Heats of Formation of Hydrofluorocarbons Obtained by Gaussian-3 and Related Quantum Chemical Computations

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The heats of formation of ~120 C_1 and C_2 hydrofluorocarbon and oxidized hydrofluorocarbon molecules, as well as of hexafluoropropene and the hexafluoropropyl radical, were computed using the Gaussian-3 (G3) method, along with two approximations to G3, denoted G3[MP2(full)] and G3(MP4SDQ), and the G2(MP2) method. The performance of G3 is clearly superior to that of the other methods when the heats of formation are computed via atomization energies, and in general, the G3 results agree with the available good-quality experimental and theoretical data to within 2 kcal mol^{-1}. The use of isodesmic reaction schemes improves the overall accuracy of the computed heats of formation and results in a consistent set of predictions that are largely method-independent. Although, for the majority of molecules, the G3 data agree well with the earlier theoretical predictions of Zachariah et al. (*J. Phys. Chem.*, **1996**, *100*, 8737), who used the bond-additivity-corrected MP4 (BAC-MP4) method, there are significant discrepancies as well. The heats of formation of a group of small molecules consisting of the fluoroacetylenes (HCCF and C_2F_2, as well as C_2H_2) and the C_2H, C_2F, and formyloxyl (HCOO) radicals were also computed using the coupled-cluster method with basis sets ranging from cc-pVDZ to aug-cc-pVQZ and cc-pCVQZ, followed by extrapolation to the CBS limit and corrections for core-valence correlation and scalar relativistic effects. The predicted CBS heats of formation (in kcal mol^{-1}) are $\Delta_f H^0_{298}(\mathrm{HCCF}) = 24.6 \pm 1.0$, $\Delta_f H^0_{298}(\mathrm{C_2F_2}) = 0.5 \pm 1.0$, $\Delta_f H^0_{298}(\mathrm{C_2H}) = 135.9 \pm 1.0$, $\Delta_f H^0_{298}(\mathrm{C_2F}) = 109.1 \pm 1.0$, and $\Delta_f H^0_{298}(\mathrm{HCOO}) = -30.1 \pm 1.0$, in good agreement with the G3 results. The current work on formyloxyl provides strong support for the experimental value of $\Delta_f H^0_0 = 28.6 \pm 0.7$ kcal mol^{-1} obtained by Langford et al. (*J. Chem. Soc., Faraday Trans.* **1997**, *93*, 3757).

Introduction

With the recent international restrictions on the production and deployment of chloro- and bromofluorocarbons (CFC's and BFC's), much effort is currently devoted to the search for suitable ozone-friendly replacements. An important use of halons, such as trifluorobromomethane (CF_3Br), has been as fire suppressants. Unfortunately, the bromine atoms that are so efficient in extinguishing flames, by removing hydrogen radicals, are also efficient catalysts of the ozone reduction process. Indeed, the ozone-depletion potential of CF_3Br is an order of magnitude greater than that of most CFC's.[1] Fluorocarbons and hydrofluorocarbons have been identified as promising candidates as fire suppressants,[2] and considerable effort is being devoted to their study, which has resulted in the generation of extensive thermochemical and kinetic databases.[3,4] Unlike CFC's and BFC's, fluorinated hydrocarbons have zero ozone-depleting potential, although they are potential greenhouse gases. Fluorocarbons are also widely used as lubricants, blowing and sterilizing agents, anaesthetics, propellants, refrigerants, and agents in the preparation of semiconductors.

There is considerable current interest in 2*H*-heptafluoropropane (CF_3CHFCF_3, FM-200) as a potential fire retardant.[5,6] Unlike bromine, fluorine forms much stronger bonds, and fluorine atoms are not recycled in the flame, as one fluorine radical will terminate just one hydrogen radical. Hence, with seven fluorines per molecule, it is not surprising that flame tests have shown CF_3CHFCF_3 to be a very effective fire retardant.[7] The pyrolysis kinetics of CF_3CHFCF_3 at 1200−1500 K have been the subject of a recent shock-tube and kinetic modeling study by Hynes et al.[8] The dominant initiation pathways were identified as HF elimination and CC bond fission, viz.

$$CF_3CHFCF_3 \rightarrow C_3F_6 + HF \qquad (1)$$

and

$$CF_3CHFCF_3 \rightarrow CF_3CHF + CF_3 \qquad (2)$$

The most important subsequent reactions are (a) the decomposition of the CF_3CHF radical

$$CF_3CHF \rightarrow CF_2{=}CHF + F \qquad (3)$$

(b) the abstraction of H from the parent molecule

$$CF_3CHFCF_3 + F \rightarrow CF_3CFCF_3 + HF$$

followed by the decomposition reactions

$$CF_3CFCF_3 \rightarrow CF_3CF\!: + CF_3 \qquad (4)$$

$$CF_3CF\!: \rightarrow CF_2{=}CF_2 \rightarrow CF_2 + CF_2 \qquad (5)$$

and the secondary reaction

$$CF_2{=}CF_2 + CF_2 \rightarrow \text{cyclo-}C_3F_6 \qquad (6)$$

and (c) the radical recombination reactions

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$$CF_3CHF + CHF_2 \rightarrow CF_3CHFCHF_2 \quad (7)$$

and

$$CF_3 + CF_3 \rightarrow CF_3CF_3 \quad (8)$$

As the thermochemistry of a number of species participating in the above reactions had been poorly characterized at the time, we carried out ab initio quantum chemical calculations concurrently with the modeling studies, generating heats of formation for most of the intermediates in reactions 1−8, as well as barrier heights and rate constants for several reactions. The theoretical work concerned with the relevant thermochemistry constitutes the major part of this paper.

In subsequent work, Hynes et al.[9] studied the kinetics of high-temperature oxidation of C_3F_6 by O(^{3}P), where the initial step is the addition of an oxygen atom across the double bond of C_3F_6.

$$CF_3CF{=}CF_2 + O \rightarrow CF_3CFCF_2O \quad (9)$$

The resulting triplet biradical could (a) simply decompose to the triplet CF_3CF: and CF_2O, (b) undergo a 1,2 F-atom shift and decompose to form CF_3CF_2 + CFO, and (c) lose fluorine to yield $CF_3CFCF{=}O$ + F. Some of these reactions were also studied using ab initio techniques, and the thermochemical information generated was subsequently used in the kinetic modeling studies of Hynes et al.[9]

The most recent work in this area has been the shock-tube kinetic study[10] of the high-temperature reaction of H atoms with hexafluoropropene (C_3F_6) over the temperature range of 1250−1550 K, in an effort to understand the role that C_3F_6 plays in a flame, given that it is a pyrolysis product of 2*H*-heptafluoropropane. Addition of H across the double bond yields CF_3CHFCF_2 or CF_3CFCHF_2, which can then decompose by CC bond scissions to yield CF_3 + $CHFCF_2$, CF_3CHF + CF_2, etc., or after F loss, CF_2CHF + CF_2. Again, ab initio calculations were performed to compute, in particular, the heats of formation of the hexafluoropropyl radicals.

The current work, including the computation of heats of formation of C1, C2, and C3 halons (closed-shell singlets, radicals, and carbenes), therefore, complements and extends the thermochemical database representing ∼30 years of experimental work by numerous scientists, as well as ab initio theoretical work principally by Westmoreland, Zachariah, and co-workers[2,3,11−13] and by Francisco and co-workers[14−17] over the last 7 years. Initially, during 1998, we undertook the computation of the heats of formation of those halons that were of immediate importance in the kinetic modeling studies using the approximate Gaussian-2 technique, G2(MP2).[18] In an effort to maximize the accuracy of the computations, where possible, we calculated the heats of formation of the species of interest via suitable isodesmic reactions, i.e., utilizing G2(MP2) heats of reactions in conjunction with accepted literature values for all other species in the reactions. Although this approach is generally more accurate than using computed atomization energies, its accuracy is also limited by the reliability of the available literature data.

An important advance in the computation of thermochemistry, especially that of fluorine-containing molecules was made, however, by the introduction of Gaussian-3 (G3) theory[19] toward the end of 1998. It has been demonstrated to be significantly more accurate than Gaussian-2 (G2)[20] as well as computationally cheaper. This has subsequently prompted us to recalculate, using G3, all heats of formation that we previously obtained at the G2(MP2) level, as well as those of a number of other C_1 and C_2 halons of general interest, in particular those included in the set of molecules studied by Zachariah et al.[3] by the bond-additivity-corrected MP4 (BAC-MP4) method.[21−23] We also present two approximate schemes derived from G3 that enabled us to reduce the computational cost of G3 and, therefore, to obtain heats of formation for larger molecules, viz., those with more than six heavy atoms, on modest workstations.

Theory and Computational Methods

Recent advances in computational quantum chemistry have made the ab initio calculation of heats of formation via the computation of atomization energies a realistic endeavor. The Gaussian methods G2[20] and more recently G3,[19] developed by Pople and co-workers, achieve this end via accurate estimates of the atomic and molecular energies in a near-complete one-particle basis and incorporation of an empirical (higher-level) correction term. The former aim is achieved by correcting the energy obtained in a quadratic configuration-interaction (QCISD(T)) calculation in a small split valence + polarization functions basis (6-311G(d,p) or 6-31G(d)) by MP4 and MP2 estimates of the changes in the energy with systematic enlargement of the basis sets. Alternatively, as pioneered by Martin,[24,25] Dixon, Feller,[26,27] and others,[28,29] the same high level of theory [mostly the coupled-cluster (CCSD(T)) method] is employed in successively larger correlation-consistent basis computations, such that the computed energies can be confidently extrapolated to an effectively complete basis limit. Using computed atomization energies at 0 K in conjunction with experimental heats of formation of the elements in their atomic states, the heats of formation of the molecules at 0 K and hence at 298 K are readily obtained, as discussed in detail by Curtiss et al.,[30] by calculating also the appropriate thermal contributions to the atomic and molecular enthalpies.

