Ab Initio Calculations and Internal Rotor: Contribution for Thermodynamic Properties S°_{298} and $C_p(T)$'s ($300 < T/K < 1500$): Group Additivity for Fluoroethanes

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Ab initio calculations are performed on nine fluorinated ethane compounds and thermodynamic properties (S°_{298} and $C_p(T)$'s $300 < T/K < 1500$) are calculated. Geometries of stable rotational conformers and transition states for internal rotation are optimized at the RHF/6-31G* (6-31G(d)) and MP2/6-31G* levels of theory. Harmonic vibrational frequencies are computed at the RHF/6-31G* level of theory. Potential barriers for internal rotations are calculated at the MP2/6-31G*//MP2/6-31G* level. Parameters of the Fourier expansion of the hindrance potential are tabulated. Standard entropies (S°_{298}) and heat capacities ($C_p(T)$'s, $300 < T/K < 1500$) are calculated using the rigid-rotor-harmonic-oscillator approximation with direct integration over energy levels of the intramolecular rotation potential energy curve. Heats of formation are adopted from literature evaluation and BAC-MP4 ab initio calculations. Thermodynamic properties for fluorinated carbon groups C/C/F/H2, C/C/F2/H, and C/C/F3 are determined by existing thermodynamic group parameter of C/C/H3 and data on CH_2FCH_3, CHF_2CH_3, and CF_3CH_3, respectively: no fluorine or other halogen is on the methyl carbon adjacent to the carbon bonded to the fluorine(s). Six interaction terms in addition to the above groups are developed to account for repulsion and steric effects. Interaction terms are required to accurately estimate $\Delta H_f{}^\circ_{298}$, S°_{298}, and $C_p(T)$'s ($300 < T/K < 1500$) for fluoroethanes where fluorine(s) are on carbons adjacent to a carbon bonded to fluorine(s).

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. Example includes HFC-134a (CH_2FCF_3), a replacement for CFC-12 (CF_2Cl_2) in domestic refrigeration and automobile air conditioning units.[1] A number of studies on thermodynamic property data have been reported for these species by experiment and *ab initio* calculations. Chen et al.[2] studied and recommended thermodynamic properties (ΔH_f°, S°, $C_p(T)$'s for 0−1500 K) for six fluoroethanes in which at least one of the internally rotating groups is a symmetric top. Zachariah et al. reported thermochemical data on about 100 closed and open shelled fluorocarbon species using BAC-MP4 method.[3] Chen et al. studied the structures, moments of inertia, and frequencies at the RHF/6-31G* level of theory, and barriers for internal rotation at the MP4/6-311G**//6-31G* level of theory, as well as estimated thermodynamic properties and functions of 1,1,2-trifluoroethane and 1,1,2,2-tetrafluoroethane.[4] Berry et al. reported enthalpies of formation ($\Delta H_f{}^\circ_{298}$) for ethane and the complete series of fluoroethanes, $C_2H_xF_{6-x}$, $x = 0-5$ by *ab initio* G2, G2(MP2), CBS-4, and CBS-Q quantum mechanical protocols and the parametarized BAC-MP4 procedure.[5] Marshall et al. have reported C−H bond dissociation enthalpies at 298 K for a variety of C_1-C_4 hydrofluorocarbons using MP2/6-311+G(3df,2p)//MP2/6-31G(d) level of theory and isodesmic reactions.[6] These *ab initio* studies are quite valuable; however, it is difficult to extend these beyond 3 or 4 carbon species, and a method is needed to accurately estimate thermodynamic properties of fluoroenated and other halogenated species.

The group additivity method,[7] which is an easy, inexpensive, and accurate calculation for hydrocarbons and oxygenated hydrocarbons,[8] is not accepted as accurate for these fluorocarbons where average errors are several kcal/mol with maximum errors exceeding 5 kcal/mol. Accuracy of conventional group additivity method is unacceptable by the standards set by the above research studies.

In this study, RHF/6-31G* and MP2/6-31G* calculations are applied on nine HFCs, CH_3CH_2F,CH_2FCH_2F, CH_3CHF_2, CH_2FCHF_2, CH_3CF_3, CHF_2CHF_2, CH_2FCF_3, CHF_2CF_3, and CF_3CF_3 to obtain potential barriers for internal rotations. Standard entropies (S°_{298}) and heat capacities ($C_p(T)$'s, $300 < T/K < 1500$) are calculated using the rigid-rotor-harmonic-oscillator approximation on the basis of the information obtained from the *ab initio* studies. Heats of formation for CH_3CH_2F, CH_3CHF_2, CH_3CF_3, CH_2FCF_3, CHF_2CF_3, CF_3CF_3 are adopted from the literature study evaluation of Chen et al.[2], $DH_f{}^\circ_{298}$ value for CH_2FCH_2F is adopted from BAC-MP4 *ab initio* calculation,[3,9] and $\Delta H_f{}^\circ_{298}$ of CH_2FCHF_2 and CHF_2CHF_2 are average values of Lacher et al.[10] and Chen et al.[4]

Group values are estimated for C/C/F/H2, C/C/F2/H, and C/C/F3 based on the selected molecules, CH_3CH_2F, CH_3CHF_2, and CH_3CF_3, where there are no fluorine atoms on the carbon adjacent to the carbon containing the fluorine atom(s). Group additivity corrections (fluorine interaction terms) are determined for F/F, 2F/F, 3F/F, 2F/2F, 3F/2F, and 3F/3F. Consider 1,1-difluoroethane with groups C/C/F2/H and C/C/H3 and 1,2-difluoroethane with groups C/C/F/H2 and C/C/F/H2. For 1,1-difluoroethane, the C/C/F2/H group data includes steric, electronic, and polar effects of the two fluorine atoms, but the C/C/F/H2 groups on 1,2-difluoroethane do not include steric, electronic, and polar effects resulting from F−F interactions on the adjacent

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carbons. We develop interaction groups to account for these effects. The use of a modified group additivity for the properties of C_1 to C_n fluorocarbons is valuable, and the tabulated data and databases allow easy estimation of the thermodynamic property data for a large number of fluorocarbons.

