtain $\sum D_0°(H_2CO) = 358.5$ kcal/mol. This value gives $\Delta H_f°(CH_2O) = -26.3 \pm 0.3$ kcal/mol (using a value of $\Delta H_f(O) = 58.99$ kcal/mol). This can be compared to experimental values of -26.8 ± 1.5 kcal/mol[1] and -25.0 ± 0.1 kcal/mol.[4] If we use the large experimental ZPE (16.53), we obtain $\Delta H_f°(CH_2O) = -25.8 \pm 0.3$. Thus, our ability to distinguish between the two experimental values taken from the JANAF tables depends critically on which of the two slightly different zero point energies we choose.

Similar data is presented for HCO ($^2A'$) in Table 5, where the experimental geometry is due to Brown and Ramsay[38] and the experimental frequencies were taken from work by Sappey and Crosley.[39] The heat of formation can be calculated in a manner parallel to the approach followed for the other four molecules. The CCSD(T) CBS(aDTQ/mix)/CVQZ atomization energy, $\sum D_e(HCO)$, is 278.8 kcal/mol, including a 0.3 kcal/mol spin−orbit correction which was subtracted from the raw theoretical value. The zero-point energy (taken as $^1/_2\sum\nu_i$) is 7.69 kcal/mol, whereas Clabo et al.[37] list a slightly larger value of 8.16 kcal/mol. These give $\sum D_0°(HCO)$ values in the range 270.6−271.1 kcal/mol and $\Delta H_f°$ values of $9.5-10.0 \pm 0.3$ kcal/mol. The JANAF value is 10.3 ± 1.9 kcal/mol. The theoretical heats of formation for these five small molecules are tabulated in Table 6, where it can be seen that the calculated values all fall within the experimental error bars and in many cases possess smaller uncertainties.

It is useful to note that we can also calculate the bond energy in CO quite reliably with this method. The value for D_e is 259.75 kcal/mol, including all corrections, and $D_0° = 256.6$ kcal/mol, compared to an experimental value for $D_0°$ of 256.2 ± 0.1 kcal/mol.

CF and CF_2. Experimental heats of formation for the two smallest fluorinated species, CF ($^2\Pi$) and CF_2 ($^1A_1$), are not known with the same accuracy as the $\Delta H_f°$s of the five molecules considered thus far. Table 7 contains the results of open-shell calculations on CF at the R/UCCSD(T) and UCCSD(T) levels of theory. Using the mixed CBS extrapolation and a CVQZ estimate of core/valence effects, we obtain a value of $D_e = 132.6$ kcal/mol, compared to the adjusted "experimental" value of 133.1 kcal/mol. If we subtract 0.47 kcal/mol for spin−orbit effects and include a ZPE of 1.87 kcal/mol, we obtain $D_0° = 130.3$ kcal/mol, in good agreement with the value of $D_0°$ reported by Huber and Herzberg of 130.8 kcal/mol. The agreement is poorer with the 128.3 ± 2 kcal/mol value obtained from the JANAF tables. We, thus, obtain $\Delta H_f°(CF) = 58.2 \pm 0.5$ kcal/mol (using $\Delta H_f(F) = 18.47 \pm 0.07$ kcal/mol). This can be compared to the JANAF value of 60.1 ± 2 kcal/mol at 0 K. We prefer our value based on the more accurate dissociation energy. The error due to the different ways to

TABLE 6: Theoretical and Experimental Heats of Formation at 0 K

molecule	CCSD(T) calcd[a]	exp.[b]	ZPE	S.O.
H		51.63		
C		169.98 ± 0.1		0.08
O		58.99		0.22
F		18.47 ± 0.07		0.38
CH	141.7 ± 0.3	141.20 ± 4.2	4.04	0.04
CH_2	93.1 ± 0.4	92.2 ± 1.09	10.55	0.08
CH_4	−16.6 ± 0.7[c]	−16.0 ± 0.1	27.09[c]	0.08
	−16.0 ± 0.7[d]		27.71[d]	
CH_2O	−26.3 ± 0.3[e]	−26.8 ± 1.5	16.13[e]	0.30
	−25.8 ± 0.3[f]	−25.0 ± 0.1	16.53[f]	
HCO	10.0 ± 0.3[g]	10.3 ± 1.9	8.61[g]	0.30
	9.5 ± 0.3[h]		7.69[h]	
CF	58.2 ± 0.5	60.1 ± 2	1.87	0.47
CF_2	−46.6 ± 0.7	−43.6 ± 1.5	4.29	0.85
		−44.0 ± 2		
		49 ± 3		
FCO	−44.1 ± 0.5	−41 ± 15	5.02	0.68
CF_2O	−145.2 ± 0.8	−152.0 ± 0.4	8.75	1.07
	−145.5 ± 1.0[i]	−148.4 +1.4/−0.7		
CF_2H_2	−107.2 ± 0.6	−105.9 ± 0.4	20.13	0.85
CO	−27.1 ± 0.2	−27.2 ± 0.04	3.10	0.30