Direct use of atomization energies for the computation of heats of formation of chemical accuracy (usually understood to be ∼1 kcal mol^{-1}) requires, of course, the same level of accuracy in the computed atomization energies. For small molecules, this is achievable. For example, for the Gaussian data set of 299 molecules, on average, the G2 and G3 atomization energies have been found to be within 1.48 and 1.02 kcal mol^{-1} of experiment.[19] More recently, Martin and Oliveira,[24] using a range of extrapolation schemes for CCSD(T) energies, demonstrated an even higher level of accuracy of 0.24 kcal mol^{-1} in the computation of heats of formation of some 30 small first- and second-row molecules.

The major part of the work reported in this paper was carried out using the G3 and G2(MP2) levels of theory. Unfortunately, given the current limitations of our computing resources, it was not practicable to carry out G3 calculations for molecules with more than six heavy atoms. To treat larger molecules, we propose two approximations to G3 in the spirit of G3(MP2)[31] and G2(MP2)[18] that, in our view, retain the major advantages of G3 while offering considerable reductions in computational cost. To develop and justify the proposed approximations, we write the (vibrationless) equilibrium G3 energy (at the MP2/6-31G(d) geometry), E_e(G3), as

$$E_e(\mathrm{G3}) = E[\mathrm{QCISD(T)/6\text{-}31G(d)}] + \Delta E(+) + \Delta E(\mathrm{2df,p}) + \Delta E(\mathrm{G3large}) + E(\mathrm{SO}) + E(\mathrm{HLC}) \quad (10)$$

where $\Delta E(+)$, ΔE(2df,p), ΔE(G3large), E(SO), and E(HLC) are corrections for diffuse, higher polarization, and larger basis set effects (that include core−valence correlation and nonadditivity), spin−orbit, and the so-called "higher-level" corrections, respectively, as defined by Curtiss et al.[19] In G3, $\Delta E(+)$ and ΔE(2df,p) are evaluated at the MP4(SDTQ) level, while ΔE(G3large) is obtained from MP2 energies, including MP2-(full)/G3large. As the most expensive step in a G3 calculation is the MP4(SDTQ)/6-31G(2df,p) computation of the energy in ΔE(2df,p), which is dominated by the evaluation of the triple excitations' contribution, an obvious and reasonable approximation to G3 is to calculate the contributions to ΔE(2df,p), or even both $\Delta E(+)$ and ΔE(2df,p), at a lower level, such as MP4(SDQ), MP3, or even MP2. Thus, we define the G3(MP4SDQ) approximation as

$$E_e[\text{G3(MP4SDQ)}] = E[\text{QCISD(T)/6-31G(d)}] + \Delta E(+)_{\text{MP4SDQ}} + \Delta E(\text{2df,p})_{\text{MP4SDQ}} + \Delta E(\text{G3large}) + E(\text{SO}) + E(\text{HLC}) \quad (11)$$

The MP2 alternative then trivially results in the G3[MP2(full)] approximation

$$E_e\{\text{G3[MP2(full)]}\} = E[\text{QCISD(T)/6-31G(d)}] + E[\text{MP2(full)/G3large}] - E[\text{MP2/6-31G(d)}] + E(\text{SO}) + E(\text{HLC}) \quad (12)$$

The G3[MP2(full)] method is, of course, closely related to the G3(MP2)[31] method. In the latter, the MP2 correction does not include core−valence correlation, and thus, the G3large basis is reduced to the smaller G3MP2large set.

The proposed G3[MP2(full)] and G3(MP4SDQ) methods can be further improved by optimizing the HLC terms, as done for G3(MP2). As discussed in the following section, to minimize the deviation between the G3 and G3(MP4SDQ) or G3[MP2-(full)] heats of formation for the molecules studied in this work, we propose an adjustment to the HLC terms of the atoms only, viz., to C and D, in the expression

$$E(\text{HLC atoms}) = -Cn_\beta - D(n_\alpha - n_\beta) \quad (13)$$

For G3(MP4SDQ), these are (in mE$_h$) $C = 5.708$ and $D = 0.922$, while for G3[MP2(full)], they are $C = 6.461$ and $D = 0.979$. The equilibrium geometries and vibrational frequencies in all of these approximate G3 schemes are identical to those defined by G3.

A group of small molecules, namely, the closed-shell HCCH, HCCF, and FCCF acetylenes, and the HCC, FCC, and the formyloxyl (HCOO) radicals, were chosen for a more extensive computational study, in which their heats of formation were computed by a complete basis set extrapolation technique, as recommended by Dixon and Feller.[26] In this work, the equilibrium geometries were optimized at the CCSD(T)/cc-pVTZ level. The zero-point vibrational energies of these molecules (with the exception of HCOO) were calculated at the MP2/cc-pVTZ level and scaled by a factor of 0.96, as in previous work by our group.[32] [A very similar factor, 0.9646, was proposed by Pople et al.[33] for the scaling of zero-point energies obtained at the MP2(full)/6-31G(d) level.] The open-shell coupled-cluster and MP2 calculations were carried out using the restricted formalisms, viz., RCCSD(T) and ROMP2. As discussed in a subsequent section, the HCOO frequencies were taken from the published work of Rauk et al.[34]

The electronic energies of the molecules and their constituent atoms were computed at the valence (R)CCSD(T) level using the sequence of (diffuse function) augmented correlation-consistent basis sets aug-cc-pVxZ, $x = 2$ (D), 3 (T), and 4 (Q).[35,36] The resulting energies $E(x)$ were then fitted to a mixed exponential/Gaussian function

$$E(x) = A + B\exp(1 - x) + C\exp[-(x - 1)^2] \quad (14)$$

and to the asymptotic formula

$$E(x) = A + B/(l_{\max} + 1/2)^4 \quad (15)$$

where A, B, and C are (fitted) constants and $l_{\max}$ is the highest angular momentum quantum number in the basis set. The constant A thus represents the complete basis set (CBS) limit to the valence (R)CCSD(T) energy ($x \rightarrow \infty$). Using the notation of Dixon and Feller,[26] the resulting extrapolated energies are denoted CBS(aDTQ/mix) and CBS(aTQ/$l_{\max}$), indicating the extrapolation technique and the sequence of basis sets used. Note that the $l_{\max}$-type fit utilizes only the (augmented) triple and quadruple-ζ basis sets. The extrapolated energies were then corrected for core−valence correlation (CV corr) using the cc-pCVQZ basis,[37,38] by computing the difference between the all-electron (R)CCSD(T)/cc-pCVQZ and valence (R)CCSD(T)/cc-pVQZ energies. The energies were further corrected for scalar relativistic effects, by computing, using first-order perturbation theory, the Darwin and mass-velocity contributions.[39,40] As in our previous work on the heats of formation of halocarbenes,[32] these relativistic corrections were computed at the complete-active-space second-order perturbation theory (CASPT2) level of theory[41,42] with full-valence complete-active-space self-consistent-field (CASSCF)[43,44] reference states using the G3large basis.

After combining the molecular electronic and zero-point vibrational energies and correcting the computed atomic energies for spin−orbit coupling, the atomization energies at 0 K, ΣD_0, and hence the heats of formation at 0 K, were computed. By adding to $\Delta_f H_0^0$ the appropriate enthalpy differences ($H_{298} - H_0$), for which accurate experimental values are available in the case of the elements and which can be readily calculated for the molecule of interest from the rotational constants and vibrational frequencies, the heats of formation at 298 K are readily obtained, as discussed in detail by Curtiss et al.[30]

All Gaussian3 and related calculations were carried out using the Gaussian 98 programs.[45] The (R)CCSD(T) and ROMP2 computations of the CBS studies were performed using the MOLPRO,[46−48] CADPAC6,[49] and ACES2[50] programs, while MOLCAS4[51] was used to carry out the CASPT2 relativistic correction calculations. All computations were performed on DEC alpha 600/5/333 and COMPAQ XP1000/500 workstations of the Theoretical Chemistry group at the University of Sydney.

