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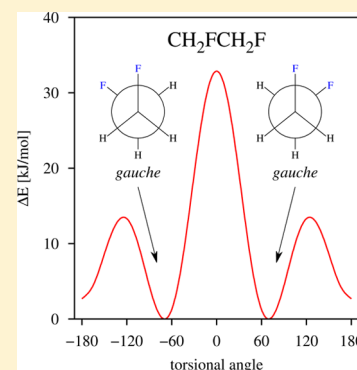
High-Accuracy Theoretical Thermochemistry of Fluoroethanes

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S Supporting Information

ABSTRACT: A highly accurate coupled-cluster-based *ab initio* model chemistry has been applied to calculate the thermodynamic functions including enthalpies of formation and standard entropies for fluorinated ethane derivatives, $C_2H_xF_{6-x}$ ($x = 0-5$), as well as ethane, C_2H_6 . The invoked composite protocol includes contributions up to quadruple excitations in coupled-cluster (CC) theory as well as corrections beyond the nonrelativistic and Born–Oppenheimer approximations. For species CH_2F-CH_2F , CH_2F-CHF_2 , and CHF_2-CHF_2 , where *anti/gauche* isomerism occurs due to the hindered rotation around the C–C bond, conformationally averaged enthalpies and entropies at 298.15 K are also calculated. The results obtained here are in reasonable agreement with previous experimental and theoretical findings, and for all fluorinated ethanes except CH_2FCH_3 and C_2F_6 this study delivers the best available theoretical enthalpy and entropy estimates.



■ INTRODUCTION

Since the 1990s hydrofluorocarbons (HFCs) and perfluorocarbons (PFCs) have been widely used in industrial and domestic refrigerants, foam blowing agents or propellant gases as ozone friendly replacements for chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs), and other ozone depleting substances. Although HFCs have low ozone depleting potential, their global warming potential¹ is considerable because of their long atmospheric lifetime and strong infrared absorption capability.² For instance, according to the most recent report of the Intergovernmental Panel on Climate Change (IPCC),³ hydrofluoroethanes remain in the atmosphere for 1.5 to 47.1 years, while perfluoroethane, C_2F_6 , has an extremely high lifetime of about 10,000 years.

Furthermore, the radiative efficiencies of these molecules (from 0.09 up to $0.23 \text{ Wm}^{-2} \text{ ppb}^{-1}$) are approximately 6500–16500 times larger⁴ than that of the reference CO_2 ($1.4 \times 10^{-4} \text{ Wm}^{-2} \text{ ppb}^{-1}$). Nevertheless, the total concentration of these species in the atmosphere is still considered to be low, and their contribution to the positive radiative forcing (RF)³ is not (yet) considerable.

At the same time, being popular replacements, the emission of HFCs and PFCs has been steadily increasing in the past two decades and, due to their possible impact on climate change, these species are covered by the Kyoto protocol.⁵ For instance, from the 1990s to 2011 the atmospheric concentration of 1,1,1,2-tetrafluoroethane (CF_3CH_2F), a replacement for dichlorodifluoromethane (CF_2Cl_2) in air conditioners, has increased from 0.09 to 62.7 ppt.^{3,4} Besides CF_3CH_2F , the abundance of several frequently used HFCs, e.g., 1,1,1-trifluoroethane (CF_3CH_3), pentafluoroethane (CF_3CHF_2), and 1,1-difluoroethane (CHF_2CH_3), has already reached or even exceeded the value of 10 ppt. Therefore, it is expected that

the rapid growth of the atmospheric concentration of these species will substantially increase their contribution to the future RF,³ making them an important factor in climate change.

The precise knowledge of kinetic and thermodynamic quantities of atmospherically important reactions and the corresponding species is of utmost importance for the so-called chemistry-climate models⁶ developed to study and understand the effects of anthropogenic activities on climate change. Although the relevant physicochemical parameters are often available in several databases, for example, NIST-JANAF tables,⁷ JPL,⁸ Burcat's compendium,⁹ and ATcT,¹⁰ many discrepancies exist, and in many cases a number of data points are associated with a relatively large uncertainty. Re-evaluation of these properties and, consequently, resolving the discrepancies among them can be performed in a straightforward manner by means of composite computational approaches^{11–19} capable of producing highly accurate and reliable thermochemical data.