Calculation Methods

Thermodynamic Properties (Standard entropies ($S°_{298}$) and Heat Capacities ($C_p(T)$'s, $300 < T/K < 1500$) Using *ab Initio* Calculations. All *ab initio* calculations are performed using the Gaussian94[11] system of programs on a DEC Alpha 200 work station. Equilibrium and saddle-point geometries are completely optimized using the closed shell restricted Hartree–Fock (RHF) method and second-order Møller–Plesset (MP2) perturbation theory with analytical gradients with the 6-31G* basis set (HF/6-31G* and MP2/6-31G*).

Energies for equilibrium structures and saddle-point structures between rotational conformers are calculated at the MP2/6-31G* level of theory. Vibrational frequencies are calculated for all rotational conformers and saddle-points using analytical second derivatives at the HF/6-31G* level. Zero point vibrational energies (ZPVE) are scaled by the factor of 0.89 as recommended[12] because of the systematic overestimation of the HF–SCF determined harmonic vibrational frequencies by about 10%.

The scaled harmonic vibrational frequencies from the HF6-31G* level of calculations and the moments of inertia of molecular structures optimized at MP2/6-31G* are used to calculate the entropies and heat capacities.

Calculation of Hindered Rotational Contribution to Thermodynamic Parameters. A technique for the calculation of thermodynamic functions from hindered rotations with arbitrary potentials has been developed.

The technique employs expansion of the hindrance potential in a Fourier series, calculation of the Hamiltonian matrix in the basis of the wave functions of free internal rotation, and subsequent calculation of energy levels by direct diagonalization of the Hamiltonian matrix. The torsional potential calculated at discrete torsional angles is represented by a truncated Fourier series. All potential curves of rotational barrier vs dihedral angle are fit by a cosine curve. The specific fit function for CH_2FCH_2F, CHF_2CH_2F, and CHF_2CHF_2 is

$$V(\text{Ø}) = a_0 + a_1 \cos(\text{Ø}) + a_2 \cos(2\text{Ø}) + a_3 \cos(3\text{Ø}) \quad (1)$$

for CH_2FCH_3, CHF_2CH_3, CF_3CH_3,CF_3CH_2F,CF_3CHF_2, and CF_3CF_3 is

$$V(\text{Ø}) = a_0 + a_3 \cos(3\text{Ø}) \quad (2)$$

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

Evaluation of the matrix elements of individual cosine terms in the basis of the free rotor wave functions is straightforward. The terms cos(mØ) induce transitions with $\Delta K = \pm m$, where K is the rotational quantum number. Moreover, the matrix element does not depend on K, which leads to a simple form of the Hamiltonian matrix. The matrix has a band structure and consists of diagonal terms that are equal to those of the free rotor and subdiagonals of constant values that correspond to a different terms in the potential expansion.

The Hamiltonian matrix is then truncated to the size of $2K_{max} + 1$, where K_{max} is the maximum rotational quantum number considered. The choice of the size of the truncated matrix is made by checking the independence of the thermodynamic properties calculated on $K_{max.}$ The truncated matrix (in reduced dimensionless form) is diagonalized, and the eigenvalues are used to calculate the partition function, entropy, heat capacity, etc. This is accomplished using direct summation over the calculated energy levels according to standard expressions of statistical thermodynamics.[13]

Group Values and Group Additivity Correction Term Estimation. Selection (definition) of the initial groups is critical to development of a group additivity scheme for accurate property estimation. We develop a new set of fluorocarbon alkane groups derived from use of thermodynamic property data on molecules where there are only hydrogen atoms on the carbons which are adjacent to the carbon atom bonded to fluorines. The properties of the C/C/F/H2, C/C/F2/H, of C/C/F3 groups, for example, are derived from fluoroethane (CH_2FCH_3), 1,1-difluoroethane (CHF_2CH_3), 1,1,1-trifluoroethane (CF_3CH_3), respectively. There are no fluorines, other halogens, or bulky groups/fragments on the carbon atoms adjacent to the carbon atoms containing the fluorine(s) in the defining group. $H_f°_{298}$ and C_p's of C/C/F/H2 are calculated on the basis of

$$(CH_3CH_2F) = (C/C/H3) + (C/C/F/H2) \quad (3)$$

$S°_{298}$ of C/C/F/H2 is calculated on the basis of

$$(CH_3CH_2F) = (C/C/H3) + (C/C/F/H) - R\ln(\sigma) \quad (4)$$

where $R = 1.987$ cal/mol K, and σ is symmetry number, which is 3 for CH_3CH_2F. The group values of C/C/F2/H and C/C/F3 are also estimated in the same manner.

Thermodynamic properties of fluoroethanes with no fluorine on the carbon atoms adjacent a carbon with fluorine are now accurately predicted; but an adjustment needs to be made for fluoroethane species where there are fluorine atoms on an adjacent carbon, such as 1,2-difluoroethane, or 1,1,2-trifluoroethane. This adjustment comes in the form of an interaction term to count the total number of fluorine atoms on each of the two adjacent carbon atoms. No interaction term is needed when there are no fluorine(s) on adjacent carbons.

Our assumption is based on the known accuracy and validity of group additivity for hydrocarbon and oxyhydrocarbons with gauche interactions.[7,8] Conventional group additivity does not, however, work for fluorocarbons or other halocarbons. Group additivity does not incorporate effects of nonnext nearest neighbors. Consider the two molecules 1,1-difluoroethane and 1,2-difluoroethane and the groups that are used to estimate the respective properties.

compound	1,1-difluoroethane, CHF_2-CH_3	1,2-difluoroethane, CH_2FCH_2F
groups	C/C/F2/H	C/C/F/H2
	C/C/H3	C/C/F/H2

In the 1,1-difluoroethane isomer, the C/C/F2/H group knows and incorporates polar, electronic, and steric interactions between the two fluorines as well as adjacent hydrogens and carbons. In the 1,2-difluoroethane isomer, C/C/F/H2 groups do not recognize or incorporate any interactions (polar, steric, etc.) between the two fluorines.

In this paper, we define and develop groups and a limited set of interaction terms which can be used with Benson type group additivity scheme for calculation of the thermodynamic properties of multifluoro alkanes.

