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Thermodynamic Properties $\Delta H_f{}^\circ{}_{298}$, $S^\circ{}_{298}$, and $C_p(T)$ for 2-Fluoro-2-Methylpropane, $\Delta H_f{}^\circ{}_{298}$ of Fluorinated Ethanes, and Group Additivity for Fluoroalkanes

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G2(MP2) composite calculations are performed to obtain thermodynamic properties ($\Delta H_f{}^\circ{}_{298}$, $S^\circ{}_{298}$ and $C_p(T)$'s of 2-fluoro-2-methylpropane. $\Delta H_f{}^\circ{}_{298}$ is calculated from the G2(MP2) calculated enthalpy of reaction ($\Delta H_{rxn}{}^\circ{}_{298}$) and use of isodesmic reactions. Standard entropy ($S^\circ{}_{298}$ in cal/(mol·K)) and heat capacities ($C_p(T)$'s in cal/(mol·K)) are calculated using the rigid-rotor−harmonic-oscillator approximation with direct integration over energy levels of the intramolecular rotation potential energy curve. These thermodynamic properties are used to estimate data for the C/C3/F group. Enthalpies of formation ($\Delta H_f{}^\circ{}_{298}$ in kcal/mol) for 1,2-difluoroethane (−102.7), 1,1,2-trifluoroethane (−156.9), 1,1,2,2- and 1,1,1,2-tetrafluoroethane (209.6 and 213.3), and pentafluoroethane (−264.1), are calculated using total energies obtained from G2(MP2) composite ab initio methods. Isodesmic reactions with existing literature values of $\Delta H_f{}^\circ{}_{298}$ for ethane, 1-fluoroethane, 1,1-difluoroethane and 1,1,1-trifluoroethane are used. Fluorine/fluorine interaction terms, F/F, 2F/F, 3F/F, 2F/2F, and 3F/2F, where "/" indicates interaction for alkane compounds, for $\Delta H_f{}^\circ{}_{298}$ are reevaluated based on $\Delta H_f{}^\circ{}_{298}$ of the above five fluoroethanes. Thermodynamic properties ($\Delta H_f{}^\circ{}_{298}$, $S^\circ{}_{298}$ and $C_p(T)$'s ($300 \leq T/\mathrm{K} \leq 1500$)) for fluorinated carbon groups, C/C3/F, C/C2/F/H, C/C2/F2, are calculated using data from ab initio methods and existing literature data. Fluorine−methyl (alkyl) group additivity corrections for gauche interactions are also evaluated.

Introduction

Chlorofluorocarbons (CFCs) are being replaced by hydrofluorocarbons (HFCs) and hydrochlorofluorocarbons (HCFCs) because of their non or less adverse effects on the stratospheric ozone layer. Examples include HFC-134a (CH_2FCF_3), a replacement for CFC-12 (CF_2Cl_2) in domestic refrigeration and automobile air conditioning units,[1] HFC-227ea (CF_3CFHCF_3), a replacement for Halon 1301 (CF3Br) fire suppressant,[2,3] and CFC114 (CF_2ClCF_2Cl), a refrigerant.[3]

Thermodynamic properties ($\Delta H_f{}^\circ{}_{298}$, $S^\circ{}_{298}$, and $C_p(T)$'s) of these hydrofluorocarbons are important for evaluation of their suitability in these large-scale engineering applications and are also needed for analysis of their reaction pathways in the atmospheric and combustion environments—their ultimate environmental suitability. There are limited experimental studies in the literature on the thermodynamic properties of these HFCs. The limited data are probably due to a number of reasons: the stability and inertness of the HFCs and thus lack of concern for their effects on the environment, recent needs for species with improved atmospheric acceptability and thus limited availability, and their commercial value and hence possible proprietary considerations.

One method that has recently been applied to estimation of thermodynamic properties is the use of ab initio or density functional calculations. These methods are proving quite valuable for small molecules, up to nine or so heavy atoms, but accurate calculation techniques are much more expensive for larger molecules. The group additivity method[4] is an easy, inexpensive, and accurate calculation technique to estimate the thermodynamic properties for larger molecules, and it has been extensively employed for hydrocarbons and oxygenated hydrocarbons.[5] Group additivity is not as acceptable for fluorocarbons, where average errors on fluoroethanes are several kcal/mol with maximum errors in excess of 10 kcal/mol. One objective of our research is to modify and improve the application of halocarbon group additivity for use in understanding and modeling atmospheric and combustion chemistry of these molecules. We have determined that the errors are dramatically reduced by using a modified group additivity which uses redefined group values relative to those derived by Benson and incorporates interaction terms. These terms provide a correction for the interaction between halogens, fluorines in this case, which are on adjacent carbons. This modified group additivity was recently shown to work well for chlorocarbons.[6] Group additivity serves as a reasonable method for estimation of molecules with higher carbon or fluorine number where ab initio calculation methods, which properly account for long-range correlation effects, are not currently available.[7]

In this study G2(MP2) composite calculations[8] are performed and data are analyzed with isodesmic reactions to obtain thermodynamic properties of 2-fluoro-2-methylpropane: $\Delta H_f{}^\circ{}_{298,}$ entropy ($S^\circ{}_{298}$), and heat capacities ($C_p(T)$). $\Delta H_f{}^\circ{}_{298}$ for fluoroethanes 1,2-difluoroethane, 1,1,2-trifluoroethane, 1,1,2,2-tetrafluoroethane, 1,1,1,2-tetrafluoroethane, and pentafluoroethane are also evaluated using G2(MP2) calculations and isodesmic reactions. A combination of our previous work on thermodynamic properties of fluoroethanes and fluoropropanes, plus the improved $\Delta H_f{}^\circ{}_{298}$ values of fluoroethanes and 2-methyl-2-fluoropropane of this study, allow determination of accurate group additivity and interaction terms for primary, secondary, and tertiary fluoroalkanes.