Results and Discussion

Heats of Formation from G3 and Related Atomization Eenergies. The G3 energies (including zero-point vibrational contributions) for the C$_1$ and C$_2$ halons are listed in Tables 1 and 2, respectively, along with the heats of formation at 298 K that were obtained from atomization energies computed at the G3, G3[MP2(full)], G3(MP4SDQ), and G2(MP2) levels of theory. The appropriate atomic data used in the computation of the molecular atomization energies and heats of formation are given in Table S1 of the Supporting Information. As the geometries of the majority of these molecules, calculated at the SCF/6-31G(d) level, were published by Zachariah et al.,[3] the MP2(full)/6-31G(d) geometries obtained in our work are not included in this paper. However, as all rotational constants and vibrational frequencies are given in Tables S2−S4 of the Supporting Information, any additional thermochemical data could readily be generated by the interested reader. Tables 1

TABLE 1: C_1 Fluorohydrocarbons: G3 Energies and Computed and Literature Values of Heats of Formation (in kcal mol^{-1} unless Indicated Otherwise)

molecule	E_0(G3)/E_h	$\Delta_f H^0_{298}$ G3	$\Delta_f H^0_{298}$ G3[MP2(full)]	$\Delta_f H^0_{298}$ G3(MP4SDQ)	$\Delta_f H^0_{298}$ G2[a]	$\Delta_f H^0_{298}$ G2(MP2)	$\Delta_f H^0_{298}$ literature[b]	diff G3 − lit
CH_4	−40.45762	−18.1	−17.5	−18.7	−18.6	−18.1	−17.90 ± 0.08[c]	−0.2
CH_3F	−139.64964	−56.9	−56.3	−57.3	−58.3	−58.6	−55.6 ± 2.0[d]	−1.3
CH_2F_2	−238.86227	−108.4	−107.9	−108.8	−110.8	−111.6	−108.1 ± 0.4[d]	−0.3
CHF_3	−338.08656	−167.1	−166.9	−167.6	−170.9	−171.8	−166.7 ± 0.6[d]	−0.4
CF_4	−437.30780	−223.9	−223.7	−224.7	−228.6	−230.1	−223.0 ± 0.4[d]	−0.9
							−223.1 ± 1.1[e]	−0.8
CH_3	−39.79329	34.0	34.5	33.4	35.1	35.6	35.1 ± 0.1[f]	−1.1
CH_2F	−138.98968	−7.7	−7.4	−8.3		−7.9	−7.8 ± 2.0[g]	0.1
CHF_2	−238.20132	−58.6	−58.6	−59.2		−60.6	−59.2 ± 2.0[g]	0.6
CF_3	−337.41737	−112.2	−112.3	−112.9	−114.7	−115.8	−112.8[h]	−0.6
							−112.5 ± 1.0[i]	−0.5
CH_2 ($^1A_1$)	−39.10301	101.9	102.2	101.2	101.4	101.7	101.7 ± 0.7[j]	0.2
							102.6 ± 1.0[k]	−0.7
CHF	−138.34011	34.8	34.7	34.4	31.7	32.6	34.2 ± 3.0[l]	0.6
							35.1 ± 1.0[k]	−0.3
CF_2	−237.60041	−46.6	−47.2	−47.0	−48.2	−50.7	−44.6[m]	−2.0
							−44.0[l]	−2.6
							−45.9 ± 0.3[i]	−0.7
CH	−38.45831	141.1	141.3	140.4	141.9	142.2	142.0 ± 0.1[c]	−0.9
CF	−137.72111	58.0	57.6	57.4		57.0	59.4 ± 0.3[i]	−1.4
CH_2O	−114.43106	−26.6	−26.5	−26.3	−27.9	−26.5	−26.0 ± 1.5[n,o]	−0.6
CHFO	−213.66577	−92.0	−92.0	−91.7		−93.0	−90.0 ± 3.6[c,o]	−2.0
							−91.6 ± 1.7[p]	0.4
CF_2O	−312.88194	−145.7	−145.7	−145.5	−148.6	−147.8	−152.7 ± 0.4[c]	7.0
							−145.9 ± 0.8[q]	0.2
CHO	−113.79156	9.7	9.4	10.0	9.3	10.8	9.96 ± 0.20[f]	−0.3
CFO	−213.00549	−42.7	−43.0	−42.4		−43.0	−38.5 ± 1.7[r]	−4.9
							−44.0 ± 0.5[q]	1.3
CH_3OH	−115.62921	−48.1	−47.3	−47.8	−49.4	−47.8	−48.1 ± 0.1[s,o]	0.0
CH_2FOH	−214.84531	−101.9	−101.1	−101.4		−102.9		
CHF_2OH	−314.07127	−161.6	−161.0	−161.2		−163.9		
CF_3OH	−413.29243	−218.3	−217.7	−218.1		−222.1	−217.7 ± 2.0[p]	−4.8
CH_3OF	−214.71751	−21.5	−20.1	−21.1		−21.9	−17.3 ± 3.0[t,o]	−4.2
CH_2FOF	−313.92729	−71.2	−69.9	−70.7		−73.1		
CHF_2OF	−413.14211	−123.9	−122.7	−123.6		−126.4		
CF_3OF	−512.35912	−178.0	−176.8	−177.8		−183.0	−173.0 ± 2.0[p]	4.8
CH_3O	−114.96272	4.9	5.6	4.3		7.0	4.1 ± 0.2[u]	0.8
CH_2FO	−214.17891	−48.9	−48.4	−49.3		−48.3		
CHF_2O	−313.38786	−98.0	−97.6	−98.6		−99.0		
CF_3O	−412.60361	−151.2	−150.9	−151.9		−153.8	−149.2 ± 2.0[p]	5.5
CH_2OH	−114.97710	−3.9	−3.4	−3.7	−3.8	−2.1	−2.9 ± 1.0[f]	−1.0
CHFOH	−214.18595	−53.0	−52.6	−52.7		−54.9		
CF_2OH	−313.40523	−108.7	−108.3	−108.4		−110.0		
CH_2OF	−214.05996	26.1	27.3	26.5		27.2		
CHFOF	−313.25679	−15.3	−14.2	−15.3		−18.0		
CH_3OOH	−190.72485	−30.1	−28.7	−29.0		−28.9	−33.2[v]	3.1
							−31.3 ± 2.0[n,o]	1.2
CF_3OOH	−488.37663	−193.1	−191.8	−192.2		−194.9		
CH_3OO	−190.09001	2.9	4.1	3.0		5.7	2.2[v]	0.7
CF_3OO	−487.73047	−152.9	−151.9	−153.0		−154.7	−144.0 ± 3.0[t,o]	−8.9
HCOOH	−189.65671	−90.6	−90.2	−89.4	−92.5	−85.6	−90.5 ± 0.1[n,o]	−0.1
FCOOH	−288.87711	−146.9	−146.6	−145.8		−145.4		
HCOO ($^2A_1$)	−188.98028	−31.1	−30.3	−29.7		−26.8	−37.7 ± 3.0[w]	5.6
							−29.3 ± 1.0[x]	−2.8
FCOO ($^2B_2$)	−288.19901	−86.5	−86.1	−85.5		−85.5		
CH_2OHOH	−190.82596	−93.9	−92.8	−92.6		−92.7	−93.5 ± 2.0[y]	−0.4
CF_2OHOH	−389.27646	−212.3	−211.3	−211.1		−213.7		
OCH_2OH	−190.15797	−39.9	−39.0	−39.5		−37.0		
OCF_2OH	−388.59024	−146.9	−146.2	−146.7		−139.3		

[a] G2 results from refs 12, 20, and 52. [b] Experimental value unless otherwise indicated by italics and footnotes. [c] Reference 53. [d] Reference 54. [e] CCSD(T)/CBS computations, ref 55. [f] Reference 56. [g] Reference 57. [h] Reference 58. [i] CCSD(T)/CBS computations, ref 27, with thermal corrections from this work. [j] Reference 59. [k] CCSD(T)/CBS computations, ref 32. [l] Reference 60. [m] Reference 61. [n] Reference 62. [o] Error as given in ref 3. [p] Reference 63. [q] CCSD(T)/CBS computations, ref 26, with thermal corrections from this work. [r] Reference 64. [s] Reference 65. [t] Reference 66. [u] Reference 67. [v] Reference 68. [w] Reference 69. [x] Reference 70. [y] Reference 71.

and 2 also contain current literature data, i.e., experimental values and/or the results of accurate, high-level ab initio computations. In the majority of cases, the G3 heats of formation agree with the literature values to ~1 kcal mol^{-1}, once allowance is made for the quoted uncertainties in the latter. However, in some instances, larger discrepancies, in excess of 2 kcal mol^{-1}, are noted, e.g., for CF_2O, CFO, CF_2CF_2, CF_3O, and HCOO. The first three of these molecules were recently the subject of an extensive theoretical study by Dixon, Feller, and Sandrone,[26,27] who concluded that the heats of formation

TABLE 2: C_2 Fluorohydrocarbons: G3 Energies and Computed and Literature Values of Heats of Formation (in kcal mol^{-1} unless Indicated Otherwise)