The interaction values between fluorines attached to two adjacent carbons (F/F, 2F/F, 3F/F, 2F/2F, 3F/2F, and 3F/3F)

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

species	$\nu1$[b]	$\nu2$	$\nu3$	$\nu4$	$\nu5$	$\nu6$	$\nu7$	$\nu8$	$\nu9$	$\nu10$	$\nu11$	$\nu12$	$\nu13$	$\nu14$	$\nu15$	$\nu16$	$\nu17$	$\nu18$
CH_3CH_2F	274	440	878	972	1169	1240	1310	1422	1547	1588	1627	1645	1683	3212	3242	3274	3280	3301
CH_2FCH_2F	150	348	541	956	1002	1212	1231	1251	1383	1425	1563	1607	1658	1662	3242	3258	3299	3313
CH_3CHF_2	258	408	503	614	948	1072	1254	1283	1298	1540	1558	1603	1630	1633	3229	3302	3306	3324
CH_2FCHF_2	128	263	462	522	627	1003	1211	1245	1260	1292	1386	1492	1570	1632	1664	3274	3327	3344
CH_3CF_3	251	392	392	585	585	646	908	1095	1095	1415	1415	1430	1601	1627	1627	3246	3330	3330
CHF_2CHF_2	96	220	390	455	533	585	679	1225	1257	1276	1286	1304	1463	1526	1556	1657	3343	3353
CH_2FCF_3	117	233	382	446	578	594	723	928	1098	1234	1344	1363	1460	1472	1622	1663	3286	3348
CHF_2CF_3	81	225	263	393	455	565	626	634	791	962	1266	1309	1363	1407	1483	1551	1641	3354
CF_3CF_3	70	230	230	378	415	415	564	564	674	674	774	888	1243	1426	1426	1434	1434	1627

[a] Nonscaled. Frequencies are calculated at the HF/6-31G* level of theory. [b] Torsional Frequencies. These frequencies are not included in the calculation of thermodynamic properties.

TABLE 2: Barriers for Internal Rotations and Zero Point Vibrational Energies

species[a]	MP2/6-31G**//HF/6-31G* (hartree)	ZPVE (kcal/mol)	rotational barrier[b] (kcal/mol)	rotational barrier[c] torsion frequency in ZPVE (kcal/mol)	other studies (kcal/mol)
CH_3CH_2F S	−178.508 73	45.897	0.000	0.000	
CH_3CH_2F E	−178.502 47	45.645	4.049	3.700	3.306[d]
CH_2FCH_2F Sa	−277.518 00	41.613	0.193	0.186	
CH_2FCH_2F Sg	−277.518 28	41.601	0.000	0.000	
CH_2FCH_2F El	−277.512 90	41.400	3.391	3.200	
CH_2FCH_2F Eh	−277.505 59	41.570	8.126	7.935	
CH_3CHF_2 S	−277.543 40	41.117	0.000	0.000	
CH_3CHF_2 E	−277.536 97	40.857	4.130	3.800	3.215[d] 3.32[f] 2.88[j] 2.61[k]
CH_2FCHF_2 Sa	−376.549 57	36.743	0.000	0.000	
CH_2FCHF_2 Sg	−376.546 99	36.766	1.651	1.643	
CH_2FCHF_2 El	−376.544 35	36.567	3.280	3.120	
CH_2FCHF_2 Eh	−376.540 05	36.693	6.095	5.932	5.61[e]
CH_3CF_3 S	−376.587 31	35.695	0.000	0.000	
CH_3CF_3 E	−376.580 94	35.426	4.073	3.754	3.167[d]
CHF_2CHF_2 Sa	−475.578 14	31.744	0.000	0.000	
CHF_2CHF_2 Sg	−475.575 54	31.818	1.709	1.697	
CHF_2CHF_2 El	−475.571 58	31.769	4.258	4.136	
CHF_2CHF_2 Eh	−475.566 72	31.875	7.403	7.281	7.11[e]
CH_2FCF_3 S	−475.589 99	31.295	0.000	0.000	
CH_2FCF_3 E	−475.583 03	31.195	4.432	4.283	4.428[d] 4.20[g] 4.23[j] 3.73[k]
CHF_2CF_3 S	−574.615 43	26.266	0.000	0.000	
CHF_2CF_3 E	−574.609 42	26.296	3.899	3.796	4.338[d] 3.40[h] 4.04[j] 3.45[k]
CF_3CF_3 S	−673.652 38	20.677	0.000	0.000	
CF_3CF_3 E	−673.646 31	20.740	3.954	3.865	4.300[d] 3.67[i] 4.11[j] 3.62[k]

[a] S at the end of species stands for "staggered", E stands for "eclipsed", Sa stands for "anti staggered", Sg stands for "gauche staggered", El stands for "eclipsed low", whose energy barrier is lower than the other eclipsed position, Eh stands for "eclipsed high", whose energy barrier is higher than the other eclipsed position. See Figure 1 for definition of geometric nomenclature. [b] Rotational barriers are calculated as the difference in total energies plus scaled (0.89) zero point vibrational energies. The corresponding torsional frequency is excluded in the calculation of ZPVE. [c] Rotational barriers are calculated as the difference in total energies plus scaled (0.89) zero point vibrational energies, where the corresponding torsional frequency is included in the ZPVE for comparison to other studies. [d] Reference 2. [e] MP4/6-311G**//6-31G*.[4] [f] Reference 13. [g] Reference 14. [h] Reference 15. [i] Reference 16. [j] MP2/6-311++G(3df,3p)//MP2/6-31G(d,p) method. ZPVE is included.[17] [k] MP2/6-311++G(3df,3p)//MP2/6-31G(d,p) method. ZPVE and thermal correction are included.[17]

are calculated from differences between the defined fluorinated hydrocarbon group values and thermodynamic properties of the parent compounds. For example, $H_f°_{298}$ and C_p's for the F/F interaction are estimated by

$$(CH_2FCH_2F) = (C/C/F/H2)2 + (F/F) \qquad (5)$$

$S°_{298}$ for the F/F interaction is calculated by

$$(CH_2FCH_2F) = (C/C/F/H2)2 - R\ln(\sigma) + (F/F) \qquad (6)$$

where $R = 1.987$ cal K^{-1} mol^{-1} and $\sigma = 2$ for CH_2FCH_2F. Other interaction values are also estimated in the same manner.

Results and Discussion

Rotational Barriers. The barriers for internal rotations are calculated as the difference between the total energy of each conformation and that of the global equilibrium plus the scaled ZPVE difference (see Table 2). The curves are fit by a truncated Fourier series 1 and 2.

