Halon Thermochemistry: *Ab Initio* Calculations of the Enthalpies of Formation of Fluoromethanes

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Atomic equivalent (AEQ), BAC-MP4, G2(MP2), G2, CBS-4, CBS-Q, and CBS-QCI/APNO molecular orbital calculations were used to calculate enthalpies of formation in the series of fluoromethanes, CH_xF_{4-x}, $x = 0-4$. While the computed $\Delta_f H°$(BAC-MP4) and $\Delta_f H°$(CBS-4) were in close agreement with experiment, errors in enthalpies from the other five methods were relatively high. In particular, enthalpies of formation calculated with the G2(MP2) and G2 procedures exhibited systematic deviations from experiment which were linearly dependent upon the number of C—F bonds in the molecule. Application of isodesmic reaction calculations yielded values of $\Delta_f H°$(G2(MP2)), $\Delta_f H°$(G2), $\Delta_f H°$(CBS-Q), and $\Delta_f H°$(CBS-QCI/APNO) that were in remarkably close agreement with experiment. This technique had no significant effect on the quality of results from the AEQ, BAC-MP4, and CBS-4 methods.

Introduction

Because of their well-documented catalytic activities in the depletion of stratospheric ozone,[1] the use of CF_3Br and other halon fire suppression agents has been severely restricted in recent years.[2] Fluorocarbons (FC's) and hydrofluorocarbons (HFC's) are among the potential safe alternative flame suppressants.[3] The utilization of kinetic modeling to assess the mechanism and effectiveness of various replacement agents requires a large body of accurate thermochemical and kinetic data, which is not currently available for the FC's and HFC's.

The relative paucity of accurate experimental data on these compounds can, in principle, be remedied via the application of *ab initio* molecular orbital methods to predict enthalpies of formation and activation energies (from which kinetic rate constants can be obtained). In this investigation, we have endeavored to assess the capability of several current *ab initio* techniques to yield accurate atomization energies in the series of fluoromethanes, CH_xF_{4-x}, $x = 0-4$. The methods and results are presented below.

Theoretical Methods

The *ab initio* calculations were performed using the GAUSSIAN code[4-6] on CRAY Y-MP, CRAY X-MP, CONVEX-C3820, SUN-Sparc, HP-PARisc, and SGI Power-Challenge computers.[7]

Atom Equivalent Calculations. The atom equivalents (AEQ) method was proposed by Ibrahim and Schleyer[8] in 1985 as an inexpensive way to compute accurate enthalpies of formation from energies calculated at the HF/6-31G(d) level

TABLE 1: Computation of the C—(C)₄ Atom Equivalent (AEQ)ᵃ

	C(CH₃)₄	C(CH₃)₃-CH₂-CH₃	C(CH₃)₃-C(CH₃)₃
$\Delta_f H^0$(expt)ᵇ	-168.1 ± 0.8[31]	-186.1 ± 1.0[31]	-225.6 ± 1.4[31]
E[HF/6-31G(d)]ᶜ	-196.333818	-235.364605	-313.421136
C—(C)₄ᶜ	-37.876351	-37.873442	-37.872524

ᵃ The H—(C), C—(H)₃(C), and C—(H)₂(C)₂ equivalents of Ibrahim and Schleyer[8] were used in the computation of the C—(C)₄ equivalent. ᵇ Units: kJ/mol. The uncertainty was assigned by the source of the data. ᶜ Units: hartree (=2625.5 kJ/mol). The average value computed for C—(C)₄ (=−37.874106 hartrees) was transferred to C—(F)₄.

of *ab initio* theory. In this method the enthalpy of formation is computed by subtracting a parameter (the atom equivalent) for each atom in the molecule from its energy computed at the HF/6-31G(d) level. The atom equivalents vary with the atomic environment (e.g., the values differ for the carbon atoms in CH_4 and CH_3F). The atom equivalent parameters were derived by averaging over a large set of molecules with accurate experimental enthalpies of formation.