molecule	E_0(G3)/E_h	$\Delta_f H^0_{298}$ G3	$\Delta_f H^0_{298}$ G3[MP2(full)]	$\Delta_f H^0_{298}$ G3(MP4SDQ)	$\Delta_f H^0_{298}$ G2[a]	$\Delta_f H^0_{298}$ G2MP2	$\Delta_f H^0_{298}$ literature[b]	diff G3 − lit
CH_3CH_3	−79.72340	−20.4	−19.9	−20.9	−20.6	−19.9	−20.1 ± 1.0[c,d]	−0.3
CH_3CH_2F	−178.92623	−65.7	−65.2	−66.1	−71.2	−66.8	−66.1 ± 1.0[e]	0.4
CH_2FCH_2F	−278.12348	−107.3	−106.9	−107.6	−109.9	−110.9	*−103.7 ± 2.8*[f]	−3.6
CH_3CHF_2	−278.14559	−121.3	−120.9	−121.6	−123.9	−123.9	−119.7 ± 1.5[g]	−1.6
CHF_2CH_2F	−377.33990	−161.1	−160.7	−161.3	−164.2	−165.3	−158.9 ± 1.0[h]	−2.2
CH_3CF_3	−377.37214	−181.3	−181.0	−181.7	−184.5	−185.3	−178.2 ± 0.4[g]	−3.1
CHF_2CHF_2	−476.55281	−212.5	−212.2	−212.7	−216.7	−216.9	−209.8 ± 4.2[f]	−2.7
CH_2FCF_3	−476.56312	−219.0	−218.7	−219.3	−223.3	−224.7	−214.1 ± 2.0[g]	−4.9
CHF_2CF_3			−268.2	−268.8	−273.9		−264.0 ± 1.1[g]	
CF_3CF_3			−323.8	−324.5	−330.7		−320.9 ± 1.5[g]	
CH_3CH_2	−79.06400	28.7	29.0	28.0	29.9	30.7	28.3 ± 1.0[c,d]	0.4
CH_2FCH_2	−178.26370	−14.7	−14.4	−15.2		−14.4	−14.2 ± 2.0[i]	−0.5
CH_3CHF	−178.26902	−18.2	−18.0	−18.7		−18.0	−16.8 ± 2.0[i]	1.4
CH_2FCHF	−277.46342	−58.1	−58.0	−58.6		−59.6	*−57.0 ± 3.0*[f]	−1.1
CHF_2CH_2	−277.47984	−68.3	−68.0	−68.7		−69.5	*−68.3 ± 3.6*[f]	0.0
CH_3CF_2	−277.48538	−71.9	−71.9	−72.5		−73.5	−72.3 ± 2.0[j]	0.4
CH_2FCF_2	−376.67696	−110.0	−110.0	−110.5		−113.3	*−107.5 ± 3.6*[f]	−2.5
CHF_2CHF	−376.67800	−110.6	−110.6	−111.1		−113.6	*−109.0 ± 3.6*[f]	−1.6
CF_3CH_2	−376.70469	−127.3	−127.1	−127.7		−129.8	−123.6 ± 1.0[j]	−3.7
CF_3CHF	−475.90075	−168.3	−168.3	−168.8		−172.7	−162.7 ± 2.3[k]	−5.6
CHF_2CF_2	−475.88795	−160.3	−160.4	−160.7		−165.0	*−158.9 ± 4.5*[f]	−1.4
CF_3CF_2			−216.5	−216.9			−213.0 ± 1.0[j]	
CH_2CH_2	−78.50742	12.3	11.7	12.1	12.8	13.2	12.54 ± 0.07[l]	−0.3
CH_2CHF	−177.71256	−34.4	−35.1	−34.5	−34.9	−35.0	−33.5 ± 0.6[m]	−0.9
CHFCHF−Z	−276.90631	−73.8	−74.6	−73.9		−76.0	−71.0 ± 2.4[n]	−2.8
CHFCHF−E	−276.90730	−74.5	−75.3	−74.7		−76.9	−70.0 ± 2.4[n]	−4.5
CH_2CF_2	−276.92299	−84.5	−85.2	−84.6		−86.4	−80.4 ± 1.0[m]	−4.1
$CHFCF_2$	−376.11080	−120.1	−120.9	−120.2		−123.7	−117.4 ± 2.2[m]	−2.7
CF_2CF_2	−475.30917	−162.3	−163.2	−162.6	−165.6	−167.5	−157.4 ± 0.7[l]	−4.9
							−160.6 ± 1.5[o]	−1.7
							−160.5 ± 1.5[p]	−1.8
CH_3CH	−78.38810	87.5	87.4	87.0		87.7		
CH_2FCH	−177.59324	40.7	40.6	40.5		39.6		
CHF_2CH	−276.79333[q]	−12.1[q]						
CF_3CH	−376.01256	−58.2	−58.2	−58.5		−63.4		
CH_3CF	−177.62985	17.9	17.5	17.6		16.2		
CH_2FCF	−276.82347	−21.7	−22.1	−21.9		−25.2		
CHF_2CF	−376.02767	−67.7	−68.1	−67.9		−73.0		
CF_3CF	−475.24834	−124.0	−124.4	−124.2		−131.0		
CH_2CH	−77.83307	70.5	70.0	70.2	72.7	73.4	71.6 ± 0.8[r]	−1.1
CHFCH-Z	−177.03040	28.7	28.1	28.4		29.8		
CHFCH-E	−177.03102	28.3	27.7	27.9		29.4		
CH_2CF	−177.03465	26.0	25.3	25.6		26.9		
CHFCF-Z	−276.22409	−10.8	−11.6	−11.2		−11.7		
CHFCF-E	−276.22357	−10.4	−11.1	−10.8		−11.2		
CF_2CH	−276.23666	−18.7	−19.4	−19.1		−19.2		
CF_2CF	−375.42392	−54.0	−54.8	−54.4		−56.4	−45.9 ± 2.0[s]	−8.1
CH_3C	−77.75331	120.6	120.4	120.0		122.0		
CH_2FC	−176.95053	78.8	78.6	78.4		78.6		
CHF_2C	−276.14927	36.1	35.8	35.6		34.8		
CF_3C	−375.36705	−18.4	−18.7	−18.9		−22.0		
HCCH	−77.27596	54.9	53.6	55.3	55.8	56.3	54.2 ± 0.2[c,d]	0.7
HCCF	−176.45463	24.8	23.4	25.0		24.9	30.0 ± 5.3[l]	−5.2
FCCF	−275.62524	0.0	−1.6	−0.1		−1.1	5.0 ± 5.0[l]	−5.0
CH_2C	−77.20691	98.5	97.4	98.3		99.3		
CHFC	−176.38031	71.5	70.4	71.3		70.4		
CF_2C	−275.57646	30.4	29.2	30.2		27.5		
CCH	−76.56469	136.3	135.1	136.1	138.7	139.4	135.0 ± 1.0[t]	1.3
CCF	−175.73867	109.3	107.8	108.9		110.5	110.0 ± 5.3[f]	−0.7
CH_2CO	−152.50687	−12.1	−13.2	−11.5	−12.1	−10.4	−11.4 ± 0.4[u]	−0.7
CHFCO	−251.68018	−38.8	−39.9	−38.2		−38.9		
CF_2CO	−350.86874	−75.0	−76.0	−74.4		−76.5		
CHCO	−151.84066	40.9	39.8	41.2		43.4	41.9 ± 2.0[r]	−1.0
CFCO	−251.00583	19.3	18.1	19.6		24.1		
CH_3CHO	−153.71480	−39.8	−39.8	−39.4	−41.0	−39.1	−39.7 ± 0.1[v,d]	−0.1
CH_2FCHO	−252.90987	−80.2	−80.2	−79.7		−80.1		
CHF_2CHO	−352.12071	−130.4	−130.4	−129.8		−132.8		
CF_3CHO	−451.34093	−186.5	−186.5	−186.0		−190.3		
CH_3CFO	−252.95069	−105.8	−105.8	−105.4	−107.7	−106.2		
CH_2FCFO	−352.14170	−143.6	−143.7	−143.1		−144.7		
CHF_2CFO	−451.34766	−190.7	−190.8	−190.2		−194.6		

TABLE 2: (Continued)

molecule	E_0(G3)/E_h	$\Delta_f H^0_{298}$ G3	$\Delta_f H^0_{298}$ G3[MP2(full)]	$\Delta_f H^0_{298}$ G3(MP4SDQ)	$\Delta_f H^0_{298}$ G2[a]	$\Delta_f H^0_{298}$ G2MP2	$\Delta_f H^0_{298}$ literature[b]	diff
CF_3CFO	−550.56716	−246.3	−246.3	−245.8		−251.4		
CH_3CO	−153.07373	−2.5	−2.7	−2.1	−2.8	−0.9	−2.4 ± 0.3[r]	−0.1
CH_2FCO	−252.26707	−41.9	−42.1	−41.5		−41.7		
CHF_2CO	−351.47501	−90.3	−90.5	−89.8		−92.1		
CF_3CO	−450.69399	−145.6	−145.9	−145.2		−148.9		

[a] G2 results from refs 12, 20, and 52. [b] Experimental value unless otherwise indicated by italics and footnotes. [c] Reference 72. [d] Error as given in ref 3. [e] Reference 73. [f] BAC-MP4, ref 3. [g] Reference 74. [h] Reference 75. [i] Reference 76. [j] Reference 61. [k] Reference 77. [l] Reference 53. [m] Reference 58. [n] Reference 78. [o] CCSD(T)/CBS computations, ref 27, with thermal corrections from ref 55. [p] CCSD(T)/CBS computations, ref 55. [q] Computed at HF/6-31G(d) geometry, see text [r] Reference 56. [s] Reference 79. [t] Reference 57. [u] Reference 80. [v] Reference 62.

of these molecules at 0 K are −145.2 ± 0.8, −44.1 ± 0.5, and −159.8 ± 1.5 kcal mol^{-1}, respectively, values that differ from the accepted experimental estimates by up to 6 kcal mol^{-1} but are consistent with the G3 predictions. The theoretical value for tetrafluoroethylene has been recently confirmed by the high-level computations of Bauschlicher and Ricca,[55] who obtained $\Delta_f H^0_{298} = -160.5 \pm 1.5$ kcal mol^{-1}. The remaining problem cases, including CF_3O, will be discussed in the next section on isodesmic calculations. We note also that, for a number of systems, no errors are quoted in the literature cited, so for these, we have quoted the estimated errors of Zachariah et al.[3] On the whole, the G3[MP2(full)] and G3(MP4SDQ) results are in reasonable agreement with those obtained by the application of G3. The average absolute deviations of G3[MP2(full)] and G3(MP4SDQ) from G3 are ∼0.5 and 0.4 kcal mol^{-1}, respectively, the largest deviation being 1.6 kcal mol^{-1} in the case of FCCF. The deviations are significantly larger when the G2(MP2) and G3 results are compared, up to 6 kcal mol^{-1}. However, as discussed in the next section, the consistency between the computed heats of formation is much improved, once isodesmic reaction schemes are used.