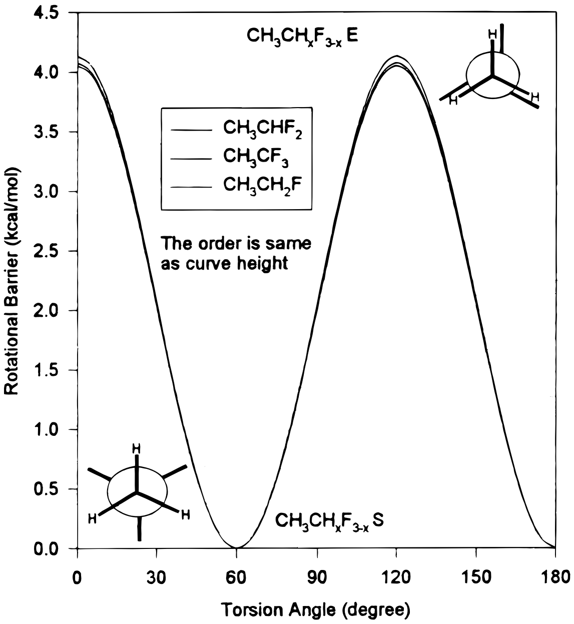

Figure 1. Potential barriers for internal rotations about C−C bonds of CH_3CH_2F, CH_3CHF_2, and CH_3CF_3.

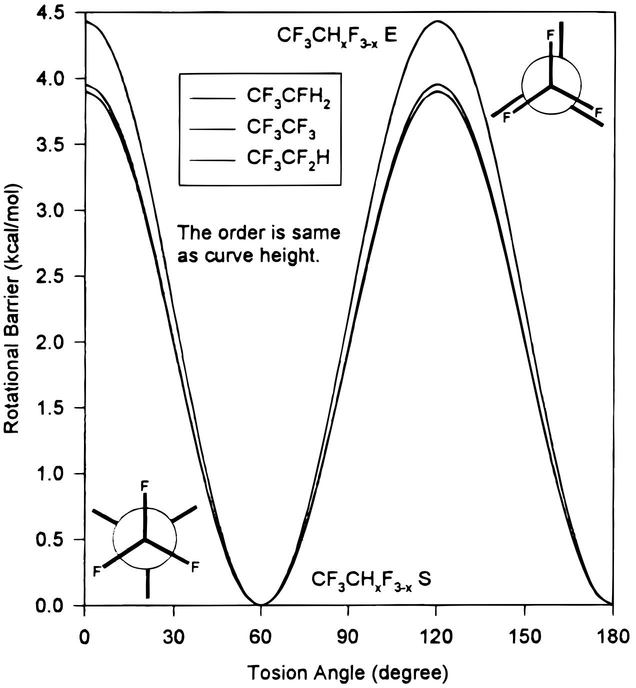

Figure 2. Potential barriers for internal rotations about C−C bonds of CH_2FCF_3, CHF_2CF_3, and CF_3CF_3.

TABLE 3: Rotational Constants[a]

species	Ia	Ib	Ic
CH_3CH_2F	36.752	9.534	8.351
CH_2FCH_2F	17.520	5.176	4.505
CH_3CHF_2	9.720	9.096	5.271
CH_2FCHF_2	9.335	3.725	2.875
CH_3CF_3	5.641	5.286	5.286
CHF_2CHF_2	5.253	3.222	2.115
CH_2FCF_3	5.492	2.866	2.826
CHF_2CF_3	3.782	2.481	2.055
CF_3CF_3	2.913	1.894	1.894

[a] Unit in gigahertz.

Figure 1 shows rotational barrier diagrams for CH_3CH_2F, CH_3CHF_2, and CH_3CF_3, with rotational barriers 4.05, 4.13, and 4.07 kcal/mol, respectively. Figure 2 shows the diagrams for CH_2FCF_3, CHF_2CF_3, and CF_3CF_3 with barriers 4.43, 3.90, and 3.95 kcal/mol, respectively. These curves are also represented by truncated Fourier series. Table 6 lists the coefficients of the respective Fourier series. Table 2 shows the comparison of calculated and experimentally determined rotational barriers. The rotational barriers estimated by Chen et al.[2] are 3.306, 3.215, 3.167, 4.428, 4.338, and 4.300 kcal/mol, respectively. The rotational barrier of CH_3CHF_2 is also experimentally investigated by Villaman et al. using wave guide microwave Fourier transform spectrometer (MWFT).[14] Their result is 3.32 kcal/mol. Our result, see column note c, Table 2, shows barriers 0.4−0.5 kcal/mol higher than Chen et al. and Villamanan et al.'s result. The rotational barrier for CH_2FCF_3, CHF_2CF_3, and CF_3CF_3 are also experimentally determined as 4.20 kcal/mol by Danti et al.,[15] as 3.40 kcal/mol by Eltayeb et al.,[16] and as 3.67 kcal/mol by Gallaher et al.[17] respectively. Our result for CHF_2CF_3 is 0.4 kcal/mol higher, while CH_2FCF_3 and CF_3CF_3 are in good agreement with the experimental results. Parra et al. recently reported rotational barrier heights of CH_3CHF_2, CH_2FCF_3, CHF_2CF_3, and CF_3CF_3 including ZPVEs and thermal corrections, using B3LYP and MP2 calculation methods with various basis sets.[18] Torsion modes were considered as harmonic oscillators in their report.[18] The values shown in Table 2 are MP2/6−4311++G(3df,3p) single point calculations with optimized geometry of MP2/6-31G(d,p). The comparison of rotational barriers with and without thermal correction for CH_2FCF_3, CHF_2CF_3, and CF_3CF_3 shows that thermal corrections decrease the barrier height by the factor of 0.5 cal/mol K. The differences between this study and their results are within 0.2 cal/mol K, except CH_3CHF_2, which has a 1.25 cal/mol K higher value in this analysis.

Figure 3 shows the rotational barrier diagram for CH_2FCH_2F. The barriers at MP2/6-31G* level are 8.13 and 3.39 kcal/mol, which are the highest rotational barrier among nine fluorinated hydrocarbons. The calculation also shows that the gauche conformer is more stable than the anti conformer by 0.193 kcal/mol. An earlier report,[19] using MP2/6-31G** basis set, also indicated that gauche conformer is 0.15 kcal/mol lower than anti conformer, A 6-311++G* level calculation resulted in similar difference of 0.197 kcal/mol.[20]

Figure 4 shows the rotational barrier diagrams for CH_2FCHF_2. The barriers are determined to be 6.09 and 3.28 kcal/mol, where Chen et al. estimated as 5.61 and 2.80 kcal/mol respectively using MP4/6-311G**//6-31G*.[4] Our estimation result is approximately 0.5 kcal/mol higher than Chen et al.'s. Figure 5 shows the rotational barrier diagrams for CHF_2CHF_2. The barriers are determined to be 7.40 and 4.26 kcal/mol, where Chen et al. estimated 7.11 and 3.90 kcal/mol respectively using MP4/6-311G**//6-31G*.[4] Our estimation is approximately 0.3 kcal/mol higher than that of Chen et al.