In this study the thermodynamic functions including enthalpies of formation at both 0 and 298.15 K as well as standard entropies for a series of fluoroethanes are computed using a composite model chemistry. Where it appears, conformational flexibility is also taken into account; that is, conformationally averaged enthalpies and entropies are calculated as well. The results obtained are compared to thermochemical quantities reported in the literature, and a careful selection of the best available data is also presented.

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METHODS

The total energies of species involved in this study were calculated using a theoretical approach mostly inspired by the Weizmann-*n* (*Wn*)^{11,12,20,21} and the HEAT family of protocols.^{13–15} The present model chemistry and its slightly modified versions were proven to provide accurate thermodynamic quantities including heats of formation at both 0 and 298 K for several small- and medium-sized species.^{22–25} The detailed description of the protocol can be found in ref 22; nevertheless, a brief outline of the utilized computational methods is given below.

Conformers and rotational barriers were determined via a systematic search performed around the torsional angle describing the rotation around the C–C bond. In these calculations the CC method with singles, doubles, and perturbative triples²⁷ [CCSD(T)] as well as the cc-pVTZ basis set^{28,29} were used. In particular, the appropriate torsional angle was changed systematically from -180 to $+180^\circ$ by a 15° increment, and the obtained conformations were partially optimized keeping only the torsional angle fixed. After the conformational search, the obtained equilibrium structures were reoptimized at the CCSD(T)/cc-pVQZ level of theory. Then, assuming the additivity of the various contributions, the total electronic energy was calculated according to the following scheme:

$$E_{\text{TOT}} = E_{\text{HF}}^\infty + \Delta E_{\text{CCSD(T)}}^\infty + \Delta E_{\text{CCSDT}} + \Delta E_{\text{CCSDT(Q)}} + \Delta E_{\text{core}}^\infty + \Delta E_{\text{ZPE}} + \Delta E_{\text{DBOC}} + \Delta E_{\text{REL}} \quad (1)$$

where E_{HF}^∞ is the basis set limit Hartree–Fock energy extrapolated from aug-cc-pVXZ³⁰ ($X = \text{T, Q, 5}$) energies using the three-point extrapolation formula of Feller,³¹ $E_{\text{HF}}^X = E_{\text{HF}}^\infty + b \cdot e^{-cX}$. $\Delta E_{\text{CCSD(T)}}^\infty$ is the correlation contribution calculated with the CCSD(T) method and extrapolated to the basis set limit using aug-cc-pVXZ ($X = \text{Q, 5}$) results along with the two-point formula of Helgaker and co-workers,³² $E_{\text{CC}}^X = E_{\text{CC}}^\infty + B \cdot X^{-3}$. ΔE_{CCSDT} is defined as $E_{\text{CCSDT}} - E_{\text{CCSD(T)}}$, where E_{CCSDT} and $E_{\text{CCSD(T)}}$ are the correlation energies calculated with the CC method with single, double, and triple excitations (CCSDT)³³ as well as at the CCSD(T) level of theory, respectively, using the cc-pVTZ basis set. $\Delta E_{\text{CCSDT(Q)}}$ = $E_{\text{CCSDT(Q)}} - E_{\text{CCSDT}}$ is obtained with the cc-pVDZ basis set, where $E_{\text{CCSDT(Q)}}$ and E_{CCSDT} are the correlation energies calculated at the CCSDT level of theory with perturbative quadruples [CCSDT(Q)]^{34–36} and the CCSDT level, respectively. For the three correlation contributions, $\Delta E_{\text{CCSD(T)}}$, ΔE_{CCSDT} , and $\Delta E_{\text{CCSDT(Q)}}$, the frozen-core approximation was invoked. $\Delta E_{\text{core}}^\infty$ is the core correlation contribution defined as the difference between all-electron and frozen-core CCSD(T) energies. The contribution was extrapolated to the basis set limit using the above formula of Helgaker et al.³² from cc-pCVTZ and cc-pCVQZ basis set results.

