

# Halon Thermochemistry: Calculated Enthalpies of Formation of Chlorofluoromethanes

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The *ab initio* G2, G2(MP2), CBS-4, CBS-Q, and BAC-MP4 methods have been used to calculate the enthalpies of formation of the series of four chloromethanes and six chlorofluoromethanes [ $\text{CH}_x\text{F}_y\text{Cl}_{4-x-y}$ ,  $x = 0-3$ ,  $y = 0-3$ ]. Calculated values of  $\Delta_f H^\circ$  using the first four *ab initio* methods exhibit comparatively large systematic negative errors compared with experimental values, up to  $-50$  kJ/mol, which are nearly linearly dependent upon the number of C–F and C–Cl bonds in the molecule. It is found for the chlorofluoromethanes that the application of bond additivity corrections (BAC's) to the *ab initio* enthalpies effectively removes systematic errors in the calculations and yields values that are in close agreement with experimentally derived heats. The rms deviations of the corrected calculated enthalpies from the experimental values are 2.4, 2.6, 3.4, 4.7, and 3.8 kJ/mol for the G2(MP2), G2, CBS-Q, CBS-4, and BAC-MP4 methods, respectively. These deviations are lower than the rms errors (6.9 kJ/mol) in the experimental enthalpies. Therefore, it is concluded that any of these calculational procedures, together with bond additivity corrections to remove systematic error, may profitably be used to obtain accurate enthalpies of formation in chlorofluorocarbon species.

## Introduction

It is well documented that chlorofluorocarbons (CFC's) and halon fire suppressants (e.g.,  $\text{CF}_3\text{Br}$ ,  $\text{CF}_2\text{ClBr}$ ,  $\text{CF}_2\text{BrCF}_2\text{Br}$ ) efficiently catalyze the destruction of stratospheric ozone.<sup>1,2</sup> Hence, their commercial use has been increasingly restricted in recent years.<sup>2,3</sup> Partially hydrogenated CFC's are more efficiently destroyed in the troposphere, which results in a diminished ozone depletion potential. Therefore, these compounds have been proposed as transitional replacements for the perhalogenated CFC's and halons.<sup>2,4</sup>

Accurate thermochemical data and rate constants are required to study the effectiveness of a proposed fire suppression agent via kinetic modeling. Unfortunately, these data are not currently available for the majority of the CFC's.

Recently, we investigated the capability of various *ab initio* quantum mechanical methods to predict accurate enthalpies of formation in the series of fluoromethanes,<sup>5</sup>  $\text{CH}_x\text{F}_{4-x}$ ,  $x = 0-4$ . Here, we report the extension of these studies to the complete series of chloromethanes and chlorofluoromethanes,  $\text{CH}_x\text{F}_y\text{Cl}_{4-x-y}$ ,  $x = 0-3$ ,  $y = 0-3$ . The results are presented below.

## Calculations

The *ab initio* calculations were performed using the GAUSSIAN code<sup>6-8</sup> on CRAY Y-MP, CRAY X-MP, CONVEX-C3820, SUN-Sparc, HP-PARisk, and SGI Power-Challenge computers.<sup>9</sup>

The G2,<sup>10</sup> the related G2(MP2),<sup>11</sup> and the CBS series<sup>12-14</sup> (CBS-4 and CBS-Q were used in this investigation) of *ab initio* protocols all involve use of a series of lower level calculations that are designed to provide estimates of the molecular energy with large basis sets and a high degree of electron correlation. The procedures are described in detail in the original references. The BAC-MP4 method<sup>15,16</sup> requires determination of electronic energies and, from these, enthalpies of formation, at the MP4/6-31G(d,p)//HF/6-31G(d) basis level, followed by empirical energy corrections dependent upon the numbers, types, and proximities of the various bonds in the molecule.

Displayed in Table 1 are the HF/6-31G(d) and MP2(FU)/6-31G(d) geometries of the 10 molecules investigated here, together with scaled (by 0.8929) HF/6-31G(d) vibrational frequencies. Also shown in the table are the experimental vibrational frequencies.<sup>17</sup> The average difference between the calculated and experimental frequencies is less than 1%. Further examination suggests that calculated vibrational frequencies less than  $1000\text{ cm}^{-1}$  are in the range 1–3% low, frequencies between 1000 and  $1500\text{ cm}^{-1}$  are roughly 1–3% high, and calculated C–H vibrational frequencies near  $3000\text{ cm}^{-1}$  are about 1% low.