Entropies ($S°_{298}$). Table 4 lists the calculation results and comparisons with previous *ab initio* calculations and experimental data. The calculation at the MP2/6-31G*//HF/6-31G* level gives good agreement for the entropies of CH_3CH_2F, CH_3CHF_2, and CH_3CF_3 with experimentally determined data[21] and the literature study.[2] The value for CH_2FCH_2F is 0.67 cal/mol K higher than suggested value by Burgess et al.[9] Their estimations are based on vibrational frequencies and moments of inertia from their *ab initio* calculations. The value for CH_2FCHF_2 shows good agreement with the suggested value by Burgess et al.,[9] but overestimates by 0.60 cal/mol K the value from MP4/6-31G** level *ab initio* calculation.[4] Our entropy for CHF_2CHF_2 has a slightly larger difference, 1.16 cal/mol

TABLE 4: Ideal Gas Phase Thermodynamic Properties[a]

species and symmetry no.		$H_f{}^{\circ}_{298}$	S°_{298}[b]	C_{p300}[b]	C_{p400}	C_{p500}	C_{p600}	C_{p800}	C_{p1000}	C_{p1500}
CH_3CH_2F	TVR[c]		61.432	12.203	15.500	18.715	21.565	26.157	29.575	34.784
(3)	internal rotor[d]		3.976	2.022	2.190	2.202	2.126	1.898	1.690	1.372
	total		63.225[e]	14.225	17.690	20.917	23.691	28.055	31.265	36.156
	Stull et al.[f]	−62.50	63.22	14.17	17.57	20.72	23.44	27.76	30.98	
	Chen et al.[g]	−62.90	63.34	14.28	17.71	20.86	23.56	27.82	31.00	35.90
CH_2FCH_2F	TVR		65.365	13.614	17.183	20.532	23.403	27.845	31.017	35.689
(2)	internal rotor		5.565	2.257	2.266	2.194	2.094	1.899	1.743	1.482
	total		69.553	15.871	19.449	22.726	25.497	29.744	32.760	37.171
	Zachariah et al.[h] & Burgess et al.[i]	−106.60	68.88	16.22		22.74		29.71	32.68	37.12
CH_3CHF_2	TVR		65.528	14.344	17.873	21.106	23.865	28.141	31.214	35.774
(3)	internal rotor		3.993	2.021	2.193	2.212	2.142	1.918	1.709	1.386
	total		67.338	16.365	20.066	23.318	26.007	30.059	32.923	37.160
	Stull et al.[f]	−118.00	67.52	16.31	19.93	23.07	25.68	29.69	32.56	
	Chen et al.[g]	−119.70	67.50	16.31	19.93	23.08	25.70	29.70	32.57	36.90
CH_2FCHF_2	TVR		69.316	15.889	19.600	22.925	25.691	29.813	32.644	36.674
(1)	internal rotor		5.182	2.628	2.730	2.687	2.575	2.296	2.037	1.588
	total		74.498	18.517	22.330	25.612	28.266	32.109	34.681	38.262
	Lacher et al.[j] and Burgess et al.[i]	−158.89	74.50	18.00		25.70		31.90	34.40	38.22
	Chen, Paddison, and Tschuikow-Roux[k]	−156.80	73.90	18.49	22.33	25.59	28.22	32.01	34.56	38.18
CH_3CF_3	TVR		68.932	16.905	20.695	23.901	26.513	30.384	33.053	36.882
(9)	internal rotor		4.022	2.032	2.198	2.210	2.134	1.906	1.697	1.377
	total		68.589	18.937	22.893	26.111	28.647	32.290	34.750	38.259
	Stull et al.[f]	−178.20	68.66	18.83	22.75	25.90	28.38	31.98	34.45	
	Chen et al.[g]	−178.20	68.67	18.84	22.75	25.90	28.38	31.98	34.44	38.00
CHF_2CHF_2	TVR		72.809	18.190	22.032	25.330	27.992	31.804	34.300	37.689
(2)	internal rotor		4.963	3.783	3.642	3.284	2.924	2.372	2.012	1.535
	total		76.395	21.973	25.674	28.614	30.916	34.176	36.312	39.224
	Zachariah et al.[h] and Burgess et al.[i]	−211.11	75.24	20.37		27.55		33.76	35.99	39.03
	Chen, Paddison, and Tschuikow-Roux[k]	−209.10	75.80	22.21	25.97	28.82	31.03	34.18	36.27	39.15
CH_2FCF_3	TVR		72.522	18.440	22.382	25.672	28.294	32.027	34.469	37.784
(3)	internal rotor		5.885	2.208	2.313	2.321	2.252	2.024	1.800	1.413
	total		76.224	20.648	24.695	27.993	30.546	34.051	36.269	39.197
	Chen et al.[g]	−214.10	75.58	20.70	24.90	28.23	30.76	34.20	36.36	39.3
CHF_2CF_3	TVR		75.957	20.747	24.794	28.048	30.566	33.998	36.115	38.799
(3)	internal rotor		6.436	2.267	2.332	2.284	2.169	1.902	1.679	1.335
	total		80.210	23.014	27.126	30.332	32.735	35.900	37.794	40.134
	Chen et al.[g]	−264.00	79.76	22.97	27.20	30.50	32.94	36.12	37.98	40.3
CF_3CF_3	TVR		79.026	23.472	27.673	30.849	33.203	36.235	37.960	39.926
(18)	internal rotor		6.602	2.266	2.334	2.291	2.181	1.915	1.688	1.308
	total		79.885	25.738	30.007	33.140	35.384	38.150	39.648	41.234
	Stull et al.[f]	−321.00	79.37	25.53	29.99	33.26	35.54	38.32	39.78	
	Chen et al.[g]	−320.90	79.30	25.52	30.01	33.29	35.60	38.40	39.87	41.40

