

Halon thermochemistry: ab initio calculations of the enthalpies of formation of fluoroethanes

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Abstract

The ab initio G2, G2(MP2), CBS-4 and CBS-Q quantum mechanical protocols and the parameterized BAC-MP4 procedure were used to calculate the enthalpies of formation ($\Delta_f H^\circ$) of ethane and the complete series of fluoroethanes, $C_2H_xF_{6-x}$, $x = 0-5$. Results from all methods exhibited significant negative deviations from experiment. With the exception of the CBS-4 and BAC-MP4 procedures, the negative errors in the calculated enthalpies were observed to be linearly dependent upon the number of C–F bonds in the molecule. Application of a bond additivity correction (BAC) parameter, Δ_{C-F} , derived in an earlier investigation of fluoro- and chlorofluoromethanes, removed some although not all of the systematic deviations. Introduction of a heavy atom interaction parameter, representing the effect of an attached carbon on the C–F bond error, yielded corrected enthalpies which agree with experiment to within the reported uncertainties. The BAC-MP4 method, which has already been parameterized with generalized BACs, yields calculated enthalpies which average approximately 10 kJ mol^{-1} below the experimental values of $\Delta_f H^\circ$ in the fluoroethanes. © 1998 Elsevier Science B.V.

Keywords: Fluoroethane; Heat of formation; Bond additivity correction; Thermochemistry; Ab initio

1. Introduction

Because of their lower ozone depletion potential, C1 and C2 hydrofluorocarbons (HFCs) have been proposed as interim replacements for the chlorofluorocarbons (CFCs) and halon fire suppressants [1]. In order to enable accurate modeling of the fire suppression capabilities of HFCs and other potential halon replacements, we have recently performed ab

initio quantum mechanical calculations of the enthalpies of formation ($\Delta_f H^\circ$) of fluoromethanes [2] and chlorofluoromethanes [3]. (The systems investigated in [3] include methane, the four fluoromethanes, the four chloromethanes, and the six mixed species.)

In this study, we extend these calculations to the C2 HFCs and report the results of G2(MP2), G2, CBS-4, CBS-Q and BAC-MP4 calculations of enthalpies of formation of ethane and the complete series of fluoroethanes, $C_2H_xF_{6-x}$, $x = 0-5$. The results are presented below.

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Table 1
Comparison of calculated relative conformational energies^a with experiment

	CH ₂ F-CH ₂ F	CH ₂ F-CHF ₂	CHF ₂ -CHF ₂
	 C ₂ C _{2h}	 C ₁ C _s	 C _{2h} C ₂
HF/6-31G(d)	-1.8 (-1.6)	8.1 (8.0)	8.3 (8.3)
BAC-MP4	0.4 (0.7)	6.7 (6.7)	6.8 (6.9)
G2/MP2	3.1 (3.4)	5.4 (5.4)	5.9 (5.9)
G2	3.2 (3.4)	5.4 (5.4)	5.9 (5.9)
CBS-4	4.2 (4.5)	4.8 (4.8)	6.7 (6.7)
CBS-Q	3.2 (3.2)	6.0 (6.0)	6.7 (6.7)
Expt.	2.5±0.4 [17]	6.7±1.7 [20]	4.9±0.8 [20]

^a $\Delta(\Delta_f H^0)$ represents the enthalpy difference of the second conformer minus that of the first, at 0 K (at 298 K in parentheses) in kJ mol⁻¹. The experiments assumed ΔH to be independent of temperature.

2. Computational methods

The ab initio calculations were performed using the GAUSSIAN code [4–6] on HP-PARisk, CRAY Y-MP, CRAY X-MP, SUN-Sparc and SGI Power-Challenge computers.¹ Details of these calculations are described in an earlier paper [2] as well as the original articles that pertain to the BAC-MP4 [7–9], G2 [10–12], and CBS family of methods [13–16].

3. Results and discussion

For each of the three molecules, 1,2-difluoroethane, 1,1,2-trifluoroethane and 1,1,2,2-tetrafluoroethane, two stable conformations can be generated by twisting about the C–C bond. Table 1 lists the relative stabilities of these conformers computed at the HF/6-31G(d), BAC-MP4, G2(MP2), G2, CBS-4 and

CBS-Q levels of theory. In general, these calculations agree with experiments [17,18] on which conformer is more stable and on the magnitude of energy that separates the two forms. An exception is the HF/6-31G(d) result for 1,2-difluoroethane where the C_{2h} conformer is calculated about 1.8 kJ mol⁻¹ more stable than the C₂ form. This disagrees with experiment, G2 and CBS results which predict the C₂ conformer to be more stable by about 3 kJ mol⁻¹. The optimized geometries of the most stable fluoroethane conformers at the HF/6-31G(d) and MP2/6-31G(d) levels are presented in Table 2. For 1,2-difluoroethane the geometry of the C₂ conformer is displayed. This conformer was also chosen for subsequent enthalpy computations.