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**TABLE 1: Optimized Geometries<sup>a</sup> and Vibrational Frequencies<sup>b,c</sup>**

formula	parameter	HF/6-31G(d)	MP2(FU)/6-31G(d)
CH <sub>3</sub> Cl	C-Cl	1.785	1.777
	C-H	1.078	1.088
	Cl-C-H	108.5	108.9
	H-C-H	110.1	110.0
	$\nu_{\text{calc}}$	699, 1016(2), 1373, 1454(2), 2917, 3010(2)	
	$\nu_{\text{expt}}$	732, 1017, 1355, 1452, 2937, 3039	
CH <sub>2</sub> Cl <sub>2</sub>	C-Cl	1.768	1.767
	C-H	1.074	1.087
	Cl-C-Cl	112.9	113.0
	H-C-Cl	108.2	108.3
	H-C-H	111.1	110.8
	$\nu_{\text{calc}}$	278, 691, 752, 889, 1174, 1295, 1445, 2980, 3053	
$\nu_{\text{expt}}$	282, 717, 758, 898, 1153, 1268, 1467, 2999, 3040		
CHCl <sub>3</sub>	C-Cl	1.763	1.765
	C-H	1.071	1.086
	Cl-C-Cl	111.3	111.2
	Cl-C-H	107.6	107.7
	$\nu_{\text{calc}}$	258(2), 360, 652, 781(2), 1249(2), 3043	
$\nu_{\text{expt}}$	261, 363, 680, 774, 1220, 3034		
CCl <sub>4</sub>	C-Cl	1.766	1.769
	$\nu_{\text{calc}}$	218(2), 311(3), 449, 806(3)	
	$\nu_{\text{expt}}$	217, 314, 458, 776	
CH <sub>2</sub> FCl	C-Cl	1.772	1.768
	C-F	1.342	1.371
	C-H	1.076	1.089
	F-C-Cl	109.9	110.1
	F-C-H	109.4	109.1
	Cl-C-H	108.0	108.3
	$\nu_{\text{calc}}$	373, 735, 998, 1095, 1239, 1374, 1490, 2964, 3036	
$\nu_{\text{expt}}$	385, 760, 1001, 1068, 1236, 1351, 1468, 2993, 3048		
CHF <sub>2</sub> Cl	C-Cl	1.759	1.759
	C-F	1.321	1.349
	C-H	1.073	1.088
	Cl-C-F	109.5	109.6
	Cl-C-H	109.3	109.7
	F-C-F	108.3	108.2
	F-C-H	110.1	109.9
	$\nu_{\text{calc}}$	357, 401, 577, 798, 1122, 1170, 1337, 1384, 3036	
$\nu_{\text{expt}}$	369, 419, 598, 806, 1115, 1178, 1312, 1343, 3026		
CF <sub>3</sub> Cl	C-Cl	1.747	1.749
	C-F	1.306	1.335
	Cl-C-F	110.3	110.4
	F-C-F	108.7	108.6
	$\nu_{\text{calc}}$	340(2), 465, 544(2), 768, 1121, 1267(2)	
$\nu_{\text{expt}}$	350, 476, 563, 782, 1105, 1212		
CHFC1 <sub>2</sub>	C-Cl	1.759	1.760
	C-F	1.329	1.359
	C-H	1.072	1.087
	Cl-C-Cl	112.1	112.1
	Cl-C-F	109.0	109.0
	Cl-C-H	108.6	108.8
	F-C-H	109.6	109.3
	$\nu_{\text{calc}}$	272, 360, 445, 723, 810, 1119, 1272, 1335, 3038	
$\nu_{\text{expt}}$	274, 365, 456, 742, 802, 1083, 1240, 1316, 3026		
CF <sub>2</sub> Cl <sub>2</sub>	C-Cl	1.752	1.755
	C-F	1.313	1.343
	Cl-C-Cl	112.3	112.4
	Cl-C-F	109.2	109.2
	F-C-F	107.9	107.6
	$\nu_{\text{calc}}$	258, 318, 422, 427, 446, 651, 924, 1138, 1218	
$\nu_{\text{expt}}$	261, 322, 433, 446, 458, 667, 922, 1101, 1159		
CFCl <sub>3</sub>	C-Cl	1.758	1.760
	C-F	1.322	1.354
	Cl-C-Cl	110.9	111.0
	Cl-C-F	108.0	107.9
	$\nu_{\text{calc}}$	243(2), 344, 390(2), 521, 863(2), 1134	
	$\nu_{\text{expt}}$	241, 350, 394, 535, 847, 1085	

<sup>a</sup> Bond lengths in Å, angles in degrees. <sup>b</sup> Scaled vibrational frequencies in cm<sup>-1</sup> (scale factor = 0.8929).