[a] Thermodynamic properties are referred to a standard state of an ideal gas of pure enantiometer at 1 atm. One torsional frequency is 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 cal/mol K. [c] The sum of contributions from translations, external rotations, and vibrations. [d] Contribution from internal rotation about C−C bond. [e] Symmetry number is taken into account ($-R$ ln(number of symmetry)) [f] Reference 20. [g] Reference 2. [h] Reference 3. [i] Reference 9. [j] Reference 10. [k] Reference. 4

TABLE 5: Comparison of Heats of Formation by G2(MP2)[BAC][a] with Previous Study[b]

compounds	G2(MP2)[BAC]	previous study
CH_3CH_2F	−64.5	−62.9[c]
CH_2FCH_2F	−105.9	−106.6[d]
CH_3CHF_2	−119.3	−119.7[c]
CH_2FCHF_2	−158.5	−158.9[d]
CH_3CF_3	−178.5	−178.2[c]
CHF_2CHF_2	−209.1	−211.1[d]
CH_2FCF_3	−215.6	−214.1[c]
CHF_2CF_3	−264.3	−264.0[c]
CF_3CF_3	−319.2	-320.9[c]

[a] Reference 5. [b] Unit in kcal/mol. [c] Reference 2. [d] Reference 9.

TABLE 6: Coefficients of Truncated Fourier Series Representation Expansions for Internal Rotation Potentials[a]

rotors	a_0	a_1	a_2	a_3
$CH_3{-}CH_2F$	2.025			2.025
$CH_2F{-}CH_2F$	2.622	1.648	1.537	2.319
$CH_3{-}CHF_2$	4.130			4.130
$CH_2F{-}CHF_2$	2.854	−1.488	−0.387	2.304
$CH_3{-}CF_3$	2.037			2.037
$CHF_2{-}CHF_2$	3.223	1.618	0.4787	2.083
$CH_2F{-}CF_3$	2.216			2.216
$CHF_2{-}CF_3$	1.900			1.900
$CF_3{-}CF_3$	1.977			1.977

[a] Unit in kcal/mol. Values of rotational barriers computed at the HF/6-31G*//MP2/6-31G* level of theory are used to calculate the coefficients. Equations 1 and 2 in text. See text.

higher, than Burgess et al.'s reported value.[9] We are 0.60 cal/mol K above the MP4/6-31G** level *ab initio* calculation.[4] Burgess et al. only indicate that standard state entropy and heat capacities were computed based on vibrational frequencies and moments of inertia from their *ab initio* calculations. We do not know if they made any attempt to incorporate a contribution for internal rotation. Our values for CH_2FCF_3, CHF_2CF_3, and CF_3CF_3 are higher by 0.64, 0.45, and 0.55 cal/mol K, respectively, compared to the values from the literature estimation.[2] Ideal gas thermodynamic functions S° and $C_p(T)$ in the temperature range 0−1500 K and 1 atm pressure are calculated in

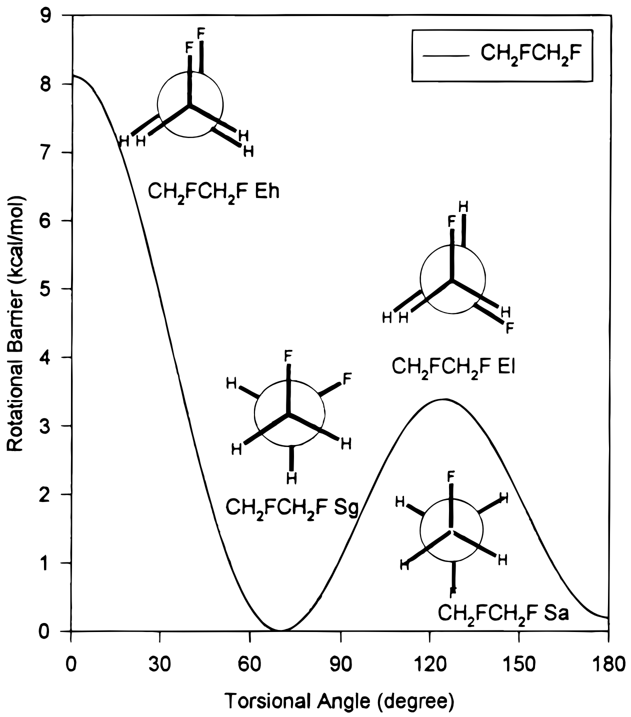

Figure 3. Potential barriers for internal rotations about C−C bonds of CH_2FCH_2F.

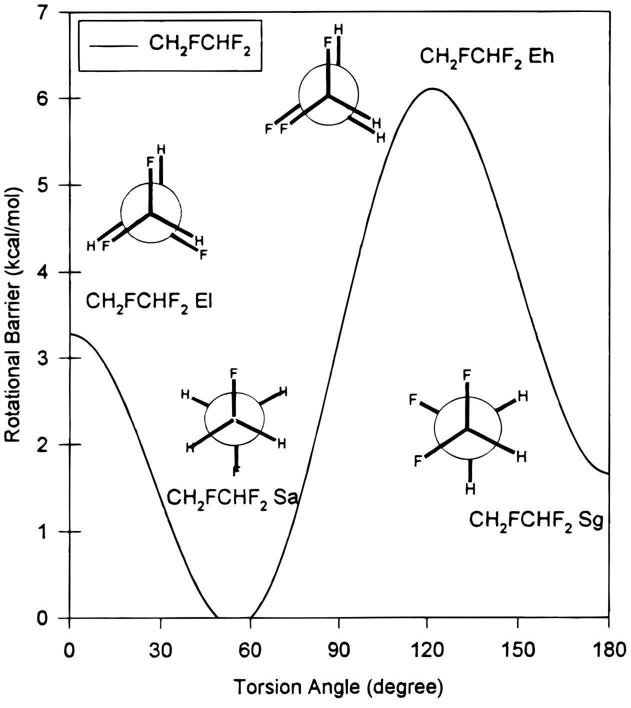

Figure 4. Potential barriers for internal rotations about C−C bonds of CH_2FCHF_2.