[a] Including complete basis set and core/valence and spin−orbit corrections. Values are based on CBS(aDTQ/mix)/CVQZ estimates of the atomization energies. Heats of formation, zero-point energies, and spin−orbit corrections are given in kcal/mol. [b] See text for references to the experimental work. [c] Using ZPE = $^1/_2\sum\nu_i$ = 27.09 kcal/mol, where ν_i are the experimental fundamentals, ref 32. [d] Using ZPE = 27.71 kcal/mol, as recommended by Grev et al., ref 33. [e] Using ZPE = $^1/_2\sum\nu_i$ = 16.13 kcal/mol, where ν_i are the experimental fundamentals, ref 32. [f] Using the recommended ZPE =16.53 kcal/mol from ref 37. [g] Using ZPE = 8.16 kcal/mol, as recommended by Clabo, ref 37. [h] Using ZPE = $^1/_2\sum\nu_i$ = 7.69 kcal/mol, where ν_i are the experimental fundamentals. [i] Using eq 4 and the theoretical value for $\Delta H_f°(CF_2O)$ = −25.8 kcal/mol.

calculate the atomic energies is small, 0.11 kcal/mol. G2 predicts a D_e(CF) value of 133.7 kcal/mol, approximately 1 kcal/mol larger than our best value.

Data for $CF_2(^1A_1)$ is provided in Table 8. As has been the case for all of the molecules considered so far, the complete basis-set CCSD(T) structure is in close agreement with the experimental geometry, which in this case was taken from work by Kirchhoff et al.[40] The CBS(aDTQ/mix)/CVQZ value of $\sum D_e$ is 258.7 kcal/mol, somewhat larger than the experimental value. Inclusion of a zero-point energy (taken as $^1/_2\sum\nu_i$) of 4.29 kcal/mol[41] and a spin−orbit correction of 0.85 kcal/mol leads to $\sum D_0°$ = 253.6 kcal/mol and $\Delta H_f°(CF_2)$ = −46.6 ± 0.7 kcal/mol. This can be compared to the JANAF value of −43.6 ± 1.5 kcal/mol; the value from photoionization measurements of C_3F_6 of −44.3 ± 1 kcal/mol,[42] and the value of −49.0 ± 3 kcal/mol from proton-transfer studies (ion cyclotron resonance measurements).[43] Our results lie directly between these various values, suggesting that the midrange is appropriate. G2 predicts a $D_e(CF_2)$ of 260.9 kcal/mol, some 2.2 kcal/mol larger than our best value.

CF_2O. At the CBS(aDTQ/mix)/CVQZ level of theory, the CF_2O ($^1A_1$) value of $\sum D_e$ is 419.8 kcal/mol, where we have subtracted 1.07 kcal/mol from the calculated value in order to account for spin−orbit effects (see Table 9). The zero-point energy (taken as $^1/_2\sum\nu_i$) is 8.75 kcal/mol,[46] yielding $\sum D_0°$ = 411.1 kcal/mol and $\Delta H_f°(CF_2O)$ = −145.2 ± 0.8 kcal/mol. The error limit is taken as one-half the spread in the CBS extrapolation methods plus the sum of the errors in the heats of formation of the atoms. For comparison, the JANAF tables give $\Delta H_f°(CF_2O)$ = −152.0 ± 0.4 kcal/mol. Asher et al. suggest a value of $\Delta H_f^{298}(CF_2O)$ = −149.1 +1.4/−0.7 kcal/mol based on photoionization mass spectrometry measurements, which can be converted to $\Delta H_f°(CF_2O)$ = −148.4 kcal/mol. Our value is in reasonably good agreement with the photoionization work.

Montgomery and co-workers[5] reported a G2 $\Delta H_f°$ of −147.7 kcal/mol and a CBS-QCI/APNO value of −145.6 kcal/mol. By using an isodesmic reaction approach (discussed below), Montgomery et al. obtained $\Delta H_f(CF_2O)$ = −143.7 kcal/mol with the G2 energies and $\Delta H_f(CF_2O)$ = −144.8 kcal/mol with the CBS-QCI/APNO energies. Schneider and Wallington[6] used a number of reactions to calculate $\Delta H_f(CF_2O)$ and obtained $\Delta H_f(CF_2O)$ = −142.8, −144.4, and −142.9 kcal/mol at their highest levels of calculation at 0 K. Schneider and Wallington[6] recommend a value of −145.3 ± 1.7 kcal/mol at 298 K.