As determined by Ibrahim and Schleyer,[8] fluorines bonded to carbon were treated as equivalent to bonded carbon atoms, i.e., $C—(H)_3F = C—(H)_3C$; $C—(H)_2(F)_2 = C—(H)_2(C)_2$; $C—(H)-(F)_3 = C—(H)(C)_3$. However, the equivalent for $C—(F)_4$ [$= C—(C)_4$] was not reported. Therefore, the $C—(C)_4$ equivalent was derived here from HF/6-31G(d) calculations on neopentane [$C(CH_3)_4$], 2,2-dimethylbutane [$CH_3C(CH_3)_2CH_2CH_3$], and 2,2,3,3-tetramethylbutane [$CH_3C(CH_3)_2C(CH_3)_2CH_3$]. An average of the computed $C—(C)_4$ values (Table 1) was chosen for the $C—(F)_4$ equivalent.

BAC-MP4 Calculations. The Melius BAC-MP4 method[9-11] was also used to compute the heats of formation of selected species. This procedure involves geometry optimization and frequency calculation at the HF/6-31G(d) basis level, followed by a single point energy evaluation at the MP4/6-31G(d,p) level using the previously optimized geometry. The MP4 energy is

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corrected for spin contamination. Empirical bond additivity corrections (BAC's) based on the type and length of bonds in the molecule are also applied. Parameters for the C—H and C—F BAC's (needed for fluoromethanes) were derived to reproduce the experimental enthalpy of formation of CH_4 and CH_3F.

G2(MP2) and G2 Calculations. The *ab initio* energies were computed at the G2[12] and G2(MP2)[13] levels of theory proposed by Pople and co-workers. Both of these methods require an MP2(full)/6-31G(d) optimized geometry for energy evaluations at various levels of theory in order to approach the computed QCISD(T)/6-311+G(3df,2p) energy.

In the G2 method several corrections are applied to the MP4-(FC)/6-311G(d,p) energy. These corrections estimate the effect of diffuse-sp and higher polarization functions on heavy atoms (computed at the MP4 level), higher order correlation (computed at the QCISD(T) level), the nonadditivity of diffuse sp and higher polarization functions (computed at the MP2 level), and the addition of a third d-function on nonhydrogen atoms and a second p-function on hydrogens (also computed at the MP2 level). Finally, the zero-point energy (calculated using scaled HF/6-31G(d) frequencies) and an empirical high-level correction are included to obtain E_0(G2), the ground state energy. The empirical correction was chosen[12] to provide equality between the G2 and the exact energies for the hydrogen atom and molecule and to yield a zero mean deviation from experiment for the calculated atomization energies of 55 small molecules whose experimental energies have been accurately measured. It is significant to this work that none of the 55 molecules in the parameterization set contains C—F bonds.

The G2(MP2) protocol[13] involves a QCISD(T)/6-311G(d,p) energy evaluation. The correction for the basis set extension to 6-311+G(3df,2p) is evaluated at the MP2 level. The zero-point energy and the empirical high-level corrections are identical to the corrections employed in the G2 method. The energies required to compute the G2(MP2) energy are a subset of the energies computed during the G2 calculations with the notable absence of the MP4/6-311G(2df,p) energy which is the largest calculation in the G2 method. Complete details of these calculations have been presented in the original papers.[12,13]

CBS Calculations. The CBS methods involve a series of calculations which are designed to recover the errors which result from incomplete convergence with respect to both the one-particle (basis set) and the *n*-particle (CI, perturbation, or coupled-cluster) expansion of the wave function. Empirical corrections, based on calibrations to the so called "G2 test set", are also included as an integral part of the CBS methodologies. A complete description of these methods can be found elsewhere.[14−15]

The unique feature of the CBS family of model chemistries is the incorporation of an algorithm for the extrapolation of second-order pair energies calculated with N natural orbitals ($e_{ij}^{(2)}(N)$) to the infinite-order pair energies at the complete basis set limit.[16] The basis of this extrapolation is the asymptotic convergence of the natural orbital expansion of pair correlation energies which is summarized in the equation below:

$$\lim_{N \to \infty} e_{ij}^{(\infty)}(N) = e_{ij}^{(\infty)}(\infty) + (\sum_{\mu=1}^{N} c_{\mu ij})^2 \left[\frac{25|S|_{ij}^2}{512(N + \delta_{ij})} \right] \quad (1)$$

where $|S|_{ij} = \int |\phi_i \phi_j|\, d\tau$ is the absolute overlap integral between orbitals ϕ_i and ϕ_j,[17] and δ_{ij} is a parameter which takes into account the exclusion of occupied orbitals from the virtual space.