Shown in Table 2 are the ground state G2, G2-MP2, CBS-4, CBS-Q, and MP4/6-31G(d,p) electronic energies of the 10

molecules. These quantities, together with calculated atomic energies, enthalpies of formation of the elements, and heat

TABLE 2: Ground State Electronic Energies<sup>a</sup> Required for Calculations of  $\Delta_f H^\circ$ 

formula	$E_0$ [G2]	$E_0$ [G2(MP2)]	$E_0$ [CBS-4]	$E_0$ [CBS-Q]	$E_0$ [MP4/6-31G(d,p)] <sup>b</sup>
CH <sub>3</sub> Cl	-499.553 824	-499.544 455	-499.568 459	-499.560 647	-499.050 199
CH <sub>2</sub> Cl <sub>2</sub>	-958.698 916	-958.681 373	-958.712 315	-958.714 758	-958.409 709
CHCl <sub>3</sub>	-1417.843 206	-1417.817 437	-1417.855 815	-1417.869 342	-1417.440 638
CCl <sub>4</sub>	-1876.984 179	-1876.950 008	-1876.999 348	-1877.021 293	-1876.467 540
CH <sub>2</sub> FCI	-598.705 574	-598.693 230	-598.733 176	-598.721 343	-598.388 234
CHF <sub>2</sub> Cl	-697.871 524	-697.855 940	-697.912 606	-697.896 463	-697.417 811
CF <sub>3</sub> Cl	-797.040 981	-797.021 993	-797.095 770	-797.074 987	-796.453 939
CHFCl <sub>2</sub>	-1057.854 684	-1057.833 921	-1057.882 081	-1057.879 403	-1057.425 750
CF <sub>2</sub> Cl <sub>2</sub>	-1157.018 311	-1156.944 124	-1157.059 939	-1157.051 827	-1156.453 861
CFCl <sub>3</sub>	-1516.999 095	-1516.969 830	-1517.027 004	-1517.033 302	-1516.458 245

<sup>a</sup> In hartrees. <sup>b</sup> Required for the BAC-MP4 calculations.