We also calculated the heat of formation of CF_2O from the isodesmic reaction

$$CH_2O + CF_2H_2 \rightarrow CF_2O + CH_4 \qquad (4)$$

used by Montgomery et al. Each side of eq 4 contains one C=O double bond and six single bonds. To use this reaction,

TABLE 7: CCSD(T) Results for CF ($^2\Pi$)[a]

basis set	energy (E_h)	geometry	method	R_e (Å)	ω_e (cm^{-1})	D_e
cc-pVDZ	−137.474921	MP2	R/U			117.39
cc-pVTZ	−137.604537	MP2	R/U			127.75
cc-pVQZ	−137.644486	MP2	R/U			130.43
aug-cc-pVDZ	−137.504054	MP2	R/U			118.74
	−137.504960	Opt.	U	1.3071	1202.5	119.24
aug-cc-pVTZ	−137.614360	MP2	R/U			128.55
	−137.614410	Opt.	U	1.2808	1295.8	128.49
aug-cc-pVQZ	−137.648402	MP2	R/U			131.02
	−137.648410	Opt.	U	1.2759	1302.5	130.92
CBS(DTQ/e^{-x})	−137.6623	MP2	R/U			
CBS(aDTQ/e^{-x})	−137.6636	MP2	R/U			
	−137.6639	Opt.	U	1.2748	1303.2	131.8
CBS(aTQ/l_{max})	−137.6681	Opt.				132.3
CBS(aDTQ/mix)	−137.6676	Opt.				132.2
CBS(aDTQ/e^{-x})/CVQZ		Opt.				132.2
CBS(TQ/l_{max})/CVQZ		Opt.				132.7
CBS(aDTQ/mix)/CVQZ		Opt.				132.6
exp.[b]				1.2718	1308.1	(133.1)

[a] D_e is in kcal/mol. The dissociation energies were computed with respect to atomic energies obtained with the same method (R/UCCSD(T) or UCCSD(T)) as the molecular energy. The optimal UMP2(FC)/cc-pVTZ bond length is 1.272907 Å. For comparison purposes, G2 yields D_e = 133.7 kcal/mol. [b] Experimental values are from Huber and Herzberg, ref 28. D_e includes a 0.47 kcal/mol spin−orbit correction to make the experimental value more directly comparable to the present theoretical values.

TABLE 8: CF_2 ($^1A_1$) CCSD(T) Results[a]

				normal modes			
basis set	energy (E_h)	R_{CF}	∠FCF	a_1	b_2	a_1	$\sum D_e$
cc-pVDZ	−237.183145	MP2[b]					
cc-pVTZ	−237.419113	MP2					
cc-pVQZ	−237.492667	MP2					
aug-cc-pVDZ	−237.239071	MP2					
	−237.240364	1.3277	104.0	635.2	1057.1	1175.5	235.54
aug-cc-pVTZ	−237.438282	MP2					
	−237.438335	1.3049	104.7	668.5	1134.2	1237.8	251.54
aug-cc-pVQZ	−237.500357	MP2					
	−237.500363	1.3008	104.8				255.82
CBS(aDTQ/e^{-x})	−237.5287	1.2998	104.8				257.2
CBS(aTQ/l_{max})	−237.5362						258.3
CBS(aDTQ/mix)	−237.5354						258.1
CBS(aDTQ/e^{-x})/CVQZ							257.8
CBS(TQ/l_{max})/CVQZ							258.8
CBS(aDTQ/mix)/CVQZ							258.7
exp.[c]		1.3035	104.8	667.0	1225.1	1114.4	(256)

[a] $\sum D_e$ (kcal/mol) was computed with respect to UCCSD(T) atoms. Bond lengths are in angstroms, and angles are in degrees. Frequencies are in cm^{-1}. The experimental frequencies correspond to harmonic frequencies. For the sake of comparison, G2 predicts $\sum D_e = 260.9$ kcal/mol. [b] The MP2/cc-pVTZ geometry is $R_{CF} = 1.2992$ Å, ∠FCF = 105.0°. [c] The experimental bond length and bond angle were taken from Kirchhoff et al. ref 39. Frequencies are ν_i values from Jacox, ref 41. $\sum D_e$ is based on the IRC measurements, ref 42, and have a quoted uncertainty of ±2 kcal/mol. This value includes a 0.85 kcal/mol spin−orbit correction to make the experimental value more directly comparable to the present theoretical values.