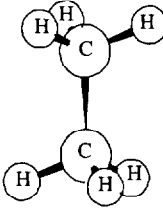
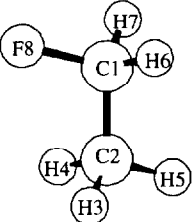
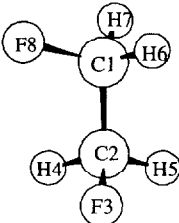
Vibrational frequencies for the optimized geometries computed at the HF/6-31G(d) level are listed in Table 3. The ground state electronic energies required for the BAC-MP4, G2(MP2), G2, CBS-4 and CBS-Q enthalpy calculations are displayed in Table 4.

The reported experimental enthalpies of formation of the fluoroethanes with their estimated uncertainties were taken from [19–22] and are presented in the second column of Table 5(A). The remaining columns of the table contain the enthalpies calculated by the various ab initio methods. For molecules with two

¹ Certain commercial equipment, instruments, or materials are identified in this paper in order to specify the experimental procedure adequately. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment are necessarily the best available for the purpose.

Table 2

Geometries^a optimized with the 6-31G(d) basis set^a

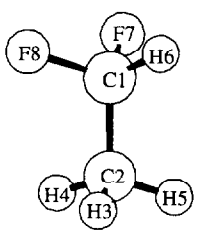
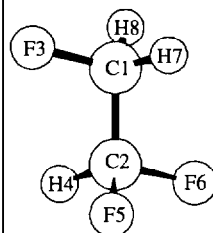
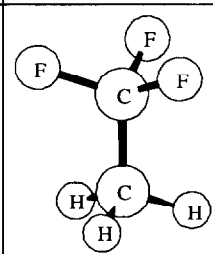
Formula		Parameter	HF	MP2
CH ₃ -CH ₃		C-H	1.086	1.093
		C-C	1.527	1.524
		C-C-H	111.2	111.2
		H-C-H	107.7	107.7
CH ₃ -CH ₂ F		C1-C2	1.512	1.509
		C1-H6,7	1.083	1.094
		C1-F8	1.373	1.399
		C2-H4,3	1.084	1.092
		C2-H5	1.086	1.093
		C1-C2-H3,4	110.5	110.2
		C1-C2-H5	110.3	110.5
		C2-C1-H6,7	111.6	111.7
		C2-C1-F8	109.5	109.2
		H5-C2-C1-F8	180.0	180.0
		H3,4-C2-C1-F8	±60.0	±59.9
		H6,7-C1-C2-H5	±60.9	±61.0
CH ₂ F-CH ₂ F		C1-C2	1.504	1.501
		C1-F8, C2-F3	1.366	1.392
		C1-H6, C2-H4	1.082	1.093
		C1-H7, C2-H5	1.083	1.095
		C1-C2-F3, C2-C1-F8	109.9	109.5
		C1-C2-H4, C2-C1-H6	110.5	110.3
		C1-C2-H5, C2-C1-H7	110.1	110.3
		F3-C2-C1-F8	-69.4	-69.0
		H4-C2-C1-F8, H6-C1-C2-F3	50.2	50.4
		H5-C2-C1-F8, H7-C1-C2-F3	171.3	171.5

stable conformers (i.e. CH₂F-CH₂F, CH₂F-CHF₂, and CHF₂-CHF₂) the listed enthalpy is a thermal average of the two computed enthalpies. The quantities in parentheses represent the deviations from experiment. The deviations in the ab initio enthalpies are also plotted in Fig. 1 (filled triangles and solid lines).