TABLE 3: Experimental and Calculated Enthalpies of Formation<sup>a</sup>

A. <i>Ab Initio</i> Enthalpies						
species	expt <sup>b</sup>	G2 <sup>c</sup>	G2(MP2) <sup>c</sup>	CBS-4 <sup>c</sup>	CBS-Q <sup>c</sup>	
CH <sub>4</sub>	-74.9(0.4)	-77.7(-2.8)	-75.6(-0.7)	-77.6(-2.7)	-74.0(0.9)	
CH <sub>3</sub> F	-232.6(8.4)	-244.1(-11.5)	-245.0(-12.4)	-236.9(-4.3)	-238.7(-6.1)	
CH <sub>2</sub> F <sub>2</sub>	-452.2(1.8)	-463.7(-11.5)	-466.9(-14.7)	-451.1(1.1)	-457.6(-5.4)	
CHF <sub>3</sub>	-697.6(2.7)	-714.0(-16.4)	-718.9(-21.3)	-696.9(0.7)	-706.7(-9.1)	
CF <sub>4</sub>	-933.0(1.7)	-956.5(-23.5)	-962.6(-29.6)	-936.6(-3.3)	-947.7(-14.7)	
CH <sub>3</sub> Cl	-83.7(2.1)	-85.5(-1.8)	-88.1(-4.4)	-88.9(-5.2)	-86.3(-2.6)	
CH <sub>2</sub> Cl <sub>2</sub>	-95.5(1.3)	-98.1(-2.6)	-105.2(-9.7)	-108.6(-13.1)	-105.6(-10.1)	
CHCl <sub>3</sub>	-103.2(1.3)	-107.6(-4.4)	-119.2(-16.0)	-126.5(-23.3)	-125.3(-22.1)	
CCl <sub>4</sub>	-96.0(2.1)	-107.7(-11.7)	-123.2(-27.2)	-143.8(-47.8)	-137.3(-41.3)	
CH <sub>2</sub> FCI	-261.9(13.0)	-273.3(-11.4)	-278.3(-16.4)	-272.5(-10.6)	-272.3(-10.4)	
CHF <sub>2</sub> Cl	-481.6(13.0)	-498.1(-16.5)	-504.7(-23.1)	-494.4(-12.8)	-495.9(-14.3)	
CF <sub>3</sub> Cl	-707.9(3.3)	-731.8(-23.9)	-739.6(-31.7)	-725.9(-18.0)	-728.2(-20.3)	
CHFCl <sub>2</sub>	-283.3(13.0)	-295.8(-12.5)	-304.7(-21.4)	-304.8(-21.5)	-301.4(-18.1)	
CF <sub>2</sub> Cl <sub>2</sub>	-491.6(8.0)	-513.9(-22.3)	-524.0(-32.4)	-522.1(-30.5)	-517.4(-25.8)	
CFCl <sub>3</sub>	-288.7(6.3)	-305.2(-16.5)	-317.8(-29.1)	-326.0(-37.3)	-318.8(-30.1)	
rms	6.9	14.5	21.5	20.7	18.8	
avg		-12.6	-19.3	-15.3	-15.3	
B. Enthalpies Calculated with Bond Additivity Corrections						
species	expt <sup>b</sup>	G2 <sup>c</sup> [BAC]	G2(MP2) <sup>c</sup> [BAC]	CBS-4 <sup>c</sup> [BAC]	CBS-Q <sup>c</sup> [BAC]	BAC-MP4 <sup>c</sup>
CH <sub>4</sub>	-74.9(0.4)	-77.7(-2.8)	-75.6(-0.7)	-77.6(-2.7)	-74.0(0.9)	-74.8(0.1)
CH <sub>3</sub> F	-232.6(8.4)	-237.6(-5.0)	-237.0(-4.4)	-235.6(-3.0)	-235.2(-2.6)	-233.8(-1.2)
CH <sub>2</sub> F <sub>2</sub>	-452.2(1.8)	-450.7(1.5)	-450.9(1.3)	-448.5(3.7)	-450.6(1.6)	-451.1(1.1)
CHF <sub>3</sub>	-697.6(2.7)	-694.5(3.1)	-695.0(2.6)	-693.1(4.5)	-696.2(1.4)	-699.5(-1.9)
CF <sub>4</sub>	-933.0(1.7)	-930.5(2.5)	-930.7(2.3)	-931.2(1.8)	-933.7(-0.7)	-934.1(-1.1)
CH <sub>3</sub> Cl	-83.7(2.1)	-82.7(1.0)	-81.6(2.2)	-78.3(5.4)	-77.8(5.9)	-84.1(-0.4)
CH <sub>2</sub> Cl <sub>2</sub>	-95.5(1.3)	-92.4(3.1)	-92.1(3.4)	-87.4(8.1)	-88.6(6.9)	-94.6(0.9)
CHCl <sub>3</sub>	-103.2(1.3)	-99.2(4.0)	-99.5(3.7)	-94.7(8.5)	-99.8(3.4)	-97.3(5.9)
CCl <sub>4</sub>	-96.0(2.1)	-96.5(-0.5)	-97.1(-1.1)	-101.3(-5.3)	-103.3(-7.3)	-84.6(11.4)
CH <sub>2</sub> FCI	-261.9(13.0)	-264.0(-2.1)	-263.7(-1.8)	-260.6(1.3)	-260.3(1.6)	-263.4(-1.5)
CHF <sub>2</sub> Cl	-481.6(13.0)	-482.3(-0.7)	-482.2(-0.6)	-481.2(0.4)	-480.4(1.2)	-483.1(-1.5)
CF <sub>3</sub> Cl	-707.9(3.3)	-709.4(-1.5)	-709.1(-1.2)	-711.4(-3.5)	-709.2(-1.3)	-710.6(-2.7)
CHFCl <sub>2</sub>	-283.3(13.0)	-283.7(-0.4)	-283.6(-0.3)	-282.3(1.0)	-280.9(2.4)	-282.2(1.1)
CF <sub>2</sub> Cl <sub>2</sub>	-491.6(8.0)	-495.3(-3.7)	-495.0(-3.4)	-498.3(-6.7)	-493.4(-1.8)	-492.3(-0.7)
CFCl <sub>3</sub>	-288.7(6.3)	-290.3(-1.6)	-290.2(-1.5)	-292.9(-4.2)	-289.8(-1.1)	-283.4(5.3)
rms	6.9	2.6	2.4	4.7	3.4	3.8
avg		-0.2	0.0	0.6	0.7	1.0

<sup>a</sup>  $\Delta_f H^\circ$  at 298.15 K in units of kJ/mol. <sup>b</sup> Values in parentheses represent reported experimental uncertainties. <sup>c</sup> Values in parentheses represent deviations from experiment.