TABLE 9: CF_2O ($^1A_1$) CCSD(T) Results[a]

		$\sum D_e$ (kcal/mol)	
basis set	energy (E_h)	R/UCCSD(T)	UCCSD(T)
cc-pVDZ	−312.331459	380.42	
cc-pVTZ	−312.642360	406.17	
cc-pVQZ	−312.740095	414.06	
aug-cc-pVDZ	−312.403332	384.60	384.46
aug-cc-pVTZ	−312.666661	408.21	407.99
aug-cc-pVQZ	−312.749753	415.51	415.28
CBS(DTQ/e^{-x})	−312.7849		417.2
CBS(aDTQ/e^{-x})	−312.7881		418.4
CBS(aTQ/l_{max})	−312.7977		419.4
CBS(aDTQ/mix)	−312.7968		419.3
CBS(aDTQ/mix)/CVQZ			420.9
exp.			(427.7)[b] (424.1)[c]

[a] Results obtained at the optimal MP2/cc-pVTZ geometry, $R_{CO} = 1.1772$ Å, $R_{CF} = 1.3145$ Å, ∠FCF = 107.6°. For comparison, G2 predicts $\sum D_e = 422.6$ kcal/mol. [b] Based on the JANAF heat of formation at 0 K, ZPE = 8.75 kcal/mol and a spin−orbit correction of 1.07 kcal/mol. [c] Based on the heat of formation from Asher et al., ref 7.

TABLE 10: CF_2H_2 ($^1A_1$) CCSD(T) Results[a]

basis set	energy (E_h)	R_{CH}/R_{CF}	∠HCH	$\sum D_e$
aug-cc-pVDZ	−238.784662	1.1018 1.3785	114.1	409.31
aug-cc-pVTZ	−238.721046	1.0908 1.3594	113.5	429.17
aug-cc-pVQZ	−238.784662	1.0895 1.3562	113.4	434.28
CBS(aDTQ/e^{-x})	−238.8133			435.8
CBS(aTQ/l_{max})	−238.8214			437.3
CBS(aDTQ/mix)	−238.8206			437.1
CBS(aDTQ/e^{-x})/CVQZ				436.9
CBS(TQ/l_{max})/CVQZ				438.3
CBS(aDTQ/mix)/CVQZ				438.1
exp.				(437.1)[b]

[a] $\sum D_e$ (kcal/mol) was computed with respect to UCCSD(T) atoms. Bond lengths are in angstroms, and angles are in degrees. CCSD(T)/aug-cc-pVDZ normal-mode frequencies (cm^{-1}) are a1 = 507.5, b2 = 1073.3, a1 = 1088.6, b1 = 1162.6, a2 = 1250.3, b2 = 1436.2, a1 = 1509.2, a1 = 3084.5, b1 = 3168.7. The CCSD(T) zero-point energy is 20.42 kcal/mol. [b] Based on JANAF tables, ref 1. $\sum D_e$ includes a 0.84 kcal/mol spin−orbit correction to make the experimental value more directly comparable to the present theoretical values

TABLE 11: Electronic Reaction Energies (kcal/mol) for[a]

$$CH_2O + CF_2H_2 \rightarrow CF_2O + CH_4$$

basis set	ΔE_{MP2}	$\Delta E_{CCSD(T)}$	difference
aug-cc-pVDZ	−26.64	−24.61	2.03
aug-cc-pVTZ	−29.31	−27.90	1.41
aug-cc-pVQZ	−29.69	−27.89	1.80

an additional set of calculations was required on CF_2H_2 ($^1A_1$). The electronic energy change with the mixed Gaussian/exponential CBS extrapolation is −27.74 kcal/mol. The CVQZ estimate of the core correlation correction is −0.30, and spin−orbit effects are negligible. Thus, the electronic $\Delta E_{Rxn-4} = -28.1$ kcal/mol.

The zero-point energy corrections for all of the molecules in eq 4 except CF_2H_2 have been discussed. The only mode for CF_2H_2 that is not known experimentally is the a_2 mode.[44] There are four known modes of similar frequency to the missing mode. For the second and third a_1 modes (1508, 1113 cm^{-1}), we calculate scale factors of 0.960 and 0.972. For the second b_1 mode (1178 cm^{-1}), we calculate a scale factor of 0.973, and for the first b_2 mode (1435 cm^{-1}), we calculate a scale factor of 0.961. Given the above, we adopted a scale factor of 0.96 for the a_2 mode, calculated at the MP2/cc-pVTZ level as 1303 cm^{-1}. This yields ZPE(CH_2F_2) = 20.13 kcal/mol or $\Delta ZPE_{Rxn-4} = -0.42$ kcal/mol, and we obtain $\Delta H°_{Rxn-4} = -28.47$ kcal/mol. The experimental heats of formation of CH_4 and CH_2O are given above. Experimentally, $\Delta H_f(CF_2H_2)$ is −105.9 ± 0.4 kcal/mol. By using Hess's Law, we calculate $\Delta H_f(CF_2O) = -143.4$ (using $\Delta H_f(CH_2O) = -25.0$ kcal/mol) or −145.2 kcal/mol (using $\Delta H_f(CH_2O) = -26.8$ kcal/mol). The latter value is in exact agreement with the value we obtained from considering the atomization energy of CF_2O. Use of our theoretical value for $\Delta H_f°(CH_2O)$, −25.8 kcal/mol, yields a $\Delta H_f°(CF_2O)$ of −144.2 kcal/mol, almost exactly the average of the values obtained from the two experimental heats of formation of formaldehyde.