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Calculation Method

1. ab initio Calculations: 2-Fluoro-2-methylpropane. The G2(MP2) composite calculation method is performed on 2-fluoro-2-methylpropane, 2-fluoropropane and a number of fluoroethanes to estimate thermodynamic properties ($\Delta H_f°_{298}$, $S°_{298}$, and $C_p(T)$'s ($300 \leq T/\mathrm{K} \leq 1500$)). All ab initio calculations are performed using the Gaussian94[9] system of programs. Thermodynamic properties for 1-fluoropropane, which were estimated in a previous study,[10] and those of fluoroethane and 2-fluoropropane are used to evaluate the accuracy of thermodynamic properties of 2-fluoro-2-methylpropane.

Enthalpy of Formation ($\Delta H_f°_{298}$) Calculations. $\Delta H_f°_{298}$'s are estimated using G2(MP2) calculations and the following isodesmic reactions.

for 1-fluoropropane

$$\mathit{CH_2FCH_2CH_3} + \mathrm{CH_3CH_3} \rightarrow \mathrm{CH_3CH_2CH_3} + \mathrm{CFH_2CH_3} \tag{1}$$

for fluoroethane

$$\mathit{CH_2FCH_3} + \mathrm{CH_4} \rightarrow \mathrm{CH_3CH_3} + \mathrm{CH_3F} \tag{2}$$

for 2-fluoropropane

$$\mathit{CH_3CFHCH_3} + \mathrm{CH_3CH_3} \rightarrow \mathrm{CH_3CH_2CH_3} + \mathrm{CFH_2CH_3} \tag{3}$$

for 2-fluoro-2-methylpropane

$$\mathit{(CH_3)_3CF} + \mathrm{CH_3CH_2CH_3} \rightarrow \mathrm{(CH_3)_3CH} + \mathrm{CH_3CFHCH_3} \tag{4}$$

The principle of isodesmic reaction is explained in previous studies.[10−13] The basic requirement of the isodesmic reaction is bond conservation, where the number of each bond type is conserved in the reaction.[12] An isodesmic reaction will lead to more accurate results if groups are also conserved in the reaction, because next nearest neighbor interactions are then conserved. Reaction 1 conserves both bonds and groups, while reactions 2−4 conserve only bond types.

G2(MP2) calculations are performed with zero point vibration energy (ZPVE) and thermal corrections determined for each of the four compounds in reaction 1; $\Delta H_{\mathrm{rxn}}°_{298}$ is then calculated. Enthalpies of formation are taken from the literature for CH_3-CH_3, $CH_3CH_2CH_3$, and CFH_2CH_3, and $\Delta H_f°_{298}$ of CFH_2CH_2-CH_3 is then calculated from the $\Delta H_{\mathrm{rxn}}°_{298}$. $\Delta H_f°_{298}$ values for fluoroethane, 2-fluoropropane, and 2-fluoro-2-methylpropane are calculated in the same manner. These values for fluoroethane and 2-fluoropropane are used to further evaluate $\Delta H_f°_{298}$ of 2-fluoro-2-methylpropane.

Rotational Barriers. Barriers for internal rotations are calculated as the difference between the total energy of each conformation calculated by MP2(full)/6-31G(d) with the scaled ZPVE calculated by HF/6-31G(d).

Standard Entropy ($S°_{298}$) and Heat Capacity ($C_p(T)$'s, $300 \leq T/K \leq 1500$), Calculations. Harmonic vibrational frequencies calculated at the HF6-31G(d) level of theory, and moments of inertia on molecular structures optimized at MP2(full)/6-31G(d) are used in calculation of the vibration frequency contribution to $S°_{298}$ and $C_p(T)$'s. Frequencies are scaled by 0.89 for ZPVE and thermal energies.

A technique for the calculation of thermodynamic functions from hindered rotations with arbitrary potentials has been described previously.[10,12−14] The potential curves of rotational barrier vs dihedral angle are fit by a truncated Fourier series:

$$V(\phi) = a_0 + a_1 \cos(\phi) + a_2 \cos(2\phi) + a_3 \cos(3\phi) \tag{5}$$

where values of the coefficients a_i are calculated to provide the minimum and maxima of the torsional potentials with allowance for a shift of the theoretical extrema angular positions.

2. Ab Initio Calculations for Enthalpies of Formations ($\Delta H_f°_{298}$) Estimation of Five Fluorinated Ethanes. $\Delta H_f°_{298}$'s of 1,2-difluoroethane, 1,1,2-trifluoroethane, 1,1,2,2-tetrafluoroethane, 1,1,1,2-tetrafluoroethane, and pentafluoroethane are calculated using the G2(MP2) composite calculation method and the following isodesmic reactions. Literature values for ethane,1-fluoroethane, 1,1-difluoroethane, and 1,1,1-trifluoroethane are then used to determine the $\Delta H_f°_{298}$'s for these five compounds as described above for 2-fluoro-2-methylpropane. This new enthalpy data is used to estimate (revise) the $\Delta H_f°_{298}$'s for fluorine−fluorine interaction terms, F/F 2F/F, 2F/2F, 3F/F, and 3F/2F.[13]

for 1,2-difluoroethane

$$\mathit{CH_2FCH_2F} + \mathrm{C_2H_6} \rightarrow \mathrm{CH_2FCH_3} + \mathrm{CH_2FCH_3} \tag{6}$$

for 1,1,2-trifluoroethane

$$\mathit{CHF_2CH_2F} + \mathrm{C_2H_6} \rightarrow \mathrm{CHF_2CH_3} + \mathrm{CH_2FCH_3} \tag{7}$$

for 1,1,2,2-tetrafluoroethane

$$\mathit{CHF_2CHF_2} + \mathrm{C_2H_6} \rightarrow \mathrm{CHF_2CH_3} + \mathrm{CHF_2CH_3} \tag{8}$$

for 1,1,1,2-tetrafluoroethane

$$\mathit{CF_3CH_2F} + \mathrm{C_2H_6} \rightarrow \mathrm{CF_3CH_3} + \mathrm{CH_2FCH_3} \tag{9}$$

for 1,1,1,2,2-pentafluoroethane

$$\mathit{CF_3CHF_2} + \mathrm{C_2H_6} \rightarrow \mathrm{CF_3CH_3} + \mathrm{CHF_2CH_3} \tag{10}$$