One observes from the RMS and average errors in Table 5(A) (also given in Table 6(A)) that the G2(MP2), G2 and CBS-Q enthalpies exhibit large negative deviations from experiment. Furthermore,

from Fig. 1(A), Fig. 1(B) and Fig. 1(D), one sees that these negative errors are systematic with an approximately linear dependence upon the number of C-F (n_{CF}) bonds in the molecule. (Fits of $\Delta_f H^0(\text{calc}) - \Delta_f H^0(\text{expt})$ vs. n_{CF} to second-order polynomials yielded statistically insignificant quadratic terms.) The CBS-4 enthalpies also show negative deviations from the experimental values. However, for this method the errors are approximately constant, as indicated by the nearly zero slope of the least squares solid line in Fig. 1(C).

Table 2
(continued)

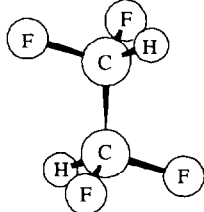
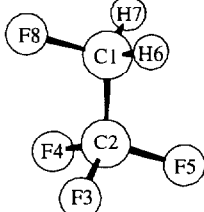
Formula		Parameter	HF	MP2
CH ₃ -CHF ₂		C1-C2	1.502	1.499
		C1-F7,8	1.346	1.373
		C1-H6	1.079	1.093
		C2-H3,4,5	1.083	1.091
		C1-C2-H3,5	110.1	110.1
		C1-C2-H4	109.3	108.6
		C2-C1-H6	113.8	114.5
		C2-C1-F7,8	110.0	109.7
		H4-C2-C1-F7,8	±58.9	±58.8
		H4-C2-C1-H6	180.0	180.0
		H3,5-C2-C1-H6	±60.2	±60.4
CH ₂ F-CHF ₂		C1-C2	1.506	1.505
		C1-F3	1.362	1.388
		C1-H7,8	1.081	1.092
		C2-H4	1.078	1.092
		C2-F5	1.338	1.364
		C2-F6	1.343	1.371
		C2-C1-F3	108.5	108.3
		C2-C1-H7	109.7	109.0
		C2-C1-H8	110.0	110.2
		C1-C2-H4	113.1	113.5
		C1-C2-F5	110.0	109.5
		C1-C2-F6	108.1	107.8
		H4-C2-C1-F3	54.3	55.0
		F5-C2-C1-F3	-67.2	-66.4
		F6-C2-C1-F3	175.1	176.0
CH ₃ -CF ₃		C-C	1.500	1.495
		C-F	1.325	1.353
		C-H	1.082	1.090
		C-C-F	111.6	111.6
		C-C-H	109.4	109.2
		F-C-F	107.2	107.2
		H-C-H	109.5	109.7

The four ab initio procedures have been found to yield very accurate enthalpies of formation in most non-halogenated species. From these results, and from previous work on fluorinated [2] and chlorinated [3] hydrocarbons it is clear that these methods exhibit severe, unacceptable errors relative to reported experimental enthalpies.

4. Bond additivity corrections

When the errors in $\Delta_f H^\circ$ are observed to be systematically dependent upon the number of bonds of a given type in a molecule, they can, in principle, be removed by the application of bond additivity corrections (BACs), originally introduced by Melius in his

Table 2
(continued)

Formula		Parameter	HF	MP2
CHF ₂ -CHF ₂		C-F	1.336	1.362
		C-C	1.510	1.511
		C-H	1.078	1.092
		C-C-F	108.5	108.2
		C-C-H	112.1	112.2
		F-C-F	108.4	108.8
		F-C-H	109.6	109.7
		H-C-C-H	180.0	180.0
		F-C-C-H	±58.8	±58.8
CH ₂ F-CF ₃		C1-C2	1.508	1.507
		C1-F8	1.356	1.382
		C1-H6,7	1.080	1.092
		C2-F3,4	1.318	1.344
		C2-F5	1.324	1.352
		F3,4-C2-C1	111.7	111.6
		F5-C2-C1	109.1	109.1
		F8-C1-C2	108.7	108.5
		H6,7-C1-C2	109.2	109.1
		F3,4-C2-C1-F8	60.5	60.5
		F5-C2-C1-F8	180.0	180.0
		H6,7-C1-C2-F5	60.4	60.3

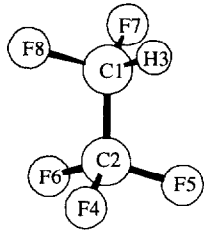
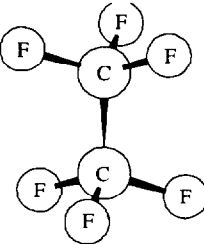
BAC-MP4 method [7–9]. The correction, Δ_{BAC} , is of the form:

$$\Delta_{\text{BAC}} = \sum_{\text{C-X}} n_{\text{C-X}} \Delta_{\text{C-X}} \quad (1)$$