Since we have already demonstrated our ability to accurately reproduce the heats of formation of CH_4 and CH_2O, we next examine $\Delta H_f(CF_2H_2)$ as a possible source of error. The CBS-

TABLE 12: FCO ($^2A''$) CCSD(T) Results[a]

basis set	energy (E_h)	R_{CO}/R_{CF}	∠FCO	normal modes			$\sum D_e$
				a_1	a_1	b_2	
cc-pVDZ	−212.621897	MP2					266.06
cc-pVTZ	−212.827977	MP2					288.19
cc-pVQZ	−212.893159	MP2					290.41
aug-cc-pVDZ	−212.668941	MP2					268.80
	−212.669860	1.1826 1.3614	127.6	596.2	974.3	1866.2	269.37
aug-cc-pVTZ	−212.844291	MP2					285.95
	−212.844349	1.1773 1.3313	127.8				285.98
aug-cc-pVQZ	−212.899575	MP2					291.49
	−212.899582	1.1709 1.3314	128.2				291.50
CBS(aDTQ/e^{-x})	−212.9254						294.3
CBS(aTQ/l_{max})	−212.9315						294.7
CBS(aDTQ/mix)	−212.9310						294.7
CBS(aDTQ/e^{-x})/CVQZ							295.5
CBS(TQ/l_{max})/CVQZ							295.9
CBS(aDTQ/mix)/CVQZ							295.9
exp.				627.5[b]	1026.1[b]	1861.6[b]	(289.3)[c] (294.1)[d]

[a] $\sum D_e$ (kcal/mol) was computed with respect to UCCSD(T) atoms. Bond lengths are in angstroms, and angles are in degrees. Frequencies are in cm^{-1}. The optimal MP2/cc-pVTZ geometry is R_{CO} = 1.1718 Å, R_{CF} = 1.3257 Å, ∠FCO = 128.2°. All calculations at the MP2 geometry used the R/UCCSD(T) method. All other used UCCSD(T). [b] Experimental ν_i from Jacox, ref 41. [c] Buckley et al., ref 45. Quoted error bars are ±2.9 kcal/mol. $\sum D_e$ includes a 0.68 kcal/mol spin−orbit correction to make the experimental value more directly comparable to the present theoretical values. [d] JANAF tables, ref 1, including a 0.68 kcal/mol spin−orbit correction. Experimental uncertainty is ±15 cal/mol.

(aDTQ/mix)/CVQZ value for $\sum D_e(CF_2H_2)$ is 437.5 kcal/mol, after subtracting a 0.84 kcal/mol spin−orbit correction (see Table 10). The zero-point energy is taken as 20.09 kcal/mol, as noted above, yielding $\sum D_0°(CF_2H_2) = 417.4$ kcal/mol and $\Delta H_f°(CF_2H_2) = -107.2 \pm 0.6$ kcal/mol. The latter value is ~1 kcal/mol more negative than the 105.9 ± 0.4 experimental value. Combining our value for $\Delta H_f°(CF_2H_2)$ in reaction 4 with $\Delta H_f°(CH_2O) = -25.0$ kcal/mol, $\Delta H_f(CH_4) = -16.0$, and $\Delta H_f°_{Rxn-4} = -28.47$ kcal/mol gives $\Delta H_f°(CF_2O) = -144.7$ kcal/mol or −146.5 kcal/mol with $\Delta H_f°(CH_2O) = -26.8$ kcal/mol. If, instead of the experimental $\Delta H_f°(CH_2O)$ values we use the −28.5 theoretical value, we arrive at $\Delta H_f°(CF_2O) =$ 145.5 kcal/mol. The latter value is now in excellent agreement with the $\Delta H_f°(CF_2O)$ value obtained from computing the total atomization energy.