3. Estimation of Groups and F−F Interactions. Groups and F−F interaction terms (corrections) for fluoroethanes are described in a previous study.[13] Thermodynamic properties of 2-fluoro-2-methylpropane, 2-fluoropropane, and 2,2-difluoropropane are chosen for derivation of the group values C/C3/F, C/C2/F/H, and C/C2/F2, respectively. Only hydrogen atoms are on the primary methyl carbons adjacent to carbon bonded to fluorine(s). This selection of the initial group values is revised from that of Benson, to provide an improved group additivity scheme for accurate property estimation.

$\Delta H_f°_{298}$ and $C_p(T)$ values for the C/C2/F/H group are calculated based on

$$(\mathrm{CH_3CFHCH_3}) = (\mathrm{C/C/H3}) \times 2 + (\mathrm{C/C2/F/H}) \tag{11}$$

$S°_{298}$ of C/C2/F/H is calculated based on

$$(\mathrm{CH_3CFHCH_3}) = (\mathrm{C/C/H3}) \times 2 + (\mathrm{C/C2/F/H}) - R\ln(\sigma) \tag{12}$$

where $R = 1.987$ cal/(mol·K), and σ is symmetry number; $\sigma = 9$ for CH_3CHFCH_3. Group values of C/C3/F and C/C2/F2 are estimated in a similar manner.

Thermodynamic properties of fluoropropanes and higher carbon number fluoroalkanes with no fluorine on the carbon atoms adjacent to a carbon bonded to fluorine(s) are now accurately predicted. F/F interaction terms described previously need to be included for fluoroalkanes where there are fluorine atoms on an adjacent carbon.

4. Fluoro−Methyl Gauche Interactions. Fluoro−methyl gauche interaction contributions to the thermodynamic parameters are estimated using data on eight fluoropropanes, 1-fluoropropane, 1,1- and 1,2-difluoropropane, 1,1,1- and 1,1,2-trifluoropropane, 1,1,1,2- and 1,1,2,2-tetrafluoropropane, and

TABLE 1: Vibrational Frequencies[a] (ν, cm^{-1})

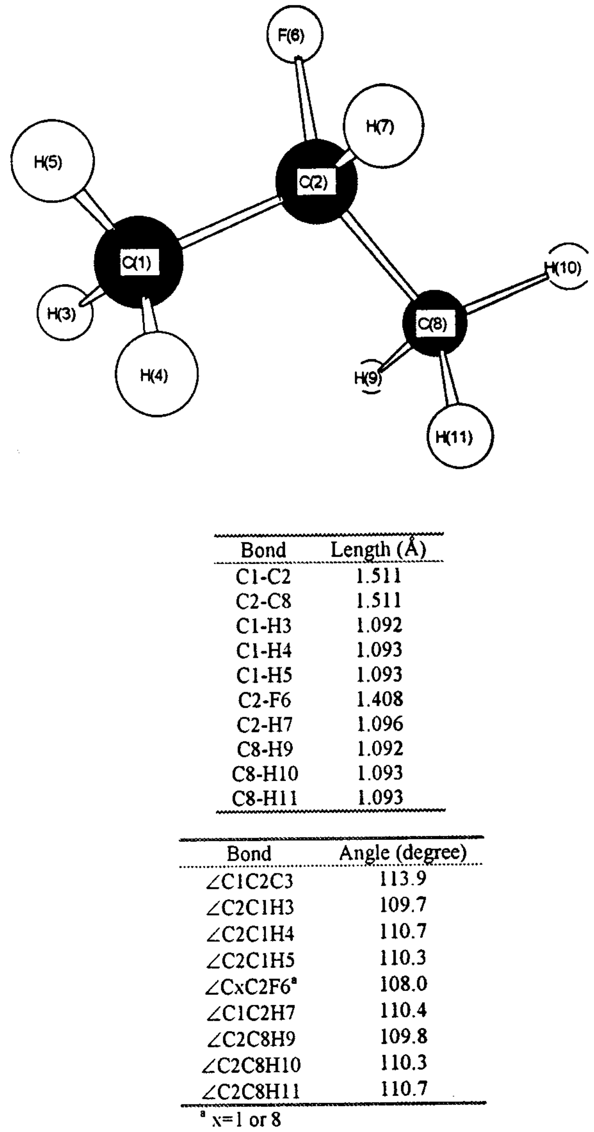
	species	
	CH_3CFHCH_3	$(CH_3)_3CF$
ν_1	233*[b]	212*[b]
ν_2	276*[b]	273*[b]
ν_3	375	273*[b]
ν_4	438	357
ν_5	512	358
ν_6	886	431
ν_7	1015	492
ν_8	1027	492
ν_9	1059	801
ν_{10}	1256	1006
ν_{11}	1279	1006
ν_{12}	1312	1016
ν_{13}	1516	1053
ν_{14}	1523	1147
ν_{15}	1572	1147
ν_{16}	1575	1370
ν_{17}	1626	1402
ν_{18}	1631	1402
ν_{19}	1635	1563
ν_{20}	1655	1563
ν_{21}	3210	1582
ν_{22}	3215	1616
ν_{23}	3241	1630
ν_{24}	3275	1630
ν_{25}	3285	1642
ν_{26}	3286	1642
ν_{27}	3292	1665
ν_{28}		3211
ν_{29}		3211
ν_{30}		3221
ν_{31}		3278
ν_{32}		3278
ν_{33}		3282
ν_{34}		3289
ν_{35}		3289
ν_{36}		3290

[a] Nonscaled. Frequencies are calculated at the HF/6-31G(d) level of theory. [b] Torsional Frequencies. These frequencies are not included in the calculation of entropies $S°_{298}$'s and heat capacities $C_p(T)$'s. Instead, an exact contribution from hindered rotations about the C−C is included. See text.