In this equation, $n_{\text{C-X}}$ is the number of a given type of bond and $\Delta_{\text{C-X}}$ is the BAC parameter representing the error associated with this bond type. The parameters are determined via a linear fit of Eq. (1) to the calculated deviations of the ab initio enthalpies from experiment. In our earlier investigation on the thermochemistry of the chlorofluoromethanes [3], it was found that, for the same four ab initio methods, the application of C–F and C–Cl BAC parameters removed all systematic error and yielded corrected enthalpies of formation whose RMS deviations from experiment were significantly below the RMS uncertainties in the literature data. It was also observed that values of $\Delta_{\text{C-H}}$ were smaller than the parameter's standard deviation and that its exclusion had no impact on the quality of the fit.

Because of the close similarity of the fluoroethanes (C2s) to the fluoromethanes (C1s) in the earlier work, it would be reasonable to expect that the same C–F BAC parameter should also correct the systematic errors found in this study. The results of this procedure are displayed in Table 6(B). The second column contains the values of $\Delta_{\text{C-F}}$ from [3], with their estimated standard deviations. The next two pairs of columns represent the RMS and average errors for the C1s and C2s, respectively. As noted above, the values of RMS1 and AVE1 demonstrate that the application of a single C–F BAC does indeed remove virtually all systematic errors in $\Delta_f H^\circ$ for the fluoromethanes; note that resulting RMS deviations are significantly smaller than the RMS experimental uncertainty of 4.1 kJ mol^{–1}. From RMS2 in Table 6, one sees, of course, that the same BAC also yields a substantial decrease in RMS deviations in the C2s. However, in contrast to the C1s, the comparatively large negative values of AVE2 reveals that not all of the negative systematic

Table 2
(continued)

Formula		Parameter	HF	MP2
CHF ₂ -CF ₃		C1-C2	1.517	1.519
		C1-H3	1.077	1.091
		C1-F7,8	1.330	1.357
		C2-F4,5	1.317	1.344
		C2-F6	1.311	1.338
		F4,5-C2-C1	109.7	109.6
		F6-C2-C1	111.4	111.0
		H3-C1-C2	111.1	111.5
		F7,8-C1-C2	108.6	108.2
		F4,5-C2-C1-H3	±59.5	±59.6
		H3-C1-C2-F6	180.0	180.0
		F7,8-C1-C2-F6	±59.2	±59.2
CF ₃ -CF ₃		C-C	1.526	1.528
		C-F	1.311	1.339
		C-C-F	109.8	109.7
		F-C-F	109.1	109.3

*Bonds in angstroms and angles in degrees.

error has been removed by the BAC. In principle, this problem could be remedied by refitting Δ_{C-F} to minimize the RMS residuals in the fluoroethanes. However, this yields a larger value for the parameter, which would overcorrect enthalpies in the C1s.

Further, it is physically unrealistic that the error due to a C–F bond should differ in the two series.

An alternative approach to eliminate the remaining systematic error would be via the addition of a second BAC, Δ_{C-C} , to account for the presence of a C–C

Table 3
Computed HF/6-31G(d) vibrational frequencies for fluoroethanes^a

Formula	Frequencies
CH ₃ -CH ₃	291, 794, 794, 948, 1194, 1194, 1382, 1410, 1468, 1468, 1473, 1473, 2857, 2862, 2901, 2901, 2924, 2924
CH ₃ -CH ₂ F	244, 393, 783, 867, 1043, 1107, 1169, 1269, 1381, 1417, 1453, 1469, 1503, 2869, 2896, 2925, 2929, 2948
CH ₂ F-CH ₂ F	134, 310, 483, 854, 894, 1081, 1099, 1117, 1235, 1272, 1395, 1434, 1481, 1484, 2895, 2909, 2946, 2959
CH ₃ -CHF ₂	230, 364, 449, 548, 846, 957, 1119, 1146, 1159, 1375, 1391, 1432, 1455, 1458, 2883, 2948, 2952, 2968
CH ₂ F-CHF ₂	114, 235, 413, 465, 559, 896, 1081, 1111, 1124, 1154, 1238, 1332, 1402, 1457, 1486, 2923, 2971, 2986
CH ₃ -CF ₃	224, 350, 350, 522, 522, 577, 811, 977, 977, 1263, 1263, 1277, 1429, 1453, 1453, 2899, 2974, 2974
CHF ₂ -CHF ₂	85, 196, 348, 406, 476, 523, 607, 1094, 1123, 1139, 1148, 1165, 1306, 1362, 1390, 1480, 2986, 2995
CH ₂ F-CF ₃	105, 208, 341, 398, 516, 530, 646, 828, 980, 1101, 1200, 1216, 1303, 1315, 1448, 1485, 2935, 2990
CHF ₂ -CF ₃	72, 201, 235, 351, 406, 505, 559, 569, 706, 859, 1131, 1169, 1217, 1256, 1324, 1385, 1466, 2996
CF ₃ -CF ₃	62, 205, 205, 337, 370, 370, 504, 504, 602, 602, 691, 793, 1110, 1274, 1274, 1280, 1280, 1453