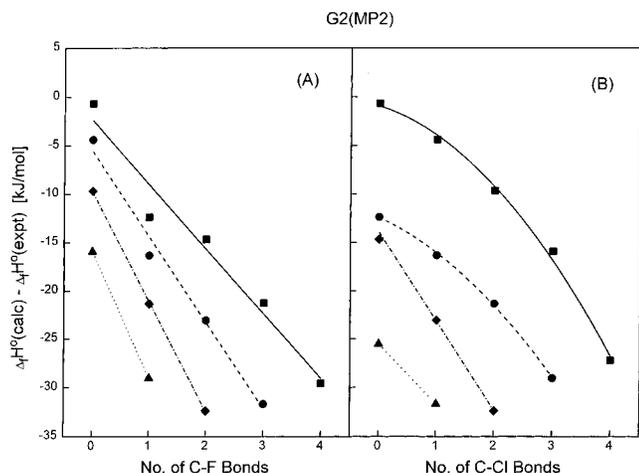
capacities, are used to derive, successively, the atomization energies ( $\sum D_0$ ) and the molecular enthalpies of formation at 0 K [ $\Delta_f H^\circ(0)$ ] and 298.15 K [ $\Delta_f H^\circ(298)$ ]. The formulas for these calculations are available elsewhere.<sup>5,18</sup>

## Results and Discussion

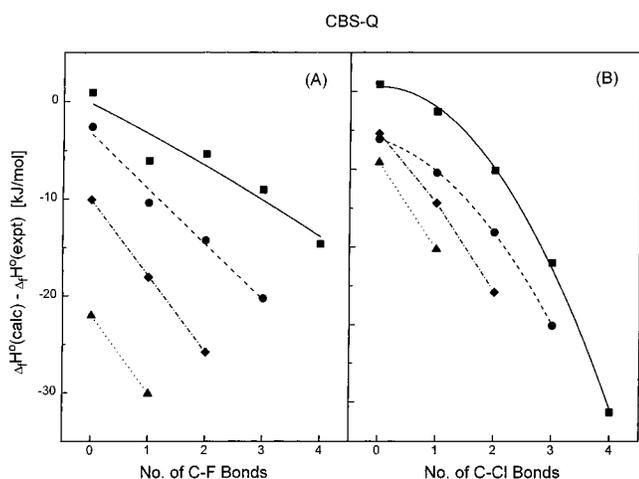
Displayed in Table 3 are the experimental and various calculated enthalpies of formation (at 298.15 K) for methane, the fluoromethanes, the chloromethanes, and the chlorofluoromethanes. The experimental enthalpies of all chlorinated species, with their reported error estimates in parentheses, were taken from the JANAF compilation,<sup>18,19</sup> as was the value for CH<sub>4</sub>. The experimental enthalpies of the fluoromethanes are

from the compilation by Kolesov.<sup>20</sup> The parenthetical values beside the calculated enthalpies represent the deviations from experimental values, [ $\Delta_f H^\circ(\text{calc}) - \Delta_f H^\circ(\text{expt})$ ].

One observes from Table 3A that enthalpies calculated by all four *ab initio* methods exhibit substantial deviations from the experimental values, with rms errors ranging from 15 to 22 kJ/mol (Table 3A). These deviations are systematic, with almost all calculated enthalpies lying lower than the reported experimental values, as evidenced by the large negative mean deviations that range from -13 to -19 kJ/mol. Furthermore, the negative deviations tend to rise with increasing halogen substitution. In our earlier investigation of the fluoromethanes,<sup>5</sup> it was found that the enthalpies determined with the computa-



**Figure 1.** (A) Deviations of  $\Delta_f H^\circ$ [G2(MP2)] from experiment as a function of the number of C–F bonds: (■) zero C–Cl bonds; (●) one C–Cl bond; (◆) two C–Cl bonds; (▲) three C–Cl bonds. (B) Deviations of  $\Delta_f H^\circ$ [G2(MP2)] from experimental values as a function of the number of C–Cl bonds: (■) zero C–F bonds; (●) one C–F bond; (◆) two C–F bonds; (▲) three C–F bonds.