Atomization Energies and Enthalpies of Formation. Atomization energies ($\sum D_0$) were computed from the calculated

energies (where calc = BAC-MP4, G2(MP2), G2, CBS-4, CBS-Q, and CBS-QCI/APNO) for the species and their constituent elements from the following expression:
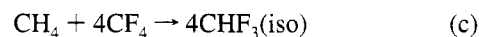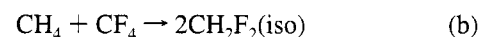
$$\sum D_0(C_xH_yF_z) = xE_0(\text{calc, C}) + yE_0(\text{calc, H}) + zE_0(\text{calc, F}) - E_0(\text{calc, } C_xH_yF_z) \quad (2)$$

Enthalpies of formation at 0 K were computed from the atomization energy and the experimental enthalpies of formation of the constituent elements via the relation

$$\Delta_f H°(C_xH_yF_z, 0\text{ K}) = x\Delta_f H°(C_{gas}, 0\text{ K}) + y\Delta_f H°(H_{gas}, 0\text{ K}) + z\Delta_f H°(F_{gas}, 0\text{ K}) - \sum D_0(C_xH_yF_z) \quad (3)$$

Standard temperature corrections[18] were applied to $\Delta_f H°(0\text{ K})$ in order to obtain $\Delta_f H°(298.15\text{ K})$.

Isodesmic Reactions. Isodesmic reactions[19,20] (in which the number of each type of bond in the reactants is preserved in the products) have been used frequently to calculate enthalpies of formation which are more accurate than can be obtained by purely *ab initio* methods. This is based upon the fact that theoretical methods such as G2 or BAC-MP4 will often yield an accurate calculated enthalpy for an isodesmic reaction even though the calculated enthalpies of the individual species involved in the reaction may be subject to systematic errors; the improved accuracy results from cancellation of these nonrandom errors. Use of this procedure requires that enthalpies of all species but one in the reaction be taken either from experiment or from prior isodesmic calculations. In this work, we have used the following reactions to obtain $\Delta H_f°$(iso):

$$3CH_4 + CF_4 \rightarrow 4CH_3F(\text{iso}) \quad \text{(a)}$$

$$CH_4 + CF_4 \rightarrow 2CH_2F_2(\text{iso}) \quad \text{(b)}$$

$$CH_4 + 4CF_4 \rightarrow 4CHF_3(\text{iso}) \quad \text{(c)}$$

where values for CH_4 and CF_4 are experimental.

Results and Discussion

Displayed in Table 2 are optimized geometries of the fluoromethanes at the HF/6-31G(d) and MP2(FU)/6-31G(d) levels and (scaled) HF/6-31G(d) frequencies for each molecule. Table 3 contains calculated HF/6-31G(d), MP4/6-31G(d,p), G2-(MP2), G2, CBS-4, CBS-Q, and CBS-QCI/APNO electronic energies. Table 4 shows a comparison of the calculated enthalpies of formation with experiment.[21,22] The enthalpies computed from isodesmic reactions using the experimental enthalpies of CH_4 and CF_4 as references are also presented in Table 4. Rms and average deviations of the calculated enthalpies from experiment are given in the two far right-hand columns of the table.