1,1,1,2,2-pentafluoropropane reported in ref 10. Contributions to the respective thermodynamic parameter are determined, on a per F−CH_3 gauche interaction basis, for each molecule, and an overall average F−CH_3 value is derived for each. Calculation of the gauche interaction for 1-fluoropropane is explained below.

Group additivity is applied first to estimate thermodynamic parameters for fluoropropane using previously estimated fluorocarbon groups and F−F interactions where appropriate; there is no F−F interaction for 1-fluoropropane. The group additivity determined thermodynamic properties are subtracted from the thermodynamic properties ($\Delta H_f°_{298}$, $S°_{298}$, and $C_p(T)$'s, $300 \le T/\mathrm{K} \le 1500$) of 1-fluoropropane. The difference in each thermodynamic property is divided by the number of gauche interactions, 1 for 1-fluoropropane.

The counting scheme for F−CH_3 gauche interactions is different from that used for hydrocarbons. The rotational barrier calculations for fluoropropanes indicate that the F−CH_3 gauche conformation has lower energy than anti-gauche conformation.[10] Gauche interactions have a stabilizing or energy lowering effect in enthalpies of formation. The number of F−CH_3 gauche interactions is therefore the maximum for each hydrofluorocarbon. Gauche interaction terms for eight fluorinated propanes are estimated and the corresponding average thermodynamic property terms are determined.



Bond	Length (Å)
C1-C2	1.511
C2-C8	1.511
C1-H3	1.092
C1-H4	1.093
C1-H5	1.093
C2-F6	1.408
C2-H7	1.096
C8-H9	1.092
C8-H10	1.093
C8-H11	1.093

Bond	Angle (degree)
∠C1C2C3	113.9
∠C2C1H3	109.7
∠C2C1H4	110.7
∠C2C1H5	110.3
∠CxC2F6[a]	108.0
∠C1C2H7	110.4
∠C2C8H9	109.8
∠C2C8H10	110.3
∠C2C8H11	110.7

[a] x=1 or 8

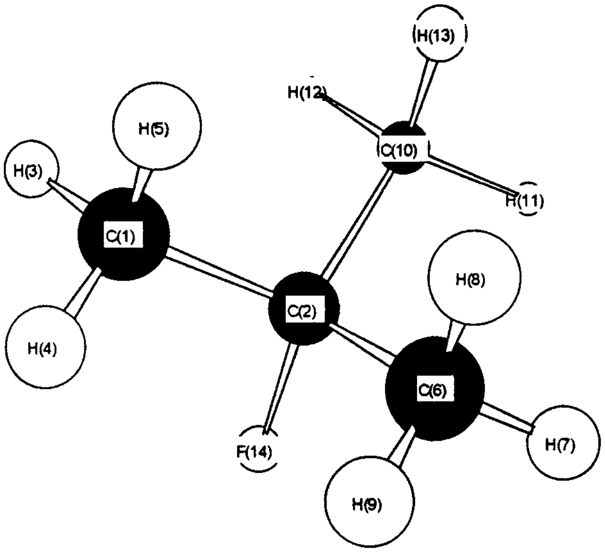
Figure 1. MP2(full)/6-31G(d) determined geometry of 2-fluoropropane (CH_3CFHCH_3), rotational constants = 8.731, 8.126, and 4.814 GHz.

Results and Discussion

1. Ab Initio Calculation Results for 2-fluoro-2-methylpropane. *Geometry and Frequencies.*

Table 1 lists the HF/6-31G(d) determined frequencies of 2-fluoropropane and 2-fluoro-2-methylpropane. Asterisks indicate torsional frequencies whose contributions to $S°_{298}$ and $C_p(T)$ are determined by an internal rotor analysis described above. Figures 1 and 2 illustrate MP2(full)/6-31G(d) determined geometries of 2-fluoropropane and 2-fluoro-2-methylpropane. The methyl groups are symmetric to the H7−C2−F6 plane in 2-fluoropropane and relative to the C2−F14 bond axis in 2-fluoro-2-methylpropane. The C−C and C−F bond lengths increase 0.05 and 0.01 Å respectively when hydrogen bonded to C2 in Figure 1 is replaced by a methyl group.

Enthalpy of Formation ($\Delta H_f°_{298}$). G2(MP2) determined total energies calculated in this study are listed in Table 2, and $\Delta H_f°_{298}$ data from the literature, for use in isodesmic reaction analysis, is tabulated in Table 3. $\Delta H_f°_{298}$ for fluoroethane, 1-fluoropropane, and 2-fluoropropane are calculated to evaluate systematic error in our estimation of $\Delta H_f°_{298}$ for 2-fluoro-2-methylpropane.



Bond	Length (Å)
C2-C_a	1.516
C1-H_x	1.093
C6-H_y	1.093
C10-H_z	1.093
C2-F14	1.418

a = 1,6 or 10
x = 3, 4 or 5
y = 7, 8 or 9
z = 11, 12 or 13

Bond	Angle (degree)
$\angle C_xC2C_y$	112.4
$\angle C_zC2F14$	106.4
∠C2C1H3	110.0
∠C2C1H4	110.0
∠C2C1H5	110.8
∠C2C6H7	110.0
∠C2C6H8	110.8
∠C2C6H9	110.0
∠C2C10H11	110.0
∠C2C10H12	110.0
∠C2C10H13	110.8

x, y, z = 1, 6 or 10

Figure 2. MP2(full)/6-31G(d) determined geometry of 2-fluoro-2-methylpropane ($(CH_3)_3CF$), rotational constants = 4.734, 4.734, and 4.544 GHz.