^a Scaled vibrational frequencies in cm⁻¹ (scale factor = 0.8929).

Table 4
Ground state electronic energies^a required for theoretical calculations of $\Delta_f H^\circ$

Species	E_0 [MP4] ^b	E_0 (G2-MP2) ^c	E_0 (G2) ^c	E_0 (CBS-4)	E_0 (CBS-Q)
CH ₃ –CH ₃	–79.504268	–79.628927	–79.630880	–79.661123	–79.629733
CH ₃ –CH ₂ F	–178.518355	–178.780125	–178.784905	–178.826645	–178.792938
CH ₂ F–CH ₂ F, C ₂	–277.528464	–277.926913	–277.934520	–277.987567	–277.951773
CH ₂ F–CH ₂ F, C _{2h}	–277.528307	–277.925717	–277.933322	–277.985952	–277.950561
CH ₃ –CHF ₂	–277.553127	–277.947537	–277.955404	–278.009455	–277.972744
CH ₂ F–CHF ₂ , C ₁	–376.560332	–377.090245	–377.100959	–377.165854	–377.127549
CH ₂ F–CHF ₂ , C _s	–376.557785	–377.088174	–377.098887	–377.164009	–377.125252
CH ₃ –CF ₃	–376.597813	–377.122026	–377.133221	–377.200227	–377.159685
CHF ₂ –CHF ₂ , C _{2h}	–475.589845	–476.251263	–476.265103	–476.341879	–476.300885
CHF ₂ –CHF ₂ , C ₂	–475.587244	–476.249031	–476.262876	–476.339335	–476.298354
CH ₂ F–CF ₃	–475.601799	–476.261476	–476.275549	–476.353260	–476.311047
CHF ₂ –CF ₃	–574.628427	–575.419525	–575.436748	–575.526124	–575.481282
CF ₃ –CF ₃	–673.666813	–674.587245	–674.607849	–674.709745	–674.660947

^a In hartree.

^b Basis set: 6-31G(d,p). Required for the BAC-MP4 calculations. Geometry optimized at the HF/6-31G(d) level.

^c Geometry optimized at the MP2/6-31G(d) level.

Table 5
Experimental and calculated enthalpies of formation^a

A. Ab initio enthalpies

Molecule	Expt.	G2(MP2)	G2	CBS-4	CBS-Q
CH ₃ –CH ₃	–84.1 ± 0.4 [19]	–83.1 (1.0)	–86.0 (–1.9)	–92.1 (–8.0)	–81.5 (2.6)
CH ₃ –CH ₂ F	–263.2 ± 1.6 [20]	–279.5 (–16.3)	–279.7 (–16.5)	–277.7 (–14.5)	–274.1 (–10.9)
CH ₂ F–CH ₂ F	–433.9 ± 11.8 [21]	–462.3 (–28.4)	–459.8 (–25.9)	–447.5 (–13.6)	–457.5 (–23.6)
CH ₃ –CHF ₂	–500.8 ± 6.3 [20]	–518.3 (–17.5)	–516.4 (–15.6)	–508.5 (–7.7)	–510.0 (–9.2)
CH ₂ F–CHF ₂	–664.8 ± 4.2 [22]	–691.7 (–26.9)	–687.0 (–22.2)	–669.1 (–4.3)	–680.0 (–15.2)
CH ₃ –CF ₃	–745.6 ± 1.6 [20]	–775.4 (–29.8)	–772.1 (–26.5)	–760.0 (–14.4)	–764.4 (–18.8)
CHF ₂ –CHF ₂	–877.8 ± 17.6 [21]	–913.2 (–35.4)	–906.6 (–28.8)	–881.3 (–3.5)	–898.6 (–20.8)
CH ₂ F–CF ₃	–895.8 ± 4.2 [20]	–940.2 (–44.4)	–934.2 (–38.4)	–912.0 (–16.2)	–925.0 (–29.2)
CHF ₂ –CF ₃	–1104.6 ± 4.6 [20]	–1153.9 (–49.3)	–1145.9 (–41.3)	–1116.1 (–11.5)	–1135.2 (–30.6)
CF ₃ –CF ₃	–1342.7 ± 6.3 [20]	–1392.9 (–30.2)	–1383.7 (–41.0)	–1348.5 (–5.8)	–1371.0 (–28.3)
RMS	± 7.7	33.4	28.4	10.9	20.9
AVE		–29.7	–25.8	–10.0	–18.4