No equilibrium structure was found at the MP2(full)/6-31G(d) level for the CHF_2CH carbene. The MP2 and the B3LYP/6-31G(d) density functional optimizations converged to difluoroethylene, CF_2CH_2. These results suggest that CHF_2CH may not exist as a distinct molecule. Nevertheless, to give an estimate of the energy of this probably metastable carbene, its G3 heat of formation was computed at the HF/6-31G(d) geometry, as at that level of theory there is a local minimum on the potential surface for CHF_2CH.

Comparison of the G3 heats of formation with the BAC-MP4 values for the C_1 and C_2 halons studied by Zachariah et al.[3] suggests remarkably good agreement on the average, the mean absolute deviation between the two sets being just 1.6 kcal mol^{-1}. Although the agreement is mostly excellent (∼1 kcal mol^{-1} or better), for a number of molecules, e.g., FCCF, CCH, CH and CH_2FOF, substantial disagreement (∼5 kcal mol^{-1}) has been noted.

Heats of Formation from G3 and Related Isodesmic Reaction Enthalpies. The calculation of accurate atomization energies, and hence heats of formation, is a stringent and demanding test of the quantum chemical methodology, as the molecules of interest and their constituent atoms need to be described in an accurate and balanced manner. It has long been recognized, however, that the computation of isodesmic reaction energies, in which the number of bond types is conserved, is much less demanding with respect to the resolution of electron correlation. Therefore, reasonably accurate predictions of heats of formation are possible by utilizing isodesmic schemes, even at relatively low levels of theory. However, the success of such an approach crucially depends on the availability of accurate thermochemical data for molecules that are chemically similar to those under study, i.e., that have the same type of bonds. Given the demonstrated accuracy of G3 theory in the calculation of atomization energies, we do not expect major improvements in the heats of formation by recalculating these from suitable isodesmic reaction energies. What we do expect, however, is a higher level of consistency between the four methods used, viz., G3, G3[MP2(full)], G3(MP4SDQ), and G2(MP2), than observed for the data in Tables 1 and 2. Therefore, the application of isodesmic schemes to the heats of formation obtained from atomization energies can also be regarded as a test of the consistency of the calculations and their results.

There are relatively few bond types among the molecules in this study (such as C−H, C−F, C−C, C═C, C−O, C═O, etc.) but, as can be noted on inspection of the data in Tables 1 and 2, the number of molecules with accurate (≤1 kcal mol^{-1}) experimental or computed heats of formation is quite small, so that not all bond types are represented by the selected set: CH_4, CF_4, CH_3, CH_2, CF_2, CF_2O, CFO, CH_3OH, CH_3O, C_2H_6, C_2H_4, and C_2H_2. Nevertheless, using these 12 molecules, it is possible to construct isodesmic reactions for the majority of the molecules studied in this work, as demonstrated by the results summarized in Table 3. For example, the heats of formation of all hydrofluoroethanes can be obtained from the computed heats of the reactions

$$C_2H_6 + \frac{x}{4}CF_4 \rightarrow C_2H_{6-x}F_x + \frac{x}{4}CH_4 \qquad (16)$$

and experimental enthalpies of formation of C_2H_6, CH_4, and CF_4. As discussed by Berry et al.,[12] such use of isodesmic reactions is equivalent to the application a bond-additivity correction to the heat of formation of the molecule of interest, i.e., $C_2H_{6-x}F_x$ in the current example. Such a bond-additivity-corrected enthalpy of formation is then written as

$$\Delta_f H^0_{298}(\mathrm{BAC}) = \Delta_f H^0_{298}(\mathrm{calc}) - \Delta_{CC} - (6-x)\Delta_{CH} - x\Delta_{CF} \qquad (17)$$

where $\Delta_f H^0_{298}$(calc) is the enthalpy of formation of $C_2H_{6-x}F_x$ calculated from its atomization energy. The bond correction parameters Δ_{CC}, Δ_{CH}, and Δ_{CF} are obtained by comparison of the calculated and experimental heats of formation of the reference molecules C_2H_6, CH_4, and CF_4, e.g.

$$\Delta_{CH} = \frac{1}{4}[\Delta_f H^0_{298}(CH_4 - \mathrm{calc}) - \Delta_f H^0_{298}(CH_4 - \mathrm{exp})] \qquad (18)$$

As expected, the G3, G3[MP2(full)], G3(MP4SDQ), and G2(MP2) heats of formation obtained from the corresponding isodesmic reaction enthalpies, as listed in Table 3, are in much closer agreement than those obtained from atomization energies. The differences are generally no greater than 0.3 kcal mol^{-1}.

TABLE 3: C_1 and C_2 Fluorohydrocarbons: Computed Heats of Formation via Isodesmic (ID) Reactions of Selected Species (in kcal mol^{-1})

molecule	eq^n	G3 ID	diff[b] ID − AE	G3[MP2(full)] ID	G3(MP4SDQ) ID	G2(MP2) ID	literature[c]	diff G3(ID) − lit
CH_3F	1	−56.5	0.4	−56.4	−56.3	−56.7	−55.6 ± 2.0	−0.9
CH_2F_2	1	−107.8	0.6	−107.7	−107.5	−108.0	−108.1 ± 0.4	0.2
CHF_3	1	−166.4	0.7	−166.5	−166.1	−166.5	−166.7 ± 0.6	0.4
CH_2F	2	−6.5	1.2	−6.7	−6.3	−6.8	−7.8 ± 2.0	1.3
CHF_2	2	−57.2	1.4	−57.5	−57.0	−57.7	−59.2 ± 2.0	2.0
CF_3	2	−110.7	1.5	−111.0	−110.6	−111.3	−112.5 ± 1.0[d]	1.8
CHF	3	35.7	0.9	35.4	36.0	35.2	35.1 ± 1.0[e]	0.6
CF_2	3	−45.5	0.9	−46.2	−45.1	−46.3	−45.9 ± 0.3[d]	1.2
CHF	4	35.1	0.3	35.5	35.6	35.7	35.1 ± 1.0[e]	0.0
CH_2O	5	−27.2	−0.6	−27.3	−27.2	−28.0	−26.0	−1.2
CHFO	5	−92.4	−0.4	−92.5	−92.3	−92.8	−90.0	−2.4
CHO	6	8.0	−1.7	7.9	8.0	7.9	10.4 ± 2.0	−0.9
CH_2FOH	7	−101.7	0.2	−101.6	−101.5	−101.5		
CHF_2OH	7	−161.2	0.4	−161.2	−161.0	−160.8		
CF_3OH	7	−217.8	0.5	−217.7	−217.7	−217.2	−213.5	−4.3
CH_2FO	8	−49.6	−0.7	−49.7	−49.4	−49.6		
CHF_2O	8	−98.6	−0.6	−98.7	−98.5	−98.6		
CF_3O	8	−151.6	−0.4	−151.7	−151.5	−151.7		
CH_3CH_2F	9	−65.2	0.5	−65.1	−65.1	−65.3	−62.9 ± 0.4	−2.3
CH_2FCH_2F	9	−106.6	0.7	−106.5	−106.3	−107.7	−103.7 ± 2.8	−2.9
CH_3CHF_2	9	−120.6	0.7	−120.5	−120.3	−120.7	−119.7 ± 1.5	−1.0
CHF_2CH_2F	9	−160.2	0.9	−160.1	−159.8	−160.4	−158.9 ± 1.0	−1.4
CH_3CF_3	9	−180.5	0.8	−180.4	−180.2	−180.4	−178.2 ± 0.4	−2.3
CHF_2CHF_2	9	−211.5	1.0	−211.3	−211.0	−210.2	−209.8 ± 4.2	−1.7
CH_2FCF_3	9	−218.0	1.0	−217.8	−217.6	−218.0	−214.1 ± 1.0	−3.9
CHF_2CF_3	9			−267.0	−266.9		−264.0 ± 1.1	1.3
CF_3CF_3	9			−322.3	−322.3		−320.9 ± 1.5	−2.1
CH_3CH_2	10	29.8	1.1	29.7	29.8	29.7	28.3	1.5
CH_2FCH_2	10	−13.4	1.3	−13.5	−13.2	−13.6	−11.40 ± 0.24	−2.0
CH_3CHF	10	−16.9	1.3	−17.1	−16.7	−17.3	−18.2 ± 1.4	1.3
CH_2FCHF	10	−56.6	1.5	−56.7	−56.3	−57.1	−57.0 ± 3.0	0.4
CHF_2CH_2	10	−67.0	1.3	−66.9	−66.8	−67.2	−68.3 ± 3.6	1.3
CH_3CF_2	10	−70.6	1.3	−70.8	−70.6	−71.0	−72.3 ± 2.0	1.8
CH_2FCF_2	10	−108.5	1.5	−108.6	−108.4	−109.1	−107.5 ± 3.6	−1.0
CHF_2CHF	10	−109.1	1.5	−109.2	−109.0	−109.4	−109.0 ± 3.6	−0.1
CF_3CH_2	10	−125.8	1.5	−125.7	−125.6	−125.8	−123.6 ± 1.0	−2.3
CF_3CHF	10	−166.7	1.6	−166.7	−166.5	−167.0	−162.7 ± 2.3	−4.0
CHF_2CF_2	10	−158.7	1.6	−158.8	−158.4	−159.3	−158.9 ± 4.5	0.2
CF_3CF_2	10			−214.6	−214.3		−213.0 ± 1.0	
CH_2CHF	11	−34.0	0.4	−34.0	−33.8	−34.0	−33.5 ± 0.6	−0.5
CHFCHF-Z	11	−73.2	0.6	−73.2	−73.0	−73.3	−71.0 ± 2.4	−2.2
CHFCHF-E	11	−73.9	0.6	−73.9	−73.8	−74.1	−70.0 ± 2.4	−3.9
CH_2CF_2	11	−83.9	0.6	−83.8	−83.7	−83.7	−80.4 ± 1.0	−3.5
$CHFCF_2$	11	−119.3	0.8	−119.2	−119.1	−119.3	−117.4 ± 2.2	−2.0
CF_2CF_2	11	−161.3	1.0	−161.2	−161.2	−160.6	−160.5	−0.8
CH_2CH	12	71.4	0.9	71.6	71.3	71.7	71.6 ± 0.8	−0.2
CHFCH-Z	12	29.8	1.1	30.0	29.7	30.0		
CHFCH-E	12	29.4	1.1	29.6	29.2	29.6		
CH_2CF	12	27.1	1.1	27.2	26.9	26.9		
CHFCF-Z	12	−9.6	1.2	−9.5	−9.7	−9.9		
CHFCF-E	12	−9.2	1.2	−9.0	−9.3	−9.4		
CF_2CH	12	−17.5	1.2	−17.3	−17.6	−17.4		
CF_2CF	12	−52.6	1.4	−52.4	−52.6	−52.9	−45.9 ± 2.0	−6.7
CH_3CH	13	88.3	0.8	88.0	88.4	88.2		
CH_2FCH	13	41.7	1.0	41.5	42.1	41.9		
CHF_2CH	13	−10.9	1.2					
CF_3CH	13	−56.9	1.3	−56.8	−56.4	−57.7		
CH_3CF	14	18.5	0.6	18.7	18.5	18.8		
CH_2FCF	14	−20.9	0.8	−20.6	−20.8	−20.9		
CHF_2CF	14	−66.7	1.0	−66.3	−66.6	−66.9		
CF_3CF	14	−122.8	1.2	−122.3	−122.6	−123.9		
HCCF	15	24.3	−0.5	24.3	24.1	24.6	30.0 ± 5.3	−5.7