The excellent agreement between the heats of formation calculated via the isodesmic reaction and the atomization energy approaches suggests that a reliable value for $\Delta H_f°(CF_2O)$ is 145.2 ± 0.8 kcal/mol. This value is in good agreement with previously reported theoretical values of Montgomery et al.[5] However, it is 3.2 kcal/mol smaller in magnitude than the value obtained from photoionization measurements and 6.8 kcal/mol smaller than the JANAF value. We suggest that the heat of formation of CF_2O be revised upward by almost 7 kcal/mol.

Isodesmic reactions, such as the one given in eq 4, are commonly assumed to minimize errors due to incomplete correlation recovery. For this particular reaction, the overall change in zero-point energy is only −0.4 kcal/mol. Consequently, even a 10−20% error in this component will have only a minor effect on ΔH_{Rxn} and we are left with correlation recovery as the most likely source of error. To test the sensitivity of ΔE to the level of theory, we compare the results of low-level correlation recovery (MP2) against high-level (CCSD(T)) findings in Table 11. As can be seen, the differences between the MP2 and CCSD(T) reaction energies are on the order of 2 kcal/mol (or 7%), regardless of which basis set is used. This is a surprisingly large amount for such a simple system. The data in Table 11 also highlights the shortcomings of combining a relatively small basis set with a high-level correlation treatment. The CCSD(T)/aug-cc-pVDZ result is in error by 3.3 kcal/mol, or 12%.

It is also possible to calculate the heat of formation of FCO. The value of $\sum D_e(FCO)$ is 296.5 kcal/mol, including core correlation and spin−orbit corrections (see Table 12). The zero-point energy (taken as $1\sum\nu_i$) is 5.02 kcal/mol,[41] giving $\sum D_0°(FCO) = 291.5$ kcal/mol and $\Delta H_f(FCO) = -44.1 \pm 0.5$ kcal/mol at 0 K. This can be compared to the JANAF value of −41± 15 kcal/mol. Buckley et al.[45] obtain −36.2 ± 2.9 kcal/mol from photoionization energy measurements, but this value is clearly too low compared to our value, suggesting that the photoionization measurements need to be reinterpreted.

Conclusions

The heats of formation of CF, CF_2, CF_2O, and a number of other small molecules have been obtained from large basis set CCSD(T) calculations, including corrections for core/valence correlation, spin−orbit, and basis set truncation effects. The results, summarized in Table 6, show that the level of theory used in the present work is in good agreement with experiment. Results based on the use of MP2/cc-pVTZ geometries were compared to results obtained from reoptimizing the geometries at the CCSD(T) level. Minimal differences were found, largely because the MP2 geometries with the cc-pVTZ basis set are fortuitously close to the CCSD(T)/aug-cc-pVQZ optimal geometries. For smaller basis sets, the error approaches 1 kcal/mol.

The calculated heats of formation can be used to calculate a variety of bond energies. The H−CO bond energy in HCO is only 15.5 kcal/mol, whereas the C−H bond energy in H_2CO is 87.3 kcal/mol. For comparison, the C−H bond energy is 80.0 kcal/mol in CH and 99.4 kcal/mol in CH_2. The C−F bond energy is only 35.4 kcal/mol in FCO but increases to 121.7 kcal/mol in CF_2O. For comparison, the C−F bond energy in

TABLE A1: Frozen-Core CCSD(T) Energies (E_h)[a]

	H (^{2}S)		C(^{3}P)	
basis	UCCSD(T)	RCCSD(T)	R/UCCSD(T)	UCCSD(T)
cc-pVDZ	−0.499278	−37.760287	−37.760314	
cc-pVTZ	−0.499810	−37.780521	−37.780660	
cc-pVQZ	−0.499946	−37.786272	−37.786434	
cc-pV5Z	−0.499994	−37.787961	−37.788124	
aug-cc-pVDZ	−0.499334	−37.764737	−37.764798	−37.764866
aug-cc-pVTZ	−0.499821	−37.781560	−37.781725	−37.781826
aug-cc-pVQZ	−0.499948	−37.786603	−37.786770	−37.786875

	O(^{3}P)		
basis	RCCSD(T)	R/UCCSD(T)	UCCSD(T)
cc-pVDZ	−74.909805	−74.909862	
cc-pVTZ	−74.973621	−74.973829	
cc-pVQZ	−74.993163	−74.993430	
cc-pV5Z	−74.999678	−74.999964	
aug-cc-pVDZ	−74.925400	−74.925567	−74.925654
aug-cc-pVTZ	−74.978558	−74.978825	−74.978952
aug-cc-pVQZ	−74.994846	−74.995134	−74.995268

	F(^{2}P)		
basis	RCCSD(T)	R/UCCSD(T)	UCCSD(T)
cc-pVDZ	−99.527502	−99.527536	
cc-pVTZ	−99.620176	−99.620301	
cc-pVQZ	−99.650202	−99.650193	
cc-pV5Z	−99.660382	−99.660559	
aug-cc-pVDZ	−99.549934	−99.550035	−99.550069
aug-cc-pVTZ	−99.627609	−99.627771	−99.627827
aug-cc-pVQZ	−99.652665	−99.652845	−99.652908

[a] Orbital symmetry and equivalence restrictions on the 2p atomic orbitals were not imposed.