B. Enthalpies calculated with bond additivity corrections

Molecule	BAC-MP4	G2(MP2) [BAC]	G2 [BAC]	CBS-4 [BAC]	CBS-Q [BAC]
CH ₃ –CH ₃	–86.9 (–2.8)	–83.1 (1.0)	–86.0 (–1.9)	–92.1 (–8.0)	–81.5 (2.6)
CH ₃ –CH ₂ F	–272.4 (–9.2)	–269.9 (–6.7)	–271.6 (–8.4)	–275.2 (–12.0)	–268.2 (–5.0)
CH ₂ F–CH ₂ F	–446.0 (–12.1)	–443.1 (–9.2)	–443.7 (–9.8)	–442.6 (–8.7)	–445.8 (–11.9)
CH ₃ –CHF ₂	–505.3 (–4.5)	–499.1 (1.7)	–500.3 (0.5)	–503.6 (–2.8)	–498.3 (2.5)
CH ₂ F–CHF ₂	–671.5 (–6.7)	–663.0 (1.8)	–662.8 (2.0)	–661.7 (3.1)	–662.4 (2.4)
CH ₃ –CF ₃	–755.4 (–9.8)	–746.7 (–1.1)	–747.9 (–2.3)	–752.6 (–7.0)	–746.9 (–1.3)
CHF ₂ –CHF ₂	–883.3 (–5.5)	–874.9 (2.9)	–874.3 (3.5)	–871.5 (6.3)	–875.2 (2.6)
CH ₂ F–CF ₃	–913.3 (–17.5)	–901.9 (–6.1)	–901.9 (–6.1)	–902.2 (–6.4)	–901.6 (–5.8)
CHF ₂ –CF ₃	–1124.1 (–19.5)	–1106.0 (–1.4)	–1105.5 (–0.9)	–1103.8 (0.8)	–1105.9 (–1.3)
CF ₃ –CF ₃	–1357.0 (–14.3)	–1335.4 (7.3)	–1335.3 (7.4)	–1333.8 (8.9)	–1335.8 (6.9)
RMS	11.5	4.9	5.3	7.2	5.3
AVE	–10.2	1.0	–1.6	–2.6	–0.8

^aEnthalpies of formation ($\Delta_f H^\circ$) at 298 K in kJ mol^{–1}. Values in parentheses represent deviations from experiment.