For this study, the enthalpies recommended in the comprehensive evaluation by Kolesov[22] were chosen as the standard values for computing the errors in the calculations. Most of the recommendations are largely based on the same sets of experimental measurements. Neugebauer and Margrave[23] measured the heat of combustion of CH_2F_2 and CHF_3. The recommendations for the heat of formation of CH_3F are based on bond additivity methods or other trends in heats of formation of fluorinated hydrocarbons. A detailed evaluation of the thermochemistry of fluoromethanes and other C1 and C2 fluorocarbons can be found elsewhere.[24]

Ab Initio Enthalpies. Inspection of Table 4 reveals that the computationally inexpensive AEQ method[8] yields enthalpies of

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TABLE 2: Optimized Geometries[a] and Vibrational Frequencies[b] Computed Using the 6-31G(d) Basis Set

	CH$_4$		CH$_3$F		CH$_2$F$_2$		CHF$_3$		CF$_4$	
parameter	HF	MP2	HF	MP2	HF	MP2	HF	MP2	HF	MP2
C−H	1.084	1.090	1.082	1.092	1.078	1.091	1.074	1.089		
C−F			1.365	1.390	1.338	1.364	1.317	1.343	1.302	1.329
H−C−H	109.5	109.5	109.8	109.9	112.5	112.8				
H−C−F			109.1	109.1	108.8	108.9	110.4	110.5		
F−C−F					108.6	108.9	108.5	108.5	109.5	109.5
frequency	1328		1059		510		492		422	
	1328		1171		1105		492		422	
	1328		1171		1123		681		610	
	1520		1474		1164		1127		610	
	1520		1476		1259		1186		610	
	2855		1476		1464		1186		896	
	2948		2887		1529		1413		1315	
	2948		2959		2942		1413		1315	
	2948		2959		3006		3037		1315	

[a] Bonds in angstroms, angles in degrees. [b] Scaled vibrational frequencies in cm^{-1} (scale factor = 0.8929).

TABLE 3: Calculated Ground State Electronic Energies[a]

method	CH$_4$	CH$_3$F	CH$_2$F$_2$	CHF$_3$	CF$_4$
E[HF/6-31G(d)][b]	−40.19517	−139.03462	−237.89635	−336.77164	−435.64521
E_0[MP4/6-31G(d,p)][c]	−40.34595	−139.34792	−238.37455	−337.41647	−436.45676
E_0(G2(MP2))	−40.40773	−139.55127	−238.71492	−337.89035	−437.06286
E_0(G2)	−40.41089	−139.55421	−238.71797	−337.89357	−437.06631
E_0(CBS-4)	−40.4281	−139.5834	−238.7596	−337.9481	−437.1342
E_0(CBS-Q)	−40.4096	−138.5619	−238.735	−337.9197	−437.1015
E_0(CBS/QCI-APNO)[d]	−40.4689	−139.7044	−238.9609	−338.2296	−437.4954

[a] Hartree units. [b] Required for the AEQ calculations. [c] Required for the BAC-MP4 calculations. [d] These values reflect an adjustment made in the zero-point energies to account for the difference between the scale factor used in the Gaussian-94 calculations (0.918 44) and the recommended value of 0.9251.[15]