TABLE 3: (Continued)

molecule	eq[n]	G3 ID	diff[b] ID − AE	G3[MP2(full)] ID	G3(MP4SDQ) ID	G2(MP2) ID	literature[c]	diff G3(ID) − lit
FCCF	15	−0.4	−0.4	−0.5	−0.8	0.3	5.0 ± 5.0	−5.4
CCH	16	136.2	−0.1	135.6	136.2	136.3	135.0 ± 1.0	1.2
CCF	16	109.4	0.1	108.6	109.4	109.2	110.0 ± 5.3	−0.6

[a] Isodesmic Reactions:

$$\left(1-\frac{x}{4}\right)CH_4 + \frac{x}{4}CF_4 \rightarrow CH_{4-x}F_x \tag{1}$$

$$CH_3 + \frac{x}{4}CF_4 \rightarrow \frac{x}{4}CH_4 + CH_{3-x}F_x \tag{2}$$

$$CH_2 + \frac{x}{4}CF_4 \rightarrow CH_{2-x}F_x + \frac{x}{4}CH_4 \tag{3}$$

$$\frac{1}{2}CH_2 + \frac{1}{2}CF_2 \rightarrow CHF \tag{4}$$

$$CF_2O + \frac{x}{4}CH_4 \rightarrow CH_xF_{2-x}O + \frac{x}{4}CF_4 \tag{5}$$

$$CFO + \frac{1}{4}CH_4 \rightarrow CHO + \frac{1}{4}CF_4 \tag{6}$$

$$CH_3OH + \frac{x}{4}CF_4 \rightarrow \frac{x}{4}CH_4 + CH_{3-x}F_xOH \tag{7}$$

$$CH_3O + \frac{x}{4}CF_4 \rightarrow \frac{x}{4}CH_4 + CH_{3-x}F_xO \tag{8}$$

$$C_2H_6 + \frac{x}{4}CF_4 \rightarrow \frac{x}{4}CH_4 + C_2H_{6-x}F_x \tag{9}$$

$$C_2H_6 + CH_3 + \frac{x}{4}CF_4 \rightarrow \left(1+\frac{x}{4}\right)CH_4 + C_2H_{5-x}F_x \tag{10}$$

$$C_2H_4 + \frac{x}{4}CF_4 \rightarrow \frac{x}{4}CH_4 + C_2H_{4-x}F_x \tag{11}$$

$$C_2H_4 + CH_3 + \frac{x}{4}CF_4 \rightarrow \left(1+\frac{x}{4}\right)CH_4 + C_2H_{3-x}F_x \tag{12}$$

$$C_2H_6 + CH_2 + \frac{x}{4}CF_4 \rightarrow \left(1+\frac{x}{4}\right)CH_4 + CH_{3-x}F_xCH \tag{13}$$

$$C_2H_6 + CF_2 + \frac{x+1}{4}CF_4 \rightarrow \left(\frac{x+3}{4}\right)CH_4 + CH_{3-x}F_xCF \tag{14}$$

$$C_2H_2 + \frac{x}{4}CF_4 \rightarrow \frac{x}{4}CH_4 + C_2H_{2-x}F_x \tag{15}$$

$$C_2H_2 + CH_3 + \frac{x}{4}CF_4 \rightarrow \left(1+\frac{x}{4}\right)CH_4 + C_2H_{1-x}F_x \tag{16}$$

[b] Difference between G3 heats of formation obtained via isodesmic (ID) reaction and atomization energy (AE). [c] Experimental value as in Tables 1 and 2, unless otherwise indicated. [d] CCSD(T)/CBS computations, ref 27, with thermal corrections from this work. [e] CCSD(T)/CBS computations, ref 32.

Clearly, considerable error cancellation occurs when we compute the heats of isodesmic reactions. It is worth noting also that all empirical HLC contributions to the Gaussian-2, -3, etc. energies completely cancel when one computes isogyric or isodesmic reaction energies. Nevertheless, the differences between the G3 heats of formation when obtained from atomization energies and isodesmic reaction enthalpies are moderately small, ∼0.9 kcal mol^{-1} on the average and no larger than 1.6 kcal mol^{-1}. This is, of course, expected, given that the heats of formation of the above 12 reference molecules are quite accurately predicted from the G3 atomization energies. On the other hand, in the case of certain heats of formation, such as those of CF_3O, CH_2FCF_3, and CF_3CHF, where initially large discrepancies (∼5 kcal mol^{-1}) between the G3 and literature values were noted (see Table 1), the application of isodesmic, viz., bond-additivity, corrections does not significantly improve the situation. We believe that, in the case of such molecules, the precision in the literature values is considerably less than implied by the quoted errors.

In Table 4, we summarize the heats of formation for the C_3 systems that were of direct interest in the kinetic modeling studies of Hynes et al.[10] The various schemes yield very consistent results in that the isodesmic heats of formation are, with one exception, within 0.2 kcal mol^{-1} of each other and up to ∼3 kcal mol^{-1} higher than those obtained from atomization energies. The variations are largest for hexafluoropropene and the hexafluoropropyl radical. Utilizing the isodesmic results, we estimate the heats of formation of these two species as −276.2 ± 2 and −266.4 ± 3 kcal mol^{-1}, on the basis of the spread of computed values and the expected intrinsic accuracy of the G3 method. Given the good agreement between the computed (isodesmic) and experimental heats of formation for

TABLE 4: C_3 Fluorohydrocarbons: G3 Energies and Computed Values of Heats of Formation from Atomization Energies (AE) and Isodesmic Reactions (ID), as Specified (in kcal mol^{-1} unless Indicated Otherwise)

		$\Delta_f H^0_{298}$ G3		$\Delta_f H^0_{298}$ G3[(MP2(full)]		$\Delta_f H^0_{298}$ G3(MP4SDQ)		$\Delta_f H^0_{298}$
molecule	E_0(G3)/E$_h$	AE	ID	AE	ID	AE	ID	expt
CH_3CHCH_2	−117.78219	4.7	5.0	3.8	4.8	4.6	5.0	4.88[b]
$CH_3CH_2CH_2$	−118.33332	24.5	25.7	24.6	25.5	23.8	25.4	23.9 ± 0.5[c]
CF_3CFCF_2	−713.01767	−277.6	−276.2	−278.3	−275.6	−277.5	−275.7	−275.3 ± 1.1[d]
CF_3CHFCF_2				−269.1	−266.5	−269.3	−266.3	

[a] Isodesmic Reactions:

$$CH_3CH_3 + CH_2CH_2 + \frac{3}{2}CF_4 \rightarrow CF_3CFCF_2 + \frac{5}{2}CH_4$$

$$2CH_3CH_3 + CH_3 + \frac{3}{2}CF_4 \rightarrow CF_3CHFCF_2 + \frac{7}{2}CH_4$$

$$CH_3CH_3 + CH_2CH_2 \rightarrow CH_3CHCH_2 + CH_4$$

$$2CH_3CH_3 + CH_3 \rightarrow CH_3CH_2CH_2 + 2CH_4$$

[b] Reference 81. [c] Reference 82. [d] Reference 83.