**Figure 2.** (A) Deviations of  $\Delta_f H^\circ$ [CBS-Q] from experimental values as a function of the number of C–F bonds: (■) zero C–Cl bonds; (●) one C–Cl bond; (◆) two C–Cl bonds; (▲) three C–Cl bonds. (B) Deviations of  $\Delta_f H^\circ$ [CBS-Q] from experimental values as a function of the number of C–Cl bonds: (■) zero C–F bonds; (●) one C–F bond; (◆) two C–F bonds; (▲) three C–F bonds.

tionally inexpensive CBS-4 protocol were within the rms experimental error. It is seen here, however, that CBS-4 enthalpies of formation show rather large negative deviations in the CFC's, which increase with the degree of chlorine substitution.

To explore the distribution of errors in these series in greater detail, it is instructive to plot the deviation from the experimental values, [ $\Delta_f H^\circ(\text{calc}) - \Delta_f H^\circ(\text{expt})$ ], as a function of one type of carbon–halogen bond while holding the number of the other C–X bond types constant, e.g., a plot of error vs  $n_{\text{CF}}$  (number of CF bonds) in the series  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_2\text{FCl}$ ,  $\text{CHF}_2\text{Cl}$ ,  $\text{CF}_3\text{Cl}$ . The deviations as a function of  $n_{\text{CF}}$  for various fixed values of  $n_{\text{CCl}}$  are shown for the G2(MP2) and CBS-Q enthalpies in Figures 1A and 2A, respectively. The equivalent curves for the G2 and CBS-4 methods, which are not shown in the interest of brevity, display similar behavior. Shown in Figures 1A and 2A are the deviations as a function of  $n_{\text{CF}}$  for various fixed values of  $n_{\text{CCl}}$ . Regression analysis reveals that for each value of  $n_{\text{CCl}}$  the negative errors in the CFC's increase linearly with the number of C–F bonds;<sup>21</sup> the same behavior was observed in the earlier investigation of the fluoromethanes<sup>5</sup> [square

**TABLE 4: Bond Additivity Corrections<sup>a</sup>**

method	$\Delta_{\text{CF}}$	$\Delta_{\text{CCl}}$
G2	−6.51(0.41)	−2.80(0.41)
G2(MP2)	−7.98(0.38)	−6.54(0.38)
CBS-4	−1.28(0.74)	−10.62(0.74)
CBS-Q	−3.51(0.55)	−8.50(0.55)

<sup>a</sup> In units of kJ/bond.

symbols in Figures 1A and 2A]. Furthermore, it was found that the slopes of the straight lines becomes more negative with increasing  $n_{\text{CCl}}$ . In Figures 1B and 2B are plotted enthalpy deviations vs  $n_{\text{CCl}}$  for fixed  $n_{\text{CF}}$ . Here, it was found that the negative error increases with degree of chlorination. However, in these graphs, particularly for  $n_{\text{CF}} = 0, 1$  [G2(MP2) and G2] and  $n_{\text{CF}} = 0, 1, 2$  [CBS-Q and CBS-4], the curves exhibited negative curvature, as seen in the figures (and verified by standard deviations in the second-order regression coefficients).

From these results, one may conclude that the calculated errors are, indeed, systematic and dependent upon the number of C–F and C–Cl bonds in the molecule. The significance of the increasingly negative slopes in Figures 1A and 2A and of the negative curvature in Figures 1B and 2B will be discussed in the next section.

**Bond Additivity Corrections.** One approach to correct systematic errors in *ab initio* estimates of enthalpies of formation is to employ the concept of bond additivity corrections (BAC's), developed by Melius and co-workers<sup>15,16</sup> for MP4/6-31G(d,p) enthalpies. In this method, which is an extension of the use of isodesmic reactions,<sup>22,23</sup> it is assumed that the deviation of calculated enthalpies from experiment is a linear function of the number of each type of bond in the molecule, as indicated in eq 1:

$$\begin{aligned} \Delta_f H^\circ(\text{BAC}) &= \Delta_f H^\circ(\text{calc}) - \sum n_i \Delta_i \\ &= \Delta_f H^\circ(\text{calc}) - [n_{\text{CH}} \Delta_{\text{CH}} + n_{\text{CF}} \Delta_{\text{CF}} + \\ &\quad n_{\text{CCl}} \Delta_{\text{CCl}}] \quad (1) \end{aligned}$$