TABLE 4: Comparison of the Calculated Enthalpies of Formation[a] with Experiment

method	CH$_4$	CH$_3$F	CH$_2$F$_2$	CHF$_3$	CF$_4$	rms	ave
			A. Experiment				
	−74.9 ± 0.4[21]	−232.6 ± 8.4[22]	−452.2 ± 1.8[22]	−697.6 ± 2.7[22]	−933.0 ± 1.7[22]	±4.1	
		B. Enthalpies from *ab Initio* Calculations					
AEQ	−71.3 (3.6)	−226.7 (5.9)	−445.6 (6.6)	−705.2 (−7.6)	975.5 (−42.5)	(19.8)	(−6.8)
BAC-MP4	−74.8 (0.1)	−233.8 (−1.2)	−451.1 (1.1)	−699.5 (−1.9)	−934.1 (−1.1)	(1.2)	(−0.5)
G2(MP2)	−75.6 (−0.7)	−245.0 (−12.4)	−466.9 (−14.7)	−718.8 (−21.2)	−962.6 (−29.6)	(18.4)	(−15.7)
G2	−77.7 (−2.8)	−244.1 (−11.5)	−463.7 (−11.5)	−714.0 (−16.4)	−956.5 (−23.5)	(14.8)	(−13.1)
CBS-4	−77.5 (−2.6)	−236.9 (−4.3)	−451.1 (1.1)	−696.9 (0.7)	−936.3 (−3.3)	(2.8)	(−1.7)
CBS-Q	−74.0 (0.9)	−238.7 (−6.1)	−457.6 (−5.4)	−706.7 (−9.1)	−947.7 (−14.7)	(8.6)	(−6.9)
CBS-APNO	−79.0 (−4.1)	−240.5 (−7.9)	−457.1 (−4.9)	−705.0 (−7.4)	−945.3 (−12.3)	(7.9)	(−7.3)
		C. Isodesmic Enthalpies					
AEQ(iso)	ref	−218.9 (13.7)	−426.2 (26.0)	−674.2 (23.4)	ref	(21.7)	(21.0)
AEQ2(iso)[b]	ref	−228.9 (3.7)	−441.4 (10.8)	−689.4 (8.2)	ref	(8.1)	(7.6)
BAC-MP4(iso)	ref	−233.6 (−1.0)	−450.6 (1.6)	−698.7 (−1.1)	ref	(1.3)	(−0.2)
G2(MP2,iso)	ref	−237.1 (−4.5)	−451.8 (0.4)	−696.4 (1.2)	ref	(2.7)	(−0.9)
G2(iso)	ref	−236.1 (−3.5)	−450.6 (1.6)	−695.7 (1.9)	ref	(2.5)	(0.0)
CBS-4(iso)	ref	−234.1 (−1.5)	−448.2 (4.0)	−693.9 (−3.8)	ref	(3.3)	(2.1)
CBS-Q(iso)	ref	−235.7 (−3.1)	−450.8 (1.5)	−696.0 (−1.7)	ref	(2.2)	(0.0)
CBS-APNO(iso)	ref	−234.4 (−1.8)	−449.0 (3.3)	−694.8 (2.9)	ref	(2.7)	(1.5)

[a] $\Delta_f H^0$ at 298.15 K and 1 atm in kJ/mol units. Numbers in parentheses represent deviations from experiment, i.e., calc − expt. [b] The carbon equivalents employed here were obtained from a linear interpolation between the equivalents C−(H)$_4$ = −37.887 963 and C−(F)$_4$ = −37.890 281 hartrees derived for CH$_4$ and CF$_4$, respectively. See text for details.

formation for the first four members of the series within ±7 kJ/mol of experiment. However, $\Delta_f H^\circ$(CF$_4$) is in serious disagreement from experiment by over −40 kJ/mol (Table 4). This large deviation is mostly due to the assumed equality of the C−(C)$_4$ and C−(F)$_4$ atom equivalents,[8] which was used here to calculate the C−(F)$_4$ parameter.

The values of $\Delta_f H^\circ$(BAC-MP4) for the series CH$_x$F$_{4-x}$ are in good agreement (Table 4) with experiment; the rms deviation for these five molecules (1.2 kJ/mol) is actually lower than average of the quoted experimental uncertainties (4.1 kJ/mol). The Melius BAC-MP4 procedure has recently been applied to calculate enthalpies of formation in an extensive set of C1 and

C2 fluorocarbons,[25] yielding an average deviation of only 6.5 kJ/mol for 44 species where experimental results have been reported. On a relative basis the MP4/6-31G(d,p) energy evaluation required for the BAC-MP4 calculations requires approximately 6 and 16 times, respectively, less computer cpu time than the G2(MP2) and G2 energies (for CHF$_3$ the MP4/6-31G(d,p), G2(MP2) and G2 energy evaluations took 52, 311, and 834 min, respectively, using GAUSSIAN-92 on a HP-PARisc computer). As mentioned earlier the G2(MP2) energies can be obtained from the *ab initio* calculations required for the G2 method with the notable exception of the largest required calculation (i.e., the MP4/6-311G(2df,p) calculation).