TABLE 5: Comparison of G2 and G3 Methods: Analysis of Atomization Energies (kcal mol^{-1}) of CH_4, CH_3F, CH_2F_2, CHF_3, and CF_4

	CH_4			CH_3F			CH_2F_2			CHF_3			CF_4		
	G2	G3	G3 − G2	G2	G3	G3 − G2	G2	G3	G3 − G2	G2	G3	G3 − G2	G2	G3	G3 − G2
AE [QCISD(T)]	401.6	382.9	−18.6	397.9	385.4	−12.5	408.2	402.9	−5.3	425.8	429.5	3.7	441.4	454.5	13.1
ΔAE [MP4/(+)]	−0.4	−1.3	−0.9	1.9	1.3	−0.6	1.6	−0.1	−1.7	−0.2	−5.1	−5.0	−2.8	−12.3	−9.5
ΔAE [MP4/(2df,p)]	5.7	26.5	20.7	10.9	24.9	14.0	16.7	23.8	7.1	23.2	23.3	0.1	30.1	23.5	−6.6
ΔAE [MP2/(large)]	4.3	2.7	−1.6	4.2	1.7	−2.5	4.2	1.5	−2.7	4.2	1.6	−2.6	4.3	2.1	−2.2
ΔAE [ZPE]	−26.8	−26.8	0.0	−23.8	−23.8	0.0	−20.2	−20.2	0.0	−15.8	−15.8	0.0	−10.7	−10.7	0.0
AE (valence)[a]	384.5	384.0	−0.5	391.1	389.5	−1.5	410.5	407.9	−2.6	437.4	433.5	−3.8	462.4	457.2	−5.2
ΔAE [CV]	0.0	1.1	1.1	0.0	1.2	1.2	0.0	1.4	1.4	0.0	1.7	1.7	0.0	1.9	1.9
ΔAE [HLC]	8.7	7.7	−1.0	8.7	8.0	−0.7	8.7	8.3	−0.4	8.7	8.6	−0.1	8.7	8.9	0.2
ΔAE [Spin−Orbit]	0.0	−0.1	−0.1	0.0	−0.5	−0.5	0.0	−0.9	−0.9	0.0	−1.2	−1.2	0.0	−1.6	−1.6
AE (total)[b]	393.2	392.8	−0.4	399.8	398.3	−1.5	419.2	416.7	−2.5	446.1	442.5	−3.5	471.1	466.4	−4.7

[a] AE (valence) = AE [QCISD(T)] + Δ*AE* [MP4/(+) + MP4/(2df,p) + MP2/(large) + ZPE]. [b] AE (total) = AE (valence) + Δ*AE* [CV + HLC + Spin−Orbit].

propene, *n*-propyl, and hexafluoropropene, we expect the computed value for hexafluoropropyl, viz., −266.4 ± 3 kcal mol^{-1}, to be similarly reliable.

Comparison of G2 and G3 Methods: Analysis of Atomization Energies of Fluoromethanes. As the results of the previous sections clearly indicate, the G3 method is superior to G2 and G2(MP2) in the prediction of heats of formation of fluorohydrocarbons from the computed atomization energies. In an effort to gain some understanding of the reasons for this, we carried out an analysis of the G2 and G3 energetics for the fluoromethanes CH_4, CH_3F, CH_2F_2, CHF_3, and CF_4, in which we compare the individual contributions to the composite G2 and G3 atomization energies.

Using the decomposition scheme of eq 10, we list in Table 5 the G2 and G3 atomization energies (AE) obtained by the appropriate QCISD(T) calculations, followed by the MP4 and MP2 corrections (for basis incompleteness) and the zero-point corrections. Up to this point, the differences between G2 and G3 are due to the different "parent" bases, 6-311G(d,p) for G2 and 6-31G(d) for G3, and the different "large" bases, 6-311+G(3df,2p) for G2 and the G3large set for G3. Note that, thus far, all correlated energies, including the MP2/(large), are valence only, and thus, the sum of these contributions is denoted AE(valence). The core−valence correlation (CV) corrections to the G3 energies are listed separately, along with the empirical HLC terms and the spin−orbit coupling corrections that are implicit in G3 and, finally, the resulting total atomization energies at 0 K. The trends displayed by the data in Table 5 are interesting and informative. The largest corrections to the QCI values of the atomization energies (apart from ZPE) are the MP4/(2df,p) terms. While these are relatively constant in the G3 calculations, ranging from 23.3 to 26.5 kcal mol^{-1}, in the case of G2, they vary from 5.7 to 30.1 kcal mol^{-1}. In contrast with these corrections, the MP4/(+) corrections are more significant for G3, especially in CHF_3 and CF_4. These trends point to some basic differences between G2 and G3 in the quality of the respective QCI energies and the relative importance of the MP4/(+) and MP4/(2df,p) corrections in the two schemes. As a further illustration of this point, Figure 1 shows a plot of the QCI atomization energies, corrected by the MP4/(+) and zero-point contributions, against the G3 total atomization energies.

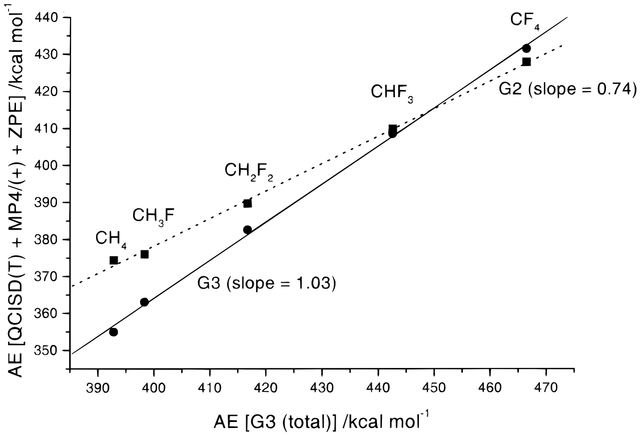

Figure 1. Comparison of G2 and G3 atomization energies of fluoromethanes: correlation of the QCISD(T) + MP4/(+) + ZPE components with the G3 total atomization energies.

TABLE 6: Computed and Extrapolated CCSD(T) Energies, Core−Valence Correlation Corrections, Zero-Point Vibrational Energies, Thermal Corrections to Enthalpies at 298 K, and Relativistic Corrections (in E_h unless Otherwise Indicated)

	CCSD(T) aug-cc-pVQZ	CCSD(T) CBS(mix)	CCSD(T) CBS(l_{max})	CV corr[a]	ZPVE kcal mol^{-1}	H_{298} kcal mol^{-1}	E_{rel}[b]
C_2H_2	−77.21098	−77.22119	−77.22182	−0.11010	16.08	18.50	−0.02956
CFCH	−176.35179	−176.37717	−176.37800	−0.17499	12.21	14.93	−0.11622
C_2F_2	−275.48392	−275.52446	−275.52548	−0.23992	8.09	11.34	−0.20291
C_2H $^2\Sigma$	−76.48915	−76.49876	−76.49922	−0.10949	8.61	10.94	−0.02957
C_2F $^2\Sigma$	−175.62574	−175.65050	−175.65120	−0.17442	5.12	8.04	−0.11722
HCOO $^2A_1$	−188.87336	−188.90056	−188.90120	−0.17690	10.07	12.70	−0.11897
HCOO $^2B_2$	−188.87499	−188.90196	−188.90261	−0.17673	11.75	14.27	−0.11885
HCOO $^2A'$	−188.87209	−188.89898	−188.89963	−0.17679	12.03	14.60	−0.11888
H	−0.49995	−0.50000	−0.50000	0.0		1.48	0.0
C	−37.78660	−37.78940	−37.78950	−0.05317		1.48	−0.01501
O	−74.99484	−75.00401	−75.00424	−0.06065		1.48	−0.05230
F	−99.65266	−99.66690	−99.66710	−0.06463		1.48	−0.08699

[a] Core−valence correlation from cc-pCVQZ calculations. [b] Scalar relativistic correction from CASPT2/G3large calculations.

The resulting QCISD(T) + MP4/(+) + ZPE energies, as obtained in the G2 and G3 calculations, correlate linearly with the benchmark G3 (total) atomization energies, but the two slopes are very different: 1.03 for G3 and 0.74 for G2. Thus, even at this base level of theory, viz., QCISD(T) + MP4/(+), the G3 values of these energies scale significantly better with the number of fluorines than the corresponding G2 values. This, of course, is also reflected in the large variation in the MP4/(2df) corrections in the case of G2, as remarked above. This behavior points to some inbalance in the QCI component of the G2 atomization energies that is due to inadequacies of the 6-311G(d,p) basis.

Core−valence correlation increases the G3 atomization energies by 1.1−1.9 kcal mol^{-1}, while spin−orbit coupling corrections change them by −0.1 to −1.6 kcal mol^{-1}, resulting in net changes of 0.3−1.0 kcal mol^{-1}. The G2 and G3 HLC contributions to the atomization energies differ by 1.0 kcal mol^{-1} at most, but such that they reduce the differences due to core−valence correlation and spin−orbit coupling. Thus, effectively, the differences between the total G2 and G3 atomization energies are almost fully reproduced by the valence calculations alone.

In summary, the shortcomings of G2 when applied to the above molecules are traced to inadequacies in the 6-311G(d,p) basis. These problems were briefly discussed by Curtiss et al. in their first paper on G3, although not actually quantified or analyzed, as in our work.