Chen et al.'s work,[4] by standard methods of statistical thermodynamics on the basis of the rigid rotor-harmonic oscillator model. The reduced moments of inertia, I_r, for internal rotation of unsymmetrical groups are calculated on the basis of the formulation of Pitzer.[22]

Heat Capacities ($C_p(T)$'s 300 < T/K < 1500). Table 4 also lists the $C_p(T)$ calculation results and comparisons with previous *ab initio* calculations and experimental data. Overall the calculation results are in good agreement with the experimental data for ($C_p(T)$'s 300 < T/K < 1500) and other *ab initio* calculations. The trends are similar to those for entropies; we estimate slightly higher values relative to the suggested values by Burgess et al.[9] for CHF_2CHF_2, but have good agreement with *ab initio* calculations of Chen et al.[4]

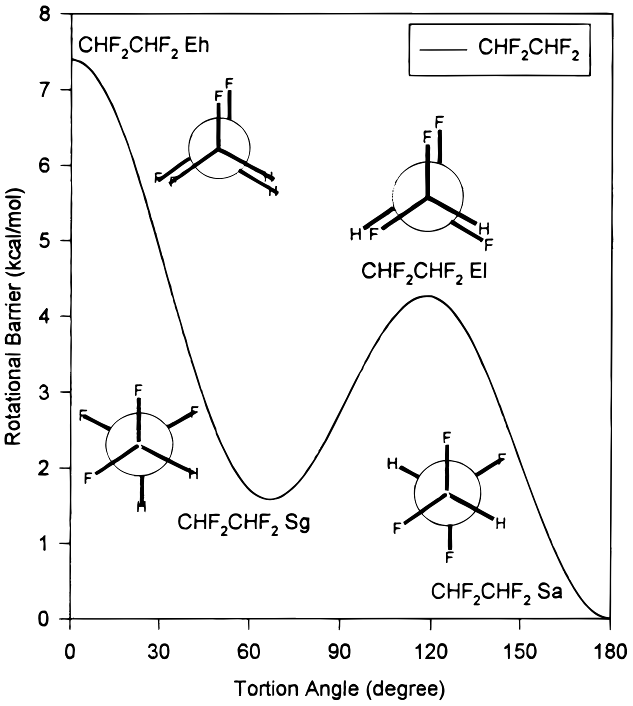

Figure 5. Potential barriers for internal rotations about C−C bonds of CHF_2CHF_2.

TABLE 7: Torsion Frequencies and Comparison of Their Contribution for Entropies $S°_{298}$ Using Torsion Frequencies and Rigid-Rotor-Harmonic-Oscillator Approximation

species	torsion frequency (cm^{-1})	$S°_{298}$ from torsion frequency (cal/mol K)	$S°_{298}$ from rigid-rotor-harmonic-oscillator approximation (this study) (cal/mol K)
CH_3CH_2F	274.4	1.772	3.976
CH_2FCH_2F	150.0	2.895	5.565
CH_3CHF_2	258.1	1.881	3.993
CH_2FCHF_2	127.9	3.202	5.182
CH_3CF_3	251.4	1.929	4.022
CHF_2CHF_2	95.7	3.768	4.963
CH_2FCF_3	117.4	3.369	5.885
CF_2HCF_3	80.9	4.099	6.436
CF_3CF_3	69.8	4.388	6.602

Table 7 lists the torsion frequencies of nine fluoroethanes and compares the torsion contribution to entropy $S°_{298}$ using the scaled torsion frequencies[12] versus our rigid-rotor-harmonic-oscillator approximation. The contribution from a torsion frequency calculation is about 2 cal/mol K lower in each case, with one exception, CHF_2CHF_2, which is only 1.195 cal/mol K lower. A comparison for heat capacity at 300 K is shown in Table 8. The C_p(300 K) contribution is approximately 0.2−0.3 cal/mol K lower in the torsion calculation. The C_p(300 K) difference for CHF_2CHF_2 is more significant (1.823 cal/mol K).

Group Additivity Values. Thermodynamic properties of fluorinated hydrocarbon groups are listed in Table 9. Heats of formation of CH_3CH_2F, CH_3CHF_2, CH_3CF_3, CH_2FCF_3, CHF_2CF_3, and CF_3CF_3 are adopted from the literature[2] values for CH_2FCH_2F are adopted from BAC-MP4 *ab initio* calculations,[3,9] and averages between the values of Lacher et al.[10] and those of Chen et al.[4] are adopted for $\Delta H_f°_{298}$ of CH_2FCHF_2 and CHF_2CHF_2. Values for the entropies and heat capacities are from this work. Heats of formation from the *ab initio*/bond additivity correction study of Berry et al.[5] are also listed for comparison.[5]

TABLE 8: Torsion Frequencies and Comparison of Their Contribution for Heat Capacities C_{P300} Using Torsion Frequencies and Rigid-Rotor-Harmonic-Oscillator Approximation

species	torsion frequency (cm^{-1})	C_{p300} from torsion frequency (cal/mol/K)	C_{p300} from rigid-rotor-harmonic-oscillator approximation (this study) (cal/mol/K)
CH_3CH_2F	274.4	1.775	2.022
CH_2FCH_2F	150.0	1.921	2.257
CH_3CHF_2	258.1	1.798	2.021
CH_2FCHF_2	127.9	1.938	2.628
CH_3CF_3	251.4	1.807	2.032
CHF_2CHF_2	95.7	1.96	3.783
CH_2FCF_3	117.4	1.946	2.208
CF_2HCF_3	80.9	1.967	2.267
CF_3CF_3	69.8	1.972	2.266

The G2(MP2)[BAC] method is chosen among his several calculation methods, G2[BAC], CBS-4, and CBS-Q. The G2(MP2)[BAC] calculations of Berry et al. give heats of formation that are consistently lower by 1−2 kcal/mol than the recommended values of Chen et al.[2] and Burgess et al.[9] Table 5 shows the comparison of $\Delta H_f{}^\circ{}_{298}$ values for all nine species.

The group values for heats of formation and entropy of C/C/H3 are taken from existing literature:[8] −10.0 kcal/mol and 30.41 cal/mol K, respectively. Group values for heats of formation are −52.9, −109.7, and −168.2 kcal/mol for C/C/F/H2, C/C/F2/H, and C/C/F3, respectively. Group values for entropy are 35.00, 39.11, and 42.54 cal/mol K, respectively. These numbers are derived from thermodynamic properties of fluoroethane (CH_2FCH_3), 1,1-difluoroethane (CHF_2CH_3), 1,1,1-trifluoroethane (CF_3CH_3), and those of C/C/H3 group.[8] The heats of formation decrease and the entropies increase with increased number of fluorines.