In the BAC-MP4 procedure,<sup>15,16</sup> the BAC parameters ( $\Delta_i$ ) are taken to be dependent upon bond length and nearest neighbors. The BAC-MP4 method has been used to calculate geometries and energies of about 100 stable and radical, C1 and C2 fluorinated hydrocarbons, including partially oxidized species. However, there is insufficient variation in the bond lengths in the CFC's (Table 1) to permit establishment of a bond length dependence from results on this series.<sup>24</sup> Consequently, in order to avoid overparametrization, we have chosen to utilize BAC's that are linearly independent, as represented by eq 1. This latter assumption is addressed further below.

We have utilized linear regression to fit eq 1 to the experimental data for the chlorine- and fluorine-substituted methanes (given in Table 3A) to obtain values for the linear BAC parameters  $\Delta_{\text{CF}}$  and  $\Delta_{\text{CCl}}$  (see Table 4) for all four *ab initio* methods. Corrected enthalpies of formation are given in Table 3B. The quantities in parentheses in Table 4 represent the standard errors in the parameters obtained from the regression analysis.<sup>25</sup> We employed the constraint  $\Delta_{\text{CH}} = 0$ , since regression analysis with unconstrained  $\Delta_{\text{CH}}$  had little impact on the standard errors (i.e.,  $\Delta_{\text{CH}} \lesssim \sigma$ ).

As seen in Table 3B, it is clear that the corrected enthalpies of formation are in extremely good agreement with experimental values. The residual rms deviations, which range from 2.4 to 4.7 kJ/mol, are almost an order of magnitude lower than errors in the uncorrected enthalpies (Table 3A), and, indeed, lie significantly below the rms experimental uncertainty of 6.9 kJ/mol.<sup>26</sup> The BAC's have also removed the systematic under-

prediction of the enthalpies of formation, as revealed by the small average errors in the corrected results. The last column in Table 3B contains the calculated BAC-MP4 enthalpies with their associated errors. The accuracy of these results is comparable to that obtained by applying BAC's to the other methods, with rms and average deviations of 3.8 and 1.0 kJ/mol, respectively. It is of further interest to note that the parameters utilized in the BAC-MP4 method were developed to yield accurate enthalpies in a wide range of compounds and were not optimized to match experimental values in this particular series of molecules.

The numerical values of the BAC parameters in Table 4 represent the magnitude of the systematic error due to each of the three types of bonds in the CFC's. As indicated above, the standard errors were essentially unaffected by whether or not  $\Delta_{\text{CH}}$  was constrained to zero. This is not surprising, since earlier computational studies<sup>10,11,27</sup> using the G2 and G2(MP2) methods have shown no inherent systematic errors in calculated atomization energies or enthalpies of formation in hydrocarbons or other C-H bond-containing compounds. The present work indicates that the same result is true for the CBS-4 and CBS-Q methods. Regression analysis using subsets of the C<sub>1</sub> CFC's also had little impact on the parameters, that is, the changes in  $\Delta_{\text{CF}}$  and  $\Delta_{\text{CCl}}$  are comparable in magnitude to  $\sigma(\Delta_{\text{CF}})$  and  $\sigma(\Delta_{\text{CCl}})$ , respectively, using only the fluoromethanes, the chloromethanes, or the three reference compounds (CH<sub>4</sub>, CF<sub>4</sub>, CCl<sub>4</sub>).

From Table 4, one observes that the systematic error (as represented by the magnitude of the BAC) for C-Cl bonds using the G2 method is substantially lower than for C-F bonds ( $|\Delta_{\text{CCl}}| < 1/2|\Delta_{\text{CF}}|$ ). By use of G2(MP2), the systematic error for C-Cl bonds is also somewhat smaller than for C-F bonds. In contrast, both CBS procedures exhibit far greater errors for C-Cl than for C-F bonds ( $|\Delta_{\text{CCl}}| \gg |\Delta_{\text{CF}}|$ ).