CF is 131.2 kcal/mol, and in CF_2 it is 124.1 kcal/mol. The CO bond energy is 179.6 kcal/mol in CH_2O and 157.9 kcal/mol in CF_2O, showing the large effect of fluorine substitution.

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References and Notes

(1) Chase, M. W., Jr.; Davies, C. A.; Downey, J. R., Jr.; Frurip, D. J.; MacDonald, R. A.; Syverud, A. N. *J. Phys. Chem. Ref. Data* **1985**, *14*, Suppl. 1 (JANAF tables).

(2) Krespan, C. G.; Dixon, D. A. *J. Fluorine Chem.* **1996**, *77*, 177.

(3) Domalski, E. S.; Hearing, E. D. *J. Phys. Chem. Data* **1993**, *22*, 805.

(4) Pedley, J. B. *Thermochemical Data and Structures of Organic Compounds*; Thermodynamics Research Center: College Station, TX, 1994; Vol. 1.

(5) Montgomery, J. A.; Michels, H. H.; Franscico, J. S. *Chem. Phys. Lett.* **1994**, *220*, 391.

(6) Schneider, W. F.; Wallington, T. J. *J. Phys. Chem.* **1994**, *98*, 7448.

(7) Asher, R. L.; Appelman, E. H.; Ruscic, B. *J. Chem. Phys.* **1996**, *105*, 9781.

(8) Petersson, G. A.; Tensfeldt, T. G.; Montgomery, J. A., Jr. *J. Chem. Phys.* **1991**, *94*, 6091.

(9) Ochterski, J. W.; Petersson, G. A.; Montgomery, J. A., Jr. *J. Chem. Phys.* **1996**, *104*, 2598.

(10) Dixon, D. A.; Feller, D.; Peterson, K. A. *J. Phys. Chem. A* **1997**, *101*, 9405.

(11) Peterson, K. A.; Xantheas, S. S.; Dixon, D. A.; Dunning, T. H., Jr. *J. Phys. Chem. A* **1998**, *102*, 2449.

(12) Kumaran, S. S.; Su, M. C.; Lim, K. P.; Michael, J. V.; Klippenstein, S. J.; DeFelice, J.; Mudipalli, P. S.; Kiefer, J. H.; Dixon, D. A.; Peterson, K. A. *J. Phys. Chem.* **1997**, *101*, 8653.

(13) Feller, D.; Peterson, K. A. *J. Chem. Phys.* **1998**, *108*, 154.

(14) Peterson, K. A.; Dunning, T. H., Jr. *J. Chem. Phys.* **1997**, *106*, 4119.

(15) Bartlett, R. J. *J. Phys. Chem.* **1989**, *93*, 1697. (b) Kucharski, S. A.; Bartlett, R. *J. Adv. Quantum Chem.* **1986**, *18*, 281. (c) Bartlett, R. J.; Stanton, J. F. In *Reviews of Computational Chemistry*; Lipkowitz, K. B., Boyd, D. B., Eds.; VCH Publishers: New York, 1995; Vol. V, Chapter 2, p 65.

(16) Dunning, T. H., Jr. *J. Chem. Phys.* **1989**, *90*, 1007. Kendall, R. A.; Dunning, T. H., Jr.; Harrison, R. J. *J. Chem. Phys.* **1992**, *96*, 6796. Woon, D. E.; Dunning, T. H., Jr. *J. Chem. Phys.* **1993**, *99*, 1914. Peterson, K. A.; Kendall, R. A.; Dunning, T. H., Jr. *J. Chem. Phys.* **1993**, *99*, 1930. Peterson, K. A.; Kendall, R. A.; Dunning, T. H., Jr. *J. Chem. Phys.* **1993**, *99*, 9790. Woon, D. E.; Dunning, T. H., Jr. *J. Chem. Phys.* **1995**, *103*, 4572.

(17) Pople, J. A.; Head-Gordon, M.; Fox, D. J.; Raghavachari, K.; Curtiss, L. A. *J. Chem. Phys.* **1989**, *90*, 5622.

(18) Curtiss, L. A.; Raghavachari, K.; Trucks, G. W.; Pople, J. A. *J. Chem. Phys.* **1991**, *94*, 7221.