$\Delta H_{rxn}°_{298}$ for reaction 3 is calculated using G2(MP2) determined total energies as

$$CH_3CH_2CH_3 + CFH_2CH_3 - (CH_3CHFCH_3 + CH_3CH_3) = 5.07\ \text{kcal/mol}$$

$\Delta H_f°_{298}$ of 2-fluoropropane is calculated using the known $\Delta H_f°_{298}$'s for ethane, propane, and fluoroethane, with the calculated $\Delta H_{rxn}°_{298}$. This analysis yields $\Delta H_f°_{298} = -72.55$ kcal/mol as shown in Table 4, and underestimates $\Delta H_f°_{298}$ by 2.40 and 3.55 kcal/mol compared with Frenkel et al. and Stull et al., respectively.[15,16] $\Delta H_f°_{298}$'s of fluoroethane and 2-fluoro-2-methylpropane are calculated in the same manner and listed in Table 4.

The isodesmic reaction to calculate $\Delta H_f°_{298}$ for 1-fluoropropane conserves both bonds and groups in reaction 1. Comparison of the calculation results with two literature evaluations shows differences of +0.37 and −0.26 kcal/mol relative to Frenkel et al. and Stull et al., respectively.[15,16] The groups used in reaction 1 include three C/C/H3's, C/C/F/H2, and C/C2/H2; groups are conserved for both reactants and products.

TABLE 2: G2(MP2) Total Energy Calculation Results

species	total energy[a]
CH_4	−40.405 849
CH_3F	−139.544 604
CH_3CH_3	−79.624 450
CFH_2CH_3	−178.775 281
CF_2HCH_3	−277.942 239
CF_3CH_3	−377.116 202
CH_2FCH_2F	−277.921 576
CHF_2CH_2F	−377.084 329
CHF_2CHF_2	−476.244 755
CF_3CH_2F	−476.254 995
CF_3CHF_2	−575.412 385
$CH_3CH_2CH_3$	−118.847 504
$CH_2FCH_2CH_3$	−217.998 301
CH_3CFHCH_3	−218.006 412
$(CH_3)_3CH$	−158.074 011
$(CH_3)_3CF$	−257.238 481

[a] ZPVE's and thermal corrections to 298 K are included. Units in hartrees. This study

TABLE 3: Literature $\Delta H_f°_{298}$ for Use in Isodesmic Reactions

compound	$H_f°_{298}$ (kcal/mol)
CH_4	−17.86[a]
CH_3F	−56.81[b]
CH_3CH_3	−20.24[a]
CFH_2CH_3	−62.90[c]
CF_2HCH_3	−119.70[c]
CF_3CH_3	−178.20[c]
$CH_3CH_2CH_3$	−24.82[a]
$CH_2FCH_2CH_3$	−67.20[a]
	−67.83[d]
CH_3CFHCH_3	−69.00[a]
	−70.15[d]
$(CH_3)_3CH$	−32.27[d]

[a] Reference 16. [b] Reference 21. [c] Reference 17. [d] Reference 15.

TABLE 4: $\Delta H_f°_{298}$ Calculation Results Using Isodesmic Reactions 1−4 and Comparison with Literature[a]

compound	calcd $\Delta H_f°_{298}$	lit. value	diff[e]
$CH_2FCH_2CH_3$	−67.46	−67.83[b]	0.37
		−67.20[c]	−0.26
CH_2FCH_3	−65.61	−62.90[d]	−2.71
		−62.50[c]	−3.11
CH_3CHFCH_3	−72.55	−70.15[b]	−2.40
		−69.00[c]	−3.55
$C(CH_3)_3F$	−81.09		

[a] Unit in kcal/mol. [b] Reference 15. [c] Reference 16. [d] Reference 17. [e] (This study) − (literature value).

Reaction 2 for fluoroethane conserves only bond types, and the calculation underestimates $\Delta H_f°_{298}$ for this compound by 2.71 and 3.11 kcal/mol when compared to Stull et al.[16] and Chen et al.[17] Groups for reactants in eq 2 are C/C/H3 and C/C/F/H2 and methane, CH_4; groups in the products are two C/C/H3's and fluoromethane, CH_3F. The unbalanced groups are C/C/F/H2 and CH_4 in reactants, and C/C/H3 and CH_3F in products.

Similarly reaction 3 for 2-fluoropropane conserves only bond types and the calculation results underestimate $\Delta H_f°_{298}$ for this compound by −2.40 and −3.55 kcal/mol in comparison with Frenkel et al.[15] and Stull et al.,[16] respectively. Groups for reactants in eq 3 are four C/C/H3's and C/C2/F/H; groups used in products are three C/C/H3's, C/C/F/H2, and C/C2/H2. The unbalanced groups are C/C/H3 and C/C2/F/H in reactants, and C/C/F/H2 and C/C2/H2 in products.

TABLE 5: Relative Barrier Heights for Internal Rotors and ZPVE

compound & rotor[a]	MP2/6-31G(d) (in hartrees)	ZPVE HF/6-31G(d) (no scale) (hartrees)	total energy[b] (hartrees)	rotational barrier height (kcal/mol)
$CH_3-CFHCH_3$ S	−217.682 706 1	0.102 981 0	−217.591 2274	
$CH_3-CFHCH_3$ E	−217.676 731 6	0.102 677 2	−217.585 051 1	3.876[c]
$CH_3-CFHCH_3$ E′	−217.676 731 6	0.102 677 2	−217.58 5051 1	3.932[d]
$CH_3-C(CH_3)_2F$ S	−256.856 998 0	0.132 414 0	−256.739 196 0	
$CH_3-C(CH_3)_2F$ E	−256.850 885 6	0.132 150 0	−256.732 888 9	3.958[c]
$CH_3-C(CH_3)_2F$ E′	−256.850 885 6	0.132 150 0	−256.732 888 9	4.037[e]

[a] S at the end of species stands for “staggered”, E stands for “eclipsed”. [b] Total energies are calculated as the difference in MP2/6-31G(d) determined total energies plus scaled ZPVE, unit in hartrees. [c] The corresponding torsional frequency, ν_1, is excluded. [d] The corresponding torsional frequency, ν_2, is excluded. [e] The corresponding torsional frequency, ν_2 or ν_3, is excluded.