As noted previously,<sup>5</sup> the bond additivity correction may represent in part the spin-orbit coupling error in the atomic halogen energies used to compute the atomization energy. If this were true, such errors would be expected to propagate in the atomization energies of chlorine-containing species in the "G2/CBS test set"<sup>10</sup> such as HCl, CH<sub>3</sub>Cl, and Cl<sub>2</sub>. Indeed, the CBS-Q method leads to atomization energy deviations [ $\sum D^\circ(\text{calc}) - \sum D^\circ(\text{expt})$ ] that increase from 4.2 kJ/mol in HCl to 7.1 kJ/mol in Cl<sub>2</sub>. These deviations can be attributed to spin-orbit coupling, since the experimental coupling correction<sup>18</sup> is known to be 3.5 kJ/mol for chlorine. By also utilizing the experimental coupling correction of 0.4 kJ/mol for carbon, one could rationalize the deviation of 5.0 kJ/mol for CH<sub>3</sub>Cl. However, such a trend is not followed in the G2(MP2) and G2 methods, since the atomization energy deviations for Cl<sub>2</sub> are actually lower than those of HCl in these methods. Similarly, we were unable to ascribe the deviations in the computed CBS-Q G2(MP2), and G2 atomization energies for fluorinated species (HF and F<sub>2</sub>) to the spin-orbit coupling effect.<sup>5</sup>

It was noted in the previous section that [ $\Delta_f H^\circ(\text{calc}) - \Delta_f H^\circ(\text{expt})$ ] is a linear function of  $n_{\text{CF}}$ , with a slope that becomes increasingly negative for higher values of  $n_{\text{CCl}}$  [Figures 1A and 2A], whereas plots of the deviation vs  $n_{\text{CCl}}$  exhibit negative curvature in some cases [Figures 1B and 2B]. The negative curvature suggests strongly that the presence of a C-Cl bond increases the negative error resulting from the addition of subsequent C-Cl bonds in the molecule. Similarly, the increasingly negative slopes of the plots of deviation vs  $n_{\text{CF}}$  implies that a C-Cl bond also increases the error due to C-F bonds in the molecule.

Hence, contrary to the assumption above (eq 1) that the errors due to each C-F and C-Cl bond are independent, there is

indeed evidence that the bonds interact. It is of interest to note that the effect of one heavy atom bond is to **increase** the negative error associated with the second bond, which is opposite to the interaction observed in the BAC-MP4 method,<sup>15,16</sup> where the net correction due to multiple heavy atom bonds is less than the sum of the independent corrections.

It would be straightforward to modify our BAC procedure to account for the adjacent bond interactions through the introduction of two additional parameters,  $f_j = f_{\text{Cl}}$ ,  $f_{\text{F}}$ , and modification of eq 1 to

$$\Delta_f H^\circ(\text{BAC}) = \Delta_f H^\circ(\text{calc}) - \sum_i [n_i \Delta_i \prod f_j] \quad (2)$$

where  $\prod f_j$  is the product over adjacent heavy atom bonds, e.g., the C-F bond correction in CHFCl<sub>2</sub> would be  $\Delta_{\text{CF}f_{\text{Cl}}^2}$ . However, as noted above, we believe that the introduction of two additional BAC interaction parameters is probably not warranted for this somewhat limited data set. It must be remembered that even with the assumption of strictly additive BAC's with no interactions (eq 1), the rms errors in corrected enthalpies of formation (Table 3B) are significantly less than the rms experimental uncertainties.

As further data are acquired for a larger set of compounds (fluorochloroethanes and the various C<sub>1</sub> and C<sub>2</sub> radical species), the efficacy of the introduction of interaction parameters to the BAC equation will be further explored.

## Summary and Conclusions

The application of *ab initio* MO methods to the determination of thermochemical properties in halocarbons have been extended to G2, G2(MP2), CBS-4, CBS-Q, and BAC-MP4 calculations of enthalpies of formation of the chlorofluoromethanes. Calculated values of  $\Delta_f H^\circ$  using the four *ab initio* methods exhibit comparatively large systematic negative errors from the experimental values, up to -50 kJ/mol, which are directly dependent upon the number of C-F and C-Cl bonds in the molecule.

The application of bond additivity corrections (BAC's) to remove the systematic errors yields corrected enthalpies that are in extremely close agreement with experimental values, with rms deviations that range from 2.4 kJ/mol [G2(MP2)] to 4.7 kJ/mol [CBS-4], which is well below the rms experimental uncertainty of 6.9 kJ/mol. The BAC-MP4 method (which has already been parametrized to remove systematic bond errors) yields comparably good agreement with experimental enthalpies. On the basis of these results, it is concluded that any of these five calculational procedures, together with bond additivity corrections to remove systematic error, may profitably be used to obtain very accurate enthalpies of formation in chlorofluorocarbon species.

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