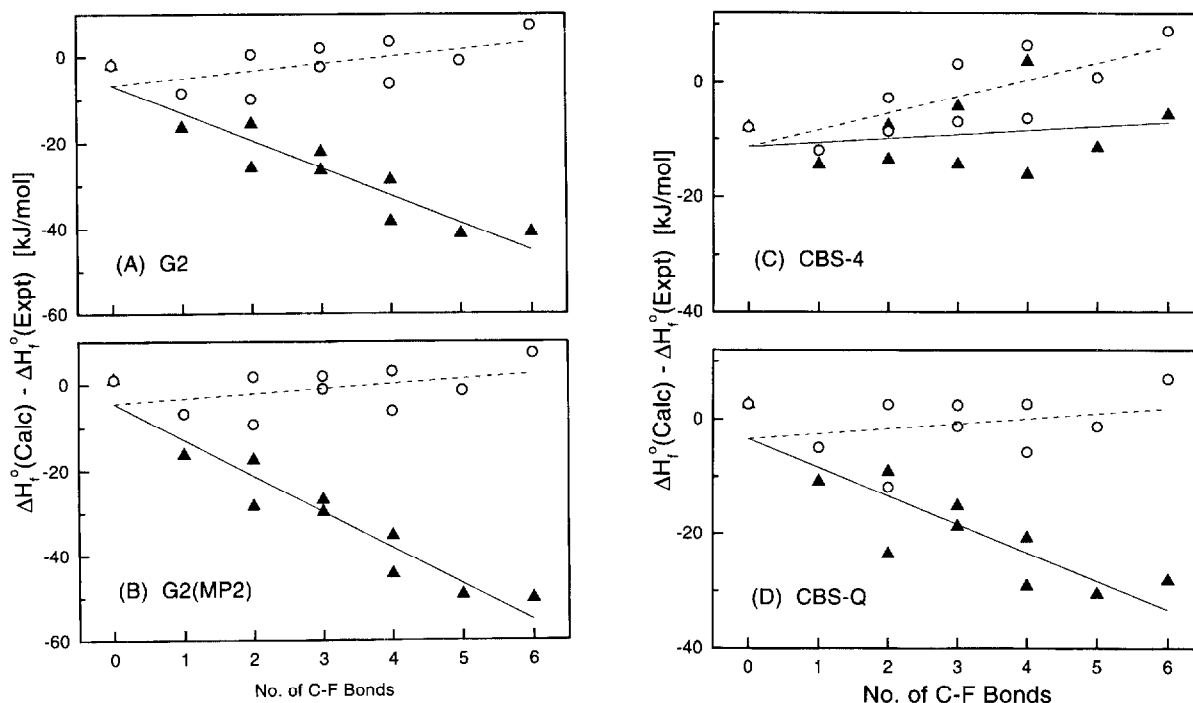


Fig. 1. Deviations of calculated enthalpies of formation of fluoroethanes from experiment: (A) G2; (B) G2(MP2); (C) CBS-4; (D) CBS-Q. (▲) Original errors; (○) BAC errors; (—) BACs plotted as a function of the number of C–F bonds; (---) errors in $\Delta_f H^\circ(\text{BAC})$.

bond in the fluoroethanes. However, this has the effect of increasing the error in ethane, where the ab initio enthalpies are in excellent agreement with experiment for all but the CBS-4 method (Table 5(A)). Furthermore, these methods have been applied with great success to the prediction of $\Delta_f H^\circ$ in numerous non-fluorinated organic species with one or more C–C bonds. Hence, the introduction of a C–C bond additivity correction would not be consistent with these earlier results.

In order to explore further the source of the remaining systematic errors in the fluoroethanes, we refer to the results of our earlier investigation of the chlorofluoromethanes [3]. In that work, it was discussed at some length how trends and curvature in plots of $\Delta_f H^\circ(\text{calc}) - \Delta_f H^\circ(\text{expt})$ vs. $n_{\text{C-F}}$ (at fixed $n_{\text{C-Cl}}$) and vs. $n_{\text{C-Cl}}$ (at fixed $n_{\text{C-F}}$) provided definitive evidence of ‘‘heavy atom’’ interactions (also utilized by Melius in the BAC-MP4 method [7–9]); i.e. the presence of one C–F bond increases the error due to either a second fluorine or a chlorine atom on the same carbon. In the earlier work, it was decided not to include heavy

atom interactions since the RMS residuals using linearly independent BACs were already below the experimental uncertainties in the chlorofluoromethanes. In contrast, for the fluoroethanes, the comparatively large residual errors (RMS2) and negative average deviations (AVE2) indicate that the introduction of a heavy atom interaction parameter is necessary in this series to account for enhanced errors due to the presence of a second carbon atom attached to the carbon containing the C–C bond. In the spirit of the BAC-MP4 procedure, one may write:

$$\Delta_{\text{BAC}} = n_{\text{C-F}} \Delta_{\text{C-F}f_{\text{C}}} \quad (2)$$

where f_{C} is the interaction parameter representing the impact of a second attached carbon on the error due to the C–F bond. This has no impact on the Cls since $f_{\text{C}} = 1$ if there is no second carbon.