TABLE 6: Ideal Gas Phase Thermodynamic Properties Obtained by G2(MP2) Calculation[a] and Their Literature Value

species and symmetry no.		$H_f°_{298}$[b]	$S°_{298}$[c]	$C_{p\ 300}$[c]	$C_{4\ p00}$	$C_{p\ 500}$	$C_{p\ 600}$	$C_{p\ 800}$	$C_{p\ 1000}$	$C_{p\ 1500}$
CH_3CFHCH_3 (9)	TVR[d]		62.16[e]	16.09	20.91	25.47	29.47	35.89	40.65	47.92
	internal rotor 1[f]		4.05	2.05	2.20	2.19	2.10	1.86	1.65	1.35
	internal rotor 2[f]		4.03	2.04	2.20	2.19	2.11	1.87	1.66	1.35
	total	−72.55	70.24	20.18	25.31	29.85	33.68	39.61	43.96	50.61
	Frenkel et al.[g]	−70.15	70.03	20.00	25.19	29.71	33.51	39.39	43.81	*j*
	Stull et al.[h]	−69.00	69.82	19.68	24.72	29.27	33.14	39.14	43.55	*j*
$(CH_3)_3CF$ (81)	TVR		62.26[e]	20.43	26.27	32.50	37.65	45.79	51.84	61.10
	internal rotor 1[i]		4.04	2.04	2.20	2.20	2.11	1.88	1.67	1.36
	internal rotor 2[i]		4.01	2.03	2.20	2.20	2.13	1.90	1.69	1.37
	internal rotor 3[i]		4.01	2.03	2.20	2.20	2.13	1.90	1.69	1.37
	total	−78.2	74.32	26.53	32.87	39.10	44.02	51.47	56.89	65.20
	Frenkel et al.[g]	*j*	74.50	26.24	32.83	38.85	43.37	*j*	*j*	*j*
$CH_3CF_2CH_3$ (18)	Frenkel et al.[g]	−124.88	72.38	22.87	28.22	32.52	36.34	41.76	45.64	51.42

[a] Thermodynamic properties are referred to a standard state of an ideal gas of pure enantiomer at 1 atm. Torsional frequencies are excluded in the calculations of entropies and heat capacities. Instead, an exact contribution from hindered rotations about the C−C is included. See text. [b] Units in kcal/mol. [c] Units in cal/(mol·K). [d] Sum of contributions from translations, vibrations, and external rotations. [e] Symmetry number is taken into account (−*R* ln(number of symmetry)). [f] Contribution from internal rotation $CH_3-CFHCH_3$. [g] Reference 15. [h] Reference 16. [i] Contribution from internal rotation $CH_3-C(CH_3)_2F$. [j] Indicates no available data.

TABLE 7: Evaluated Enthalpies of Formations ($\Delta H_f°_{298}$) for Fluorinated Ethanes and Fluorine−Fluorine Enthalpy Interaction Terms[a]

compound	this study	no. used in previous study[b]	G2(MP2)-BAC[c]	other sources
CH_2FCH_2F	−102.7	−106.6	−105.9	−103.7[d]
CHF_2CH_2F	−156.9	−157.8	−158.5	−156.8[e]
CHF_2CHF_2	−209.6	−210.1	−209.1	−209.1[e]
CF_3CH_2F	−213.3	−214.1	−215.6	−214.1[f]
CF_3CHF_2	−264.1	−264.0	−264.3	−264.0[f]

interaction terms	this study	no. used in previous study[b]
F/F[g]	3.1	−0.8
2F/F	5.7	4.8
2F/2F	9.8	9.3
3F/F	7.8	7.0
3F/2F	13.8	13.9

[a] Unit in kcal/mol. [b] Reference 13. [c] Reference 19. [d] Reference 22. [e] Reference 18. [f] Reference 17. [g] “/” indicates interaction for alkane.

The lack of group balance in reactions 2 and 3 appear to result in similar underestimation, while no underestimation is observed for the $\Delta H_f°_{298}$ of 1-fluoropropane using isodesmic reaction 1 where groups are conserved. The averaged values of underestimation in reactions 2 and 3 are 2.91 and 2.98 kcal/mol, respectively. The average error for fluoroethane and 2-fluoropropane using isodesmic reactions without group balance is 2.94 kcal/mol.

Reactions 2−4 have one fluorine on each side. Compounds with one less carbon are used as a reference compound in reactions 2−4:

(i) Methane is used as a reference compound for estimation of fluoroethane in reaction 2.

(ii) Ethane is used as a reference compound for estimation of 2-fluoropropane in reaction 3.

(iii) Propane is used as a reference compound for 2-fluoro-2-methylpropane in reaction 4.

Similar underestimation is expected for the calculation of $\Delta H_f°_{298}$ of 2-fluoro-2-methylpropane in reaction 4. $\Delta H_f°_{298}$ of 2-fluoro-2-methylpropane is estimated as −81.09 kcal/mol using an isodesmic reaction without group balance. It is adjusted by the average difference (above) of 2.94 to a recommended value of $\Delta H_f°_{298} = -78.2$ kcal/mol.

Rotational Barriers. The potential curves are fit by a truncated Fourier series represented by eq 5, with the potential coefficients, a_i, presented in the Supporting Information. Calculated torsional frequencies for 2-fluoropropane (two) and 2-fluoro-2-methylpropane (three) are not identical as shown in Table 1 and result in slightly different barrier heights as shown in Table 5.