The G2[12] and G2(MP2)[13] computational protocols proposed by Pople and co-workers have generally yielded excellent agreement with experimental atomization energies and enthalpies of formation. In the original investigations, it was found that the absolute deviation of ΣD_0 for a series of 55 first- and second-row compounds was 4.9 and 5.5 kJ/mol for the two methods, respectively; it should be noted that the G2 method was empirically parametrized specifically to minimize the mean error in the atomization energies in this series. G2 calculations of $\Delta_f H°$ in a number of other systems have also yielded excellent agreement with experiment (e.g., refs 26—27). In some molecules like SO_2 and SF_6, enthalpies calculated by the computationally less expensive G2(MP2) were significantly closer to experiment than the G2 enthalpies.

One sees from Table 4 that the rms error in $\Delta_f H°$(G2(MP2)) and $\Delta_f H°$(G2) for the five molecules is unreasonably high at above 14 kJ/mol. This is in contrast to most systems where, as discussed above, the agreement of the calculated ΣD_0 (and consequently $\Delta_f H°$) with experiment for molecules with widely varying structures is quite good.

Significantly, one finds that errors in G2(MP2) and G2 enthalpies of formation are not random in nature, as illustrated in Figure 1A, where $\Delta_f H°$(calc) — $\Delta_f H°$(expt) is plotted vs the number of C—F bonds in the molecule. It is seen quite clearly from this figure that deviations of calculated enthalpies exhibit an almost perfectly linear decrease with increasing number of C—F bonds, with slopes for the two methods: $slope_{G2(MP2)}$ = -6.67 kJ/mol/C—F bond; $slope_{G2}$ = -4.63 kJ/mol/C—F bond. Thus, deviations from experiment in calculated G2(MP2) and G2 enthalpies of formation of fluoromethanes are seen to result directly from systematic errors of these methods in the treatment of C—F bonds.

Montgomery et al.[29] recently noted that G2 atomization energies in fluoromethanes were greater than experiment (consistent with more negative enthalpies of formation) and suggested that the problem may be due to the fact that the set of 55 molecules used to parametrize the high-level correction,[12] E(HLC) = 1.14npair, where npair is the number of valence electron pairs, did not include any species with C—F bonds. We would note, however, that npair(compound) — npair(atoms) = 3 for each of the fluoromethanes. Hence a variation of the coefficient of npair in the HLC correction will change each calculated enthalpy in the series by the same amount, which will not remove the systematic variation in $\Delta_f H°$(calc) — $\Delta_f H°$(expt) with the number of C—F bonds.