Interaction Terms. Interaction term values are also listed in Table 9. The group additivity corrections for enthalpy are: -0.8, 4.8, 7.0, 9.3, 13.9, and 15.5 kcal/mol for F/F, 2F/F, 3F/F, 2F/2F, 3F/2F, and 3F/3F, respectively. Interaction values for entropies and heat capacities are small and less significant. These values are calculated by the defined fluorinated hydrocarbon group values and thermodynamic properties of the compounds. The correction values for heats of formation increase as the number of fluorine atoms increase. It is important to note that the interaction terms for heat of formation and entropy between 3F/F and 2F/2F are different, even though the interaction is between same number of fluorines. These two molecules also have the same number of F/F gauche interactions in the most stable configurations of the two isomers. The 3F/F and 2F/2F interaction terms for heat of formation correction are 7.0 and 9.3 kcal/mol, respectively. The entropy correction terms are between 0.85 and −0.45 cal/mol K, respectively. Table 10 shows groups and interaction terms which are necessary to obtain the thermodynamic properties using the modified group additivity method reported in this paper. Estimation of thermodynamic properties may not be as accurate when extended to larger fluorocarbons; this work presents group values and thus permits their use in estimations where no other data may exist. We plan to estimate the thermodynamic parameters for C3 and C4 fluorocarbons and then test this set of interaction groups, without extension on these larger molecules. We also plan to develop four additional interaction groups; three for fluoro alkenes Cd/F2, Cd/F3, and Cd/F4, plus one for fluoro acetylenes Ct/F2.

At this point we have presented groups and interaction terms for fluoro ethanes only. These groups are of use on ethanes or species where there are terminal fluoromethyl groups. Table 7 includes values of the C/C2/F/H and the C/C2/F2 groups for use in estimating larger fluoroalkanes. Our experience with chlorocarbon groups indicates that a group is needed for halocarbons where there is an gauche interaction of a halogen atom with a alkyl (methyl, first carbon of an ethyl, etc.) group containing a halogen.[23] An initial estimate of this gauche interaction term is similar to the F/F interaction value, −0.8 kcal/mol for $H_f{}^\circ{}_{298}$. Derivation and example use of the C/C2/F/H, C/C2/F2 groups and the gauche interactions will be included in future publications, along with groups and interaction terms for unsaturated fluorocarbons.

Summary

Ab initio calculations are performed on nine fluorinated hydrocarbons using the Gaussian 94[11] system of programs at the RHF/6−31G* and MP2/6-31G* levels of theory. Thermodynamic properties (heats of formation ($\Delta H_f{}^\circ{}_{298}$), standard entropies ($S^\circ{}_{298}$), and heat capacities ($C_p(T)$'s, $300 < T/\mathrm{K} <$

TABLE 9: Thermodynamic Properties of Fluorine Groups and Their Corrections

groups	$H_f{}^\circ{}_{298}{}^a$	$S^\circ{}_{298}{}^b$	$C_{p300}{}^b$	C_{p400}	C_{p500}	C_{p600}	C_{p800}	C_{p1000}	C_{p1500}
C/C/H3[c]	−10.0	30.41	6.19	7.84	9.40	10.79	13.02	14.77	17.58
C/C/F/H2	−52.9	35.00	8.04	9.85	11.52	12.90	15.04	16.50	18.58
C/C/F2/H	−109.7	39.11	10.18	12.23	13.92	15.22	17.04	18.15	19.58
C/C/F3	−168.2	42.54	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	15.45
C/C2/F2	−104.9	17.30	10.49	12.54	13.72	14.76	15.72	16.10	16.54

correction	$H_f{}^\circ{}_{298}{}^a$	$S^\circ{}_{298}{}^b$	$C_{p300}{}^b$	C_{p400}	C_{p500}	C_{p600}	C_{p800}	C_{p1000}	C_{p1500}
F/F	−0.8	0.92	−0.21	−0.25	−0.31	−0.31	−0.34	−0.24	0.01
2F/F	4.8	0.38	0.31	0.25	0.17	0.15	0.03	0.03	0.11
3F/F	7.0	0.85	−0.14	−0.2	−0.24	−0.21	−0.26	−0.21	−0.06
2F/2F	9.3	−0.45	1.61	1.21	0.77	0.48	0.09	0.01	0.06
3F/2F	13.9	0.73	0.08	−0.15	−0.3	−0.34	−0.41	−0.34	−0.13
3F/3F	15.5	0.54	0.24	−0.09	−0.28	−0.34	−0.39	−0.31	-0.13

[a] Units in kcal/mol. [b] Units in cal/mol-K. [c] Reference 8.

TABLE 10: Composition of Groups and Interaction Terms for 9 Fluoroethanes

compounds	CH_3CH_2F	CH_2FCH_2F	CH_3CHF_2	CH_2FCHF_2	CH_3CF_3	CHF_2CHF_2	CH_2FCF_3	CHF_2CF_3	CF_3CF_3
group 1	C/C/H3	C/C/F/H2	C/C/H3	C/C/F/H2	C/C/H3	C/C/F2/H	C/C/F/H2	C/C/F2/H	C/C/F3
group2	C/C/F/H2	C/C/F/H2	C/C/F2/H	C/C/F2/H	C/C/F3	C/C/F2/H	C/C/F3	C/C/F3	C/C/F3
interaction		F/F		2F/F		2F/2F	3F/F	3F/2F	3F/3F

1500) for group values of C/C/F/H2, C/C/F2/H, and C/C/F3 are defined and a set of interaction terms F/F, 2F/F, 3F/F, 2F/2F, 3F/2F, and 3F/3F are derived for use with our proposed modified group additivity. The interactions between fluorines on adjacent carbons are strong with enthalpy corrections: −0.8, 4.8, 7.0, 9.3, 13.9, and 15.5 kcal/mol for F/F, 2F/F, 3F/F, 2F/2F, 3F/2F, and 3F/3F, respectively.

Results on entropies at RHF/6-31G*//MP2/6-31G* level of calculation with direct integration over energy levels of the exact potential energy curve of the rotational barriers show slightly higher values for most HFCs in this study compared with previously determined thermodynamic properties and different level *ab initio* calculations.[2−4,21] Values of group additivity correction terms increase significantly with an increased number of adjacent fluorines for the heats of formation. Small group additivity corrections are needed for entropies and heat capacities ($C_p(T)$'s, $300 < T/\mathrm{K} < 1500$).

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