Standard Entropy ($S°_{298}$) and Heat Capacities ($C_p(T)$’s, $300 \le T/K \le 1500$). $S°_{298}$ and $C_p(T)$’s are listed in Table 6, with specific contributions from each internal rotor noted. The calculation results for 2-fluoropropane are in agreement with literature values.[15,16] The calculation results of $S°_{298}$ for 2-fluoro-2-methylpropane is about 0.2 cal/(mol·K) higher than values of Frenkel et al.,[15] and $C_p(T)$’s are about 0−0.6 cal/(mol·K) higher than values of Frenkel et al.[15]

2. *Ab Initio* Calculations for $\Delta H_f°_{298}$ Estimation of Five Fluorinated Ethanes. The G2(MP2) composite calculation method with isodesmic reactions that conserve group balance, (6)−(10), are used to estimate enthalpies of formations for five fluoroethanes: 1,2-difluoroethane, 1,1,2-trifluoroethane, 1,1,2,2-tetrafluoroethane, 1,1,1,2-tetrafluoroethane, and pentafluoroethane. The results are tabulated in Table 7. Chen et al. calculated $\Delta H_f°_{298}$ for 1,1,2-trifluoroethane and 1,1,2,2-tetrafluoroethane using the MP4/6-311G**//6-31G* calculation method and the same isodesmic reactions we chose.[18] Our G2(MP2) calculation results show good agreement with their

TABLE 8: Summary of Groups and Interactions

groups	$H_f{}^\circ{}_{298}$[a]	$S^\circ{}_{298}$[b]	$C_{p\ 300}$[b]	$C_{p\ 400}$	$C_{p\ 500}$	$C_{p\ 600}$	$C_{p\ 800}$	$C_{p\ 1000}$	$C_{p\ 1500}$
C/C/H3[c]	−10.0	30.41	6.19	7.84	9.4	10.79	13.02	14.77	17.58
C/C/F/H2[d]	−52.9	35.00	8.04	9.85	11.52	12.9	15.04	16.5	18.58
C/C/F2/H[d]	−109.7	39.11	10.18	12.23	13.92	15.22	17.04	18.15	19.58
C/C/F3[d]	−168.2	42.55	12.75	15.05	16.71	17.86	19.27	19.98	20.68
C/C2/F/H	−50.2	13.58	7.62	9.51	10.91	11.93	13.35	14.27	15.52
C/C2/F2	−104.9	17.30	10.49	12.54	13.72	14.76	15.72	16.10	16.26
C/C3/F	−48.2	−8.09	8.00	9.35	10.90	11.62	12.36	12.54	12.44
CD/H2	6.3	27.61	5.10	6.36	7.51	8.50	10.07	11.27	13.19
CD/F/H	−39.5	36.48	7.0	8.5	9.6	10.5	11.9	12.8	14.1
CD/F2	−86.8	38.55	9.1	10.8	12.0	12.8	13.9	14.5	15.2
CT/H	27.3	24.70	5.28	5.99	6.49	6.87	7.47	7.96	8.85
CT/F	2.8	32.08	7.26	7.92	8.36	8.70	9.19	9.53	10.00
interaction	$H_f{}^\circ{}_{298}$[b]	$S^\circ{}_{298}$[b]	$C_{p\ 300}$[b]	$C_{p\ 400}$	$C_{p\ 500}$	$C_{p\ 600}$	$C_{p\ 800}$	$C_{p\ 1000}$	$C_{p\ 1500}$
F/F	3.1	0.92	−0.21	−0.25	−0.31	−0.3	−0.34	−0.24	0.01
F/2F	5.7	0.38	0.3	0.25	0.17	0.15	0.03	0.03	0.1
F/3F	7.8	0.85	−0.14	−0.2	−0.24	−0.21	−0.26	−0.21	−0.06
2F/2F	9.8	−0.45	1.61	1.21	0.77	0.48	0.09	0.01	0.06
2F/3F	13.8	0.73	0.08	−0.15	−0.3	−0.34	−0.41	−0.34	−0.13
3F/3F[d]	15.5	0.54	0.24	−0.09	−0.28	−0.34	−0.39	−0.31	−0.13
F//F[e]	1.9	−7.34	−0.01	−0.10	−0.12	−0.09	−0.03	0.03	0.10
2F//F	8.9	−3.70	0.51	0.15	−0.02	−0.07	−0.07	−0.03	0.05
2F//2F	16.1	−2.62	1.12	0.37	0.02	−0.11	−0.15	−0.10	0.00
F///F[f]	−0.5	−5.17	−0.97	−0.72	−0.48	−0.29	−0.08	−0.02	−0.03
gauche	$H_f{}^\circ{}_{298}$[b]	$S^\circ{}_{298}$[c]	$C_{p\ 300}$[c]	$C_{p\ 400}$	$C_{p\ 500}$	$C_{p\ 600}$	$C_{p\ 800}$	$C_{p\ 1000}$	$C_{p\ 1500}$
F−CH3	0.0	−0.90	0.05	0.05	0.13	0.14	0.19	0.18	0.06

[a] Units in kcal/mol. [b] Units in cal/(mol·K). [c] Reference 5. [d] Reference 13. [e] // indicates correction for alkene group. [f] /// indicates correction for alkyne group.

data. The $\Delta H_f{}^\circ{}_{298}$ we obtain for 1,1,1,2-tetrafluoroethane and 1,1,1,2,2-pentafluoroethane are also in good agreement with Chen's recommended values.[17]