Among the CBS methods, surprisingly, the best agreement (Table 4 and Figure 1B) with experiment was obtained from the CBS-4 method which has, by far, the lowest computational requirements of the three CBS models. In the case of CF_4, for example, the CBS-4 calculations used 2 orders of magnitude less CPU time than the CBS-QCI/APNO calculations (13 min vs 21 h on the CRAY Y-MP computer). Both the CBS-Q and CBS-QCI/APNO results indicate a systematic error which is proportional to the number of C—F bonds. The CBS-4 errors, which are much smaller in magnitude than the errors in the CBS-Q and CBS-QCI/APNO calculations, appear to be more randomly distributed. This suggests that there is a favorable cancellation of errors. Indeed, Ochterski et al.[15] have commented that the systematic neglect of both the positive contributions of the polarization functions to the pair coupling terms and the negative contribution of the fourth-order triple excitations enhances the accuracy of the CBS-4 calculations.[15] This observation is particularly relevant to our application, since the high degree of polarization of the C—F bonds in the fluo-
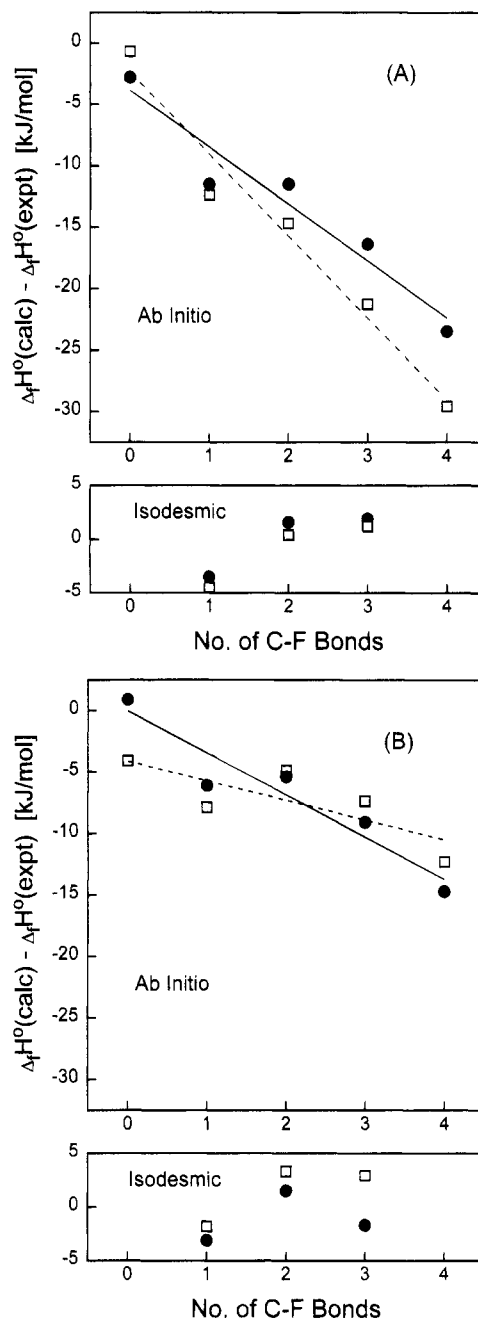

Figure 1. Deviations of calculated enthalpies of formation from experiment: (A) G2, filled circles; G2(MP2), open squares; (B) CBS-Q, filled circles; CBS-QCI/APNO, open squares.

romethanes would be expected to result in large contributions to the correlation energy from the polarization functions.

Isodesmic Enthalpies. As noted above, the application of isodesmic reactions[19,20] to the calculation of enthalpies of formation is often found to lead to significant improvements over values obtained via direct use of a given theoretical method. Displayed in section C of Table 4 are deviations in the enthalpies of formation for CH_3F, CH_2F_2, and CHF_3 calculated by each of the methods using isodesmic reactions that employ CH_4 and CF_4 as references. These results are also plotted for the G2, G2(MP2), CBS-Q, and CBS-QCI/APNO methods in Figure 1.

As shown in Table, the errors in the AEQ(iso) method actually *increase* rather markedly; this is a consequence of the very large nonsystematic error in the enthalpy of formation of CF_4, which causes large errors in the calculated enthalpies of the isodesmic reactions used to calculate $\Delta_f H°$ of the other species. The AEQ2(iso) method overcomes this error to a large

extent by using carbon equivalents for C−(H)$_4$ and C−(F)$_4$ which are specifically derived to reproduce the experimental enthalpies of formation for CH$_4$ and CF$_4$, respectively. The carbon equivalents used for the remaining fluoromethanes were obtained by a linear interpolation between the C−(H)$_4$ and C−(F)$_4$ equivalents. This procedure results in an improved agreement with experiment, but the errors in the computed enthalpies for CH$_2$F$_2$ and CHF$_3$ are at least 3 times larger than the reported experimental uncertainties.

Seen also in Table 4, there is very little change in the already excellent agreement of BAC-MP4 enthalpies with experimental values. This is not surprising since, as noted by Melius,[9] his method is basically an extension of the concept of isodesmic reactions, in which systematic errors in enthalpies of formation have been largely eliminated by the bond additivity corrections.