(19) (a) Moller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618. (b) Pople, J. A.; Binkley, J. S.; Seeger, R. *Int. J. Quantum Chem. Symp.* **1976**, *10*, 110.

(20) Feller, D.; Dixon, D. A.; Peterson, K. A. *J. Phys. Chem. A* **1998**, *102*, 7053.

(21) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T. A.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94*; Gaussian, Inc.: Pittsburgh, PA, 1995.

(22) MOLPRO is a package of ab initio molecular orbital theory programs written by H.-J. Werner and P. J. Knowles with contributions from J. Almlof, R. D. Amos, M. J. O. Deegan, S. T. Elbert, C. Hampel, W. Meyer, K. A. Peterson, R. M. Pitzer, A. J. Stone, P. R. Taylor, and R. Lindh.

(23) Hampel, C.; Peterson, K. A.; Werner, H.-J. *Chem. Phys. Lett.* **1990**, *190*, 1. Deegan, M. J. O.; Knowles, P. J. *Chem. Phys. Lett.* **1994**, *227*, 321. Knowles, P. J.; Hampel, C.; Werner, H.-J. *J. Chem. Phys.* **1993**, *99*, 5219.

(24) Feller, D. J. *Chem. Phys.* **1992**, *96*, 6104. Peterson, K. A.; Dunning, T. H., Jr. *J. Chem. Phys.* **1995**, *102*, 2032.

(25) Peterson, K. A.; Woon, D. E.; Dunning, T. H., Jr. *J. Chem. Phys.*, **1994**, *100*, 7410.

(26) Schwartz, C. *Methods in Computational Physics*; Academic Press: New York, 1963; Vol. 2.

(27) Martin, J. M. L. *Chem. Phys. Lett.* **1996**, *259*, 679.

(28) Huber, K. P.; Herzberg, G. *Molecular Spectra and Molecular Structure: Constants of Diatomic Molecules*; Van Nostrand Reinhold Co. Inc.: New York, 1979.

(29) Moore, C. E. *Atomic Energy Levels*, Natl. Stand. Ref. Data Ser. (U.S. Natl. Bur. Stand.) **1971**, 35.

(30) Jensen, P.; Bunker, P. R.; Karpfen, A.; Kofranek, M.; Lischka, H. *J. Chem. Phys.* **1990**, *93*, 6266.

(31) Gray, D. L.; Robiette, A. G. *Mol. Phys.* **1979**, *37*, 1901.

(32) Shimanouchi, T. *Tables of Molecular Vibration Frequencies Consolidated*; NSRDS−NBS 39; National Bureau of Standards: Washington, DC, 1972.

(33) Grev, R. S.; Janssen, C. L.; Schaefer, H. F., III. *J. Chem. Phys.* **1991**, *95*, 5128.

(34) Martin, J. M. L. *J. Mol. Struct. (THEOCHEM)*, in press.

(35) Lee, T. J.; Martin, J. M. L.; Taylor, P. R. *J. Chem. Phys.* **1995**, *102*, 254.

(36) Duncan, J. L. *Mol. Phys.* **1974**, *28*, 1177.

(37) Clabo, D. A.; Allen, W. D.; Remington, R. B.; Yamaguchi, Y.; Schaefer, H. F., III *Chem. Phys.* **1988**, *123*, 187.

(38) Brown, J. M.; Ramsay D. A. *Can. J. Chem.* **1975**, *53*, 2232.

(39) Sappey, A. D.; Crosley, D. R. *J. Chem. Phys.* **1990**, *93*, 7601.

(40) Kirchhoff, W. H.; Lide, D. R., Jr.; Powell, F. X. *J. Mol. Spectrosc.* **1973**, *47*, 491.

(41) Jacox, M. E. *J. Phys. Chem. Ref. Data, Monograph* **1994**, 3.

(42) Berman, D. W.; Bomse, D. W.; Beauchamp, J. L. *Int. J. Mass Spectrom. Ion Phys.* **1981**, *39*, 263.

(43) Lias, S. G.; Karpas, Z.; Liebman, J. F. *J. Am. Chem. Soc.* **1985**, *107*, 6080.

(44) Smith, M. A. H.; Rinsland, C. P.; Fridovich, B.; Rao, K. N. In *Molecular Spectroscopy: Modern research*; Rao, K. N., Ed.; Academic: New York, 1985; Vol. III, p 111.

(45) Buckley, T. J.; Johnson, R. D., III; Huie, R. D.; Zhang, Z.; Kuo, S. C.; Klemm, R. B. *J. Phys. Chem.* **1995**, *99*, 4879.

(46) Shimanouchi, T. *J. Phys. Chem. Ref. Data* **1977**, *6*, 993.