Heats of Formation by Complete Basis Set Coupled-Cluster Calculations. HCCH, HCCF, FCCF, CCH, CCF, and HCOO were selected for further study, whereby their heats of formation are calculated using the coupled-cluster RCCSD(T) method and large basis sets, allowing the sequences of atomic and molecular energies to be extrapolated to the hypothetical complete basis set (CBS) limit. These small molecules were chosen for further study partly because the experimental heats of formation of several of them (HCCF, FCCF, and CCF) are poorly characterized, with estimated errors of ∼5 kcal mol^{-1} in the literature values. The BAC-MP4 heats of formation for HCCF, FCCF, and CCH are also at significant variance with the G3 values. The formyloxyl (HCOO) radical is an unusual system in that it has several low-lying electronic states. An excellent summary of the theoretical literature on this interesting molecule is provided in a relatively recent paper by Rauk et al.,[34] who also report the results of an extensive CASPT2 and multireference CI (MRCI) study of formyloxyl. Rauk et al. were unable to conclude unequivocally whether the ground state is $^2A_1$ or $^2B_2$, because the order of the two states (separated by no more than 2.2 kcal mol^{-1}) was found to be dependent on the method of calculation, although the broken symmetry $^2A'$ state consistently appeared to be an excited state. According to G3, the ground state is $^2A_1$, but the G3 prediction of $\Delta_f H^0_{298}$ = −32.1 kcal mol^{-1} could be regarded as being equally consistent with the two conflicting literature values −37.7 ± 3.0 and −29.3 ± 1.0 kcal mol^{-1}. Consequently, formyloxyl represents an interesting and challenging application for a coupled-cluster CBS study.

TABLE 7: Atomization Energies[a] ΣD_0 at 0 K Computed at Various Levels of Theory (in kcal mol^{-1})

	CCSD(T) aug-cc-pVQZ	CCSD(T) CBS(mix)	CCSD(T) CBS(l_{max})	CCSD(T) CBS[b] + CV corr	CCSD(T) CBS[b] + CV corr + rel[c]
C_2H_2	384.02	386.85	387.12	389.34	389.04
CFCH	380.03	383.48	383.75	386.13	385.63
C_2F_2	370.85	374.91	375.18	377.75	377.06
C_2H	252.25	254.74	254.91	256.79	256.50
C_2F	245.25	248.35	248.53	250.60	250.72
HCOO $^2A_1$	364.63	367.87	367.92	369.41	369.01
HCOO $^2B_2$	363.98	367.07	367.12	368.51	368.02
HCOO $^2A'$	361.34	364.92	364.97	366.40	365.94

[a] Using atomic energies corrected for spin−orbit contributions (from ref 19). [b] Average of CBS(aDTQ/mix) and CBS(aTQ/l_{max}) results. [c] Scalar relativistic corrections from CASPT2/G3large calculations.

As indicated in the section on Computational Methods, the CBS energies of the above molecules and their constituent atoms were obtained by extrapolating the sequence of valence-correlated (R)CCSD(T) energies computed using the aug-pVxZ (x = D, T, and Q) bases, followed by corrections for core−valence correlation, scalar relativistic effects, and zero-point vibrational contributions. The latter were computed at the (RO)-MP2/cc-pVTZ level of theory, except in the case of HCOO, for which we utilized the CASPT2 harmonic frequencies of Rauk et al.,[34] all scaled by 0.96. Table 6 contains a representative part of the raw data, viz., the total valence CCSD(T) energies of the molecules obtained in the aug-cc-pVQZ basis, along with the corresponding extrapolated values and the core−valence correlation corrections, zero-point vibrational energies, thermal corrections to the enthalpies, and scalar relativistic corrections. The resulting atomization energies at 0 K are given in Table 7. Although the effect of the extrapolation on the total molecular energies is ∼10−25 kcal mol^{-1} in comparison with those obtained at the CCSD(T)/aug-cc-pVQZ level of theory, the effect on the atomization energies is a modest 3−4 kcal mol^{-1}. The mix and l_{max} methods yield comparable results, so we chose to define the CBS atomization energies as the average of the two sets of extrapolated values. Core−valence correlation further increases the atomization energies by ∼2 kcal mol^{-1}. The scalar

TABLE 8: Computed Heats of Formation at 0 and 298 K (kcal mol^{-1})

		$\Delta_f H_0^0$			$\Delta_f H_{298}^0$			
		CBS[a]	G2	G3	CBS[a]	G2	G3	expt
C_2H_2	$^1\Sigma_g$	54.2	56.0	55.1	54.0	55.8	54.9	54.2 ± 0.2[b]
CFCH	$^1\Sigma$	24.4	25.0	24.8	24.6	25.0	24.8	30.3 ± 5.3[c]
C_2F_2	$^1\Sigma_g$	−0.2	−0.7	−0.5	0.5	−0.2	0.0	−5.5 ± 5.0[c]
C_2H	$^2\Sigma$	135.1	137.8	135.4	135.9	138.7	136.3	135.0 ± 1.0[d] 114.0 ± 6.9[c]
C_2F	$^2\Sigma$	107.7	109.4	108.0	109.1	110.7	109.3	110.0 ± 5.3[e]
HCOO	$^2A_1$	−29.4	−31.2	−30.4	−30.1	−31.9	−31.1	−29.3 ± 0.7[f,] −37.7 ± 3.0[g]
HCOO	$^2B_2$	−28.4	−29.9	−28.6	−29.3	−30.7	−29.4	
HCOO	$^2A'$	−26.3	−27.9	−27.0	−27.1	−28.7	−27.8	

[a] Average of CBS(aDTQ/mix) and CBS(aTQ/l_{max}) results and including scalar relativistic corrections. [b] Reference 72. [c] Reference 53. [d] Reference 57. [e] Estimated from bond dissociation energies, ref 3. [f] Based on $\Delta_f H_0^0 = 28.6 \pm 0.7$ kcal mol^{-1} from ref 70, with thermal corrections from this work. [g] Reference 69.

relativistic corrections to the atomization energies are generally quite small, the largest correction being just −0.7 kcal mol^{-1} (for FCCF).

The heats of formation at 0 and 298 K that were computed from the atomization energies are summarized in Table 8, along with the corresponding G3 and G2 values. The agreement between the CBS and G3 results is excellent for all molecules, except HCOO, for which the deviation is 2 kcal mol^{-1}. The agreement between the G2 and CBS heats of formation is generally less good, the maximum difference being 2.8 kcal mol^{-1}. In line with previous work of this quality, we expect the CBS heats of formation to be accurate to within 1 kcal mol^{-1}, although this may prove to be a conservative estimate. In the case of acetylene, where the heat of formation is known accurately, the CBS prediction is in excellent agreement with experiment. For CCH, the theoretical results agree well with the experimental value of McMillen and Golden.[57] Given the high level of disagreement when the former are compared with the current JANAF value[53] of 114.0 ± 6.9 kcal mol^{-1}, we must conclude that the JANAF value is seriously in error. For CFCH, C_2F_2, and C_2F, the theoretical predictions, although consistent with the available experimental estimates, are expected to be more reliable than the latter. The overall agreement between the CBS and G3 results further supports the reliability of G3 in predicting heats of formation.

For formyloxyl the $^2A_1$ state is found to be the ground state, with the $^2B_2$ and $^2A'$ states being just 1.0 and 3.1 kcal mol^{-1} higher in energy at 0 K. This ordering is largely the result of the zero-point energies, as in the absence of zero-point correction the $^2B_2$ would be predicted to be the ground state. The resulting heat of formation of HCOO ($^2A_1$) at 0 K, viz., −29.4 kcal mol^{-1}, is in excellent agreement with the experimental value of −28.6 ± 0.7 kcal mol^{-1} reported by Langford et al.,[70] who used H (Rydberg) atom photofragment translational spectroscopy to deduce the OH bond dissociation energy of formic acid and hence heat of formation of formyloxyl. It is worth noting that, using G2(MP2) in conjunction with several isodesmic reactions, Yu et al.[84] deduced a value of −30.3 ± 0.7 kcal mol^{-1} for $\Delta_f H_{298}^0$, which is clearly in very good agreement with the current CBS prediction and with experiment.

Conclusion

Using the G3 and related methodologies, the heats of formation of ~120 C_1 and C_2 hydrofluorocarbons and oxidized hydrofluorocarbons, including a number of C_2 carbenes, were computed. For most molecules studied in this work, the G3 heats of formation are in good agreement with the available experimental data, attesting to the capability and reliability of G3. Indeed, there is growing evidence, in the form of accurate ab initio values, that where the discrepancy between G3 and experiment is in excess of 2 kcal mol^{-1}, it may well signal inaccuracies in the latter. Although for most molecules the G3 predictions agree well with those of the BAC-MP4 method, there are also sizable discrepancies. Given the apparent robustness of G3 and its relative ease of application, we would certainly recommend its use for the computation of thermochemical data. The use of suitable isodesmic reaction schemes, as expected, has the potential to improve the accuracy and consistency of the predictions, especially when approximate forms of G3 are used, such as G3[MP2(full)] and G3(MP4SDQ), which were explored in this work along with G2(MP2). Using this approach, the heat of formation of the hexafluoropropyl radical, an important intermediate in the high-temperature reaction of H atoms with hexafluoropropene, was computed and subsequently used in the kinetic model describing the pyrolysis of 2*H*-heptafluoropropane.[10] In addition to G3 and related applications, the heats of formation of the fluoroacetylenes (HCCF and C_2F_2 as well as C_2H_2) and the C_2H, C_2F, and formyloxyl radicals were computed using the coupled-cluster method, with extrapolations to the CBS limit. The computed heats of formation are believed to be accurate to within 1 kcal mol^{-1}, providing useful and reliable data for HCCF, C_2F_2, and C_2F, while in the case of formyloxyl, it strongly supports the experimental value of 29.3 ± 0.7 kcal mol^{-1} of Langford et al.[70]

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Supporting Information Available: Tables S1−S4 containing atomic data, rotational constants, vibrational frequencies, zero-point energies, and thermal corrections to heats of formation at 298 K. This material is available free of charge via the Internet at http://pubs.acs.org.

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