In contrast, one observes a most dramatic improvement in the quality of enthalpies of formation determined by the G2-(MP2) and G2 methods via isodesmic reaction calculations (Table 4 and Figure 1A). The average deviations for the three molecules, 2.7 and 2.5 kJ/mol, are actually substantially lower than the quoted rms errors in the measured values. The greatly improved agreement with experiment derives from the fact that, as shown above, deviations in $\Delta_f H°$(G2(MP2)) and $\Delta_f H°$(G2) result almost entirely from errors in the treatment of C−F bonds, which will cancel when isodesmic reaction calculations are employed.

Systematic errors in the CBS-Q and CBS-QCI/APNO are also reduced significantly (Table 4 and Figure 1B) due to the application of isodesmic calculations. The CBS-4(iso) errors do not improve over the already good CBS-4 results.

Thus, the errors in the computed G2, G2(MP2), CBS-Q, and CBS-QCI/APNO) enthalpies were determined to be systematic and removable by the application of isodesmic calculations. Alternatively, one could obtain the bond contributions to the computed error (Δ_{BAC}) in the enthalpies of fluoromethanes by a least-squares fit to a linear function of the form

$$\Delta_{BAC} = \sum_{C-X} n_{C-X} \Delta_{C-X} \qquad (4)$$

where Δ_{C-X} is the contribution of the C−X bond to the total error (Δ_{BAC}) and n_{C-X} is the number of C−X bonds in the molecule. For fluoromethanes: $n_{C-F} + n_{C-H} = 4$. This procedure is identical to the isodesmic calculations listed in the previous section if Δ_{C-H} and Δ_{C-F} are obtained from errors for CH$_4$ and CF$_4$, respectively. For these four methods the contributions of the C−H and C−F bonds to the errors were obtained from eq 4 by linear regression analysis of the deviations from experiment. In each case the C−H bond correction was found to be small and comparable in magnitude to the estimated errors. Therefore, the contribution from the C−F bond is the dominant source of the error in these four methods and Δ_{C-H} was set equal to zero to obtain the final results.[30] The relative deficiency of these methods with respect to the description of the C−F bond has been overlooked in the past because of the absence of fluorocarbons in the "G2/CBS test set" used in evaluating the accuracy of these methods.

As pointed out by one ot the reviewers of this article, a part of the C−F bond additivity correction can be attributed to errors in the computed atomic energies which arise due to spin contamination and/or spin−orbit (SO) coupling. For fluorine and carbon the error due to spin contamination is very small at the G2 and CBS levels of calculation. However, a significant SO coupling correction (Δ_{SO}) can be computed from the observed splittings[18] between the ground state electronic energy levels of fluorine ($\Delta_{SO} = 1.61$ kJ/mol) and carbon ($\Delta_{SO} = 0.35$

kJ/mol). For fluoromethanes the SO coupling error in fluorine can account for approximately half of the systematic error per C−F bond in the CBS-Q and CBS-QCI/APNO methods and approximately a third of the error in the G2 and G2(MP2) methods. An examination of the fluorinated species used in the "G2/CBS test set" shows that the deviations in the atomization energies [$\sum D_0$(calc) − $\sum D_0$(expt)] computed by the CBS-Q, G2(MP2), G2 and CBS-QCI/APNO methods are 3.8, 6.7, 4.1, and 0.0 kJ/mol, respectively, for HF; and 2.9, 2.9, −1.2, and 0.8 kJ/mol, respectively, for F$_2$. Thus a trend supporting an increased error with the number of fluorines in the molecule is not clearly evident from this data.

Conclusion

In conclusion, the BAC-MP4 and CBS-4 methods predict enthalpies of formation in the series of fluoromethanes which are in excellent agreement with experiment. Errors in the AEQ enthalpies appear to be random and larger. The G2(MP2), G2, CBS-Q, and CBS-QCI/APNO calculations, on the other hand, exhibit systematic errors which are linearly dependent upon the number of C−F bonds in the molecule. Enthalpies predicted by these four methods employing isodesmic reactions agree with experiment to within quoted measurement errors.

Additional calculations are planned to assess the relative capabilities of the various methods to predict accurate transition state enthalpies for reactions important in halon flame chemistry.

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