One may solve for f_{C} via linear regression (constrained to pass through the origin) to fit Δ_{BAC} to the deviations of the ab initio enthalpies from experiment, with the product $n_{\text{C-F}} \Delta_{\text{C-F}}$ as the independent variable. The resultant values of the interaction parameter

Table 6

Fluoroalkane bond additivity correction parameters and the resulting errors computed by regression analysis^a

Method	Δ_{C-F}	f_C	RMS1 ^b	AVE1 ^b	RMS2 ^c	AVE2 ^c
Expt.			± 4.1		± 7.7	
A. Ab initio						
G2(MP2)	0.0	0.0	18.4	–15.7	33.4	–29.7
G2	0.0	0.0	14.8	–13.1	28.4	–25.8
CBS-4	0.0	0.0	2.8	–1.7	10.9	–10.0
CBS-Q	0.0	0.0	8.6	–6.9	20.9	–18.4
B. Δ_{C-F}						
G2(MP2) [BAC]	-7.98 ± 0.38	0.0	2.6	0.2	7.3	–5.8
G2 [BAC]	-6.51 ± 0.41	0.0	3.2	–0.1	7.6	–6.3
CBS-4 [BAC]	-1.28 ± 0.74	0.0	3.3	0.9	8.6	–6.5
CBS-Q [BAC]	-3.51 ± 0.55	0.0	1.6	0.1	9.7	–7.7
C. $\Delta_{C-F} + f_C$						
G2(MP2) [BAC]	-7.98 ± 0.38	1.20 ± 0.06	2.6	0.2	5.3	–1.6
G2 [BAC]	-6.51 ± 0.41	1.24 ± 0.08	3.2	–0.1	5.2	–1.2
CBS4[BAC]	-1.28 ± 0.74	1.92 ± 0.57	3.3	0.9	7.2	–2.6
CBS-Q [BAC]	-3.51 ± 0.55	1.67 ± 0.14	1.6	0.1	5.3	–0.8

^a Units: kJ mol^{–1}.^b Fluoromethanes (C1).^c Fluoroethanes (C2).

are shown in the third column of Table 6(C). The estimated errors in f_C may be obtained from either (a) the standard deviation of the parameter obtained from the least squares fit, or (b) the variation in the parameter when Δ_{C-F} is varied between its upper and lower limits ($\Delta_{C-F} \pm \sigma$). The estimates given in the table represent the larger of these two values. The very large value of $\sigma(f_C)$ for the CBS-4 method is a consequence of the large error in Δ_{C-F} for this method and the fact that, as mentioned above, errors in the CBS-4 enthalpies of formation are largely random.

It is very satisfying to observe from RMS2 in Table 6(C) that the RMS residuals using a C–F BAC with an f_C interaction parameter are reduced significantly. Further, the much smaller negative values of AVE2, relative to Table 6(B), indicates that almost all of the remaining systematic error has been removed from the BAC-corrected enthalpies of formation. The removal of systematic error is also demonstrated in Fig. 1, in which errors in the BAC-corrected enthalpies of formation (open circles and dashed line) are clustered about $\Delta_f H^0(\text{cal}) - \Delta_f H^0(\text{exp}) = 0$. Individual BAC-corrected enthalpies of formation in the

fluoromethanes, using Δ_{C-F} from [3] and f_C from this work (Table 6(C)) are presented in Table 5(B).

Finally, the first column of Table 5(B) contains errors in enthalpies of formation of the fluoroethanes calculated using the Melius BAC-MP4 procedure [7–9]. It was shown in [3] that calculated enthalpies using this method are in excellent agreement with experimental results for the fluoromethanes. There are, however, rather large residual systematic errors in predicted values of $\Delta_f H^0$ of the fluoroethanes, as illustrated by the RMS and average errors of 11.5 and –10.2 kJ mol^{–1}, respectively. From the table, it is seen that calculated enthalpies of the C2 series are uniformly more negative than results from the literature. Thus, it would appear that the C–C BAC and interaction parameters derived in the BAC-MP4 method to fit data in predominantly non-halogenated organics do not adequately characterize the systematic errors in fluoroethanes.

5. Summary and conclusions

Enthalpies of formation of the fluoroethanes calculated by the G2, G2(MP2), CBS-4 and CBS-Q

quantum mechanical procedures were found to exhibit substantial negative deviations from experiment which are proportional to the number of C–F bonds in the molecule. The application of a C–F bond additivity correction, $\Delta_{\text{C-F}}$, derived in an earlier investigation of fluoro- and chlorofluoromethanes, removed some, although not all, of the systematic errors. Introduction of a further heavy atom interaction parameter, f_{C} , to account for the impact of a second attached carbon on the C–F bond error, yielded BAC-corrected enthalpies with RMS errors within the reported experimental uncertainties.

Additional calculations on fluoroethylenes and acetylenes, fluorocarbon radicals and reactive transition states are in progress to assess the capability of ab initio procedures with bond additivity corrections to predict accurate enthalpies of formation in these species.

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