Berry et al. calculated the $\Delta H_f{}^\circ{}_{298}$ on fluoroethanes using G2, G2(MP2), CBS-4, and CBS-Q and the parametrized BAC-MP4 procedure.[19] The results of G2(MP2)-BAC are listed in Table 7 and range from 0.2 to 3.2 kcal/mol lower than our results. $\Delta H_f{}^\circ{}_{298}$ for 1,2 difluoroethane is calculated to be −102.7 kcal/mol, using an isodesmic reaction with group balance; this value is in good agreement with the noted experimental value of Zachariah et al., −103.7. It is, however, 3.2 kcal/mol higher than the values calculated by G2(MP2)-BAC. The value reported by Zachariah et al. as experimental results from kinetic data on dissociation of 1,1-difluoroethane and the $\Delta H_f{}^\circ{}_{298}$ of CH_2F radical recommended by Tsang.[22] Enthalpies for the remaining 1,2-substituted fluorinated ethanes listed in Table 7 are in good agreement with the G2(MP2)-BAC values of Berry et al.; CF_3CH_2F shows the next largest deviation at 2.3 kcal/mol lower than the value determined in this study.

3. Estimation of Group Additivity and Interaction (Correction) Terms. The F−F interaction terms are reevaluated using these $\Delta H_f{}^\circ{}_{298}$'s and the group values for C/C/H2/F, C/C/H/F2, and C/C/F3, estimated in the previous study.[13] Results of the interaction terms are tabulated in Table 7. The differences of interaction values are less than 1 kcal/mol with the exception of the F−F interaction, which is 3.9 kcal/mol higher in this study. This increase in evaluated F−F interaction results from an increased $\Delta H_f{}^\circ{}_{298}$ of CH_2FCH_2F (−102.7 kcal/mol) calculated in this study relative to −106.6 kcal/mol previously chosen. The thermodynamic property data used to calculate group values and interaction terms for the fluoroalkanes are listed in Table 6 and refs 10 and 13. The group values $C/C/H_3$ and $C/C_2/H_2$ are taken from existing literature.[5] Enthalpy contributions to the interaction terms determined in the previous study[13] are compared in Table 7 with the current values. Thermodynamic properties of fluorinated hydrocarbon groups and their interaction terms are listed in Table 8.

4. Estimation of F−CH_3 Gauche Interaction Effects on Thermodynamic Properties. It is of value to evaluate the importance of fluoro−methyl gauche interactions, because the group and interaction terms are determined, to a significant extent, from molecules where these gauche isomers are not present (fluoroethanes). The F−CH_3 gauche staggered conformation was reported to be more stable than anti staggered conformation in fluoropropanes,[10] where there are five molecules with F−CH_3 gauche interactions. Evaluation data for the gauche interactions are described in the calculations section above and specific data illustrated in the Supporting Information. Group additivity with no gauche interactions underestimates $\Delta H_f{}^\circ{}_{298}$ by 1 kcal/mol for 1,1-difluoropropane and overestimates $\Delta H_f{}^\circ{}_{298}$ by 1.0 and 1.9 kcal/mol for 1,1,1,2-tetrafluoropropane and 1,1,1,2,2-pentafluoropropane. Group additivity without gauche interactions overestimates $S^\circ{}_{298}$ for all fluorinated propanes, and the difference increases with number of fluorines, 0.34−2.73 cal/(mol·K). Group additivity estimation for heat capacities ($C_p(T)$'s $300 \le T/\mathrm{K} \le 1500$) shows close agreement to ab initio determined thermodynamic properties without use of gauche interactions.

The gauche correction term for $\Delta H_f{}^\circ{}_{298}$, is determined as −0.1 kcal/mol; the term does not improve accuracy significantly for enthalpy. An increase of 0.1 kcal/mol in the standard deviation between group additivity with gauche interaction and ab initio calculation results indicates the use of no correction would be better. The correction for $S^\circ{}_{298}$, which is −0.9 cal/(mol·K) per interaction, improves the group additivity estimation accuracy, as the standard deviation decreases from 1.63 to 0.66 cal/(mol·K). The group additivity determined $S^\circ{}_{298}$ for 1,1-difluoropropane is underestimated by 1.47 cal/(mol·K), and the group additivity determined $S^\circ{}_{298}$ for 1,1,1,2,2-pentafluoropropane is overestimated by 0.93 cal/(mol·K). Other differences are small, less than 0.76 cal/(mol·K). The correction factor for heat capacities ($C_p(T)$'s $300 \leq T/\mathrm{K} \leq 1500$) shows only small, inconsequential improvement. Table 8 shows final values for $F-CH_3$ gauche interactions. No correction is chosen for enthalpy of formation $\Delta H_f°_{298}$.

Summary

Thermodynamic properties ($\Delta H_f°_{298}$, $S°_{298}$, and $C_p(T)$'s ($300 \leq T/\mathrm{K} \leq 1500$)) for 2-fluoro-2-methylpropane are calculated. $\Delta H_f°_{298}$ of fluoroethane, 1-fluoropropane, and 2-fluoropropane are calculated using G2(MP2) results and isodesmic reactions. $\Delta H_f°_{298}$, of fluoroethane and 2-fluoropropane are compared with literature values and the systematic error is evaluated. Underestimation of 2.94 kcal/mol is expected for $\Delta H_f°_{298}$ of 2-fluoro-2-methylpropane with G2(MP2) calculation and isodesmic reaction without group balance. The $\Delta H_f°_{298}$ for 2-fluoro-2-methylpropane is estimated as −78.2 kcal/mol. $S°_{298}$ and $C_p(T)$'s of 2-fluoro-2-methylpropane are calculated. Thermodynamic properties for fluorinated carbon groups C/C2/F/H and C/C2/F2 are estimated using the literature data and the existing group value of C/C/H3. Those for C/C3/F are estimated from thermodynamic properties of 2-fluoro-2-methylpropane and the existing group value of C/C/H3.

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Supporting Information Available: Tables of rotational constants and gauche interaction properties. This information is available free of charge via the Internet at http://pubs.acs.org.

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