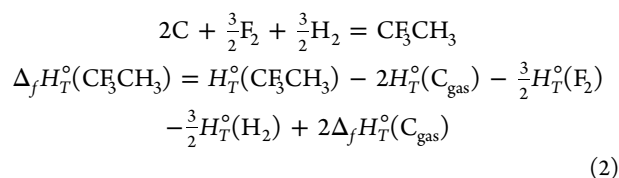
Anharmonic zero-point vibrational energies, ΔE_{ZPE} , were calculated using the resonance-independent formula of Schuurman and co-workers.³⁷ Harmonic frequencies were obtained at the CCSD(T)/cc-pVQZ level of theory, while cubic and quartic force constants as well as Coriolis couplings were taken from CCSD(T)/cc-pVTZ calculations. Due to convergence problems, cubic and quartic force constants as well as Coriolis couplings for CF_3CH_3 were obtained at the all-electron MP2/cc-pVTZ level of theory.

Diagonal Born–Oppenheimer corrections³⁸ (ΔE_{DBOC}) were calculated at the CCSD/cc-pCVTZ level of theory. The scalar relativistic effects were evaluated by determining the expectation value of the mass-velocity and one- and two-electron Darwin operators at the CCSD(T)/cc-pCVTZ level. Furthermore, for the carbon atom, the energy lowering of the lowest spin–orbit state with respect to the energy evaluated within a spin–orbit-free, scalar relativistic approximation was also considered. This contribution, $-135 \mu E_{\text{h}}$, was calculated from the experimental fine-structure splittings available in the NIST Atomic Spectra Database.³⁹

For CCSDT(Q) calculations, the MRCC⁴¹ program was invoked, while all other calculations were performed with the C_{FOUR} package.⁴²

From the computed total energies, frequencies, and rotational constants, standard enthalpies and entropies were calculated at $T = 0$ and 298.15 K at a pressure of 1 bar via the standard formulas of statistical thermodynamics within the ideal gas approximation.⁴³ It was further assumed that the excited states of the molecules studied here lie far above the ground states; therefore, the electronic contribution to the molecular partition function was set to one. For the rotational and vibrational degrees of freedom, the rigid rotor-harmonic oscillator (RRHO) approximation was invoked. To correct the errors of the RRHO model for the hindered rotations around the C–C bond in the molecules, a one-dimensional hindered rotor model (1D-HR) was applied, where the partition function calculated for the hindered rotor was used to correct the ZPE, entropy, and thermal correction values. Briefly, at the calculation of ZPE via eq 3 of ref 37, the lowest solution of the 1D-HR model was substituted for the contribution of the harmonic frequency associated with the rotational motion in the first term of the equation. Furthermore, the one-fourth of the diagonal element of the anharmonicity matrix belonging to the internal rotational motion (x_{ii} obtained with C_{FOUR}) was subtracted from the total anharmonic contribution, while the off-diagonal elements describing the interactions of the different normal modes were retained. For entropies and temperature corrections to enthalpies, the partition functions were explicitly calculated for the rotational motion considering the eigenvalues of the rotational Hamiltonian. Further details of our 1D-HR calculations can be found in refs 22–24, and 25 as well as references therein.

To obtain the heats of formation from the calculated enthalpies, the elemental reaction approach was used.^{13,22–25} For instance, the heat of formation of CF_3CH_3 was calculated according to the following scheme:



The reference state of the elements H_2 and F_2 was defined as it is standard in thermochemistry. For carbon the gaseous atom was used as a reference state. For the heat of formation of the carbon atom at 0 K, $\Delta_f H_0^\circ(\text{C}_{\text{gas}})$, the *ab initio* data of ref 44, 711.65 ± 0.32 kJ/mol was adopted. This value was established on the basis of the high-level *ab initio* atomization energy of the CO molecule using auxiliary data of $\Delta_f H_0^\circ(\text{CO}) = 113.82 \pm 0.03$ kJ/mol and $\Delta_f H_0^\circ(\text{O}) = 246.84 \pm 0.00$ kJ/mol taken from the ATcT database.¹⁰ To calculate the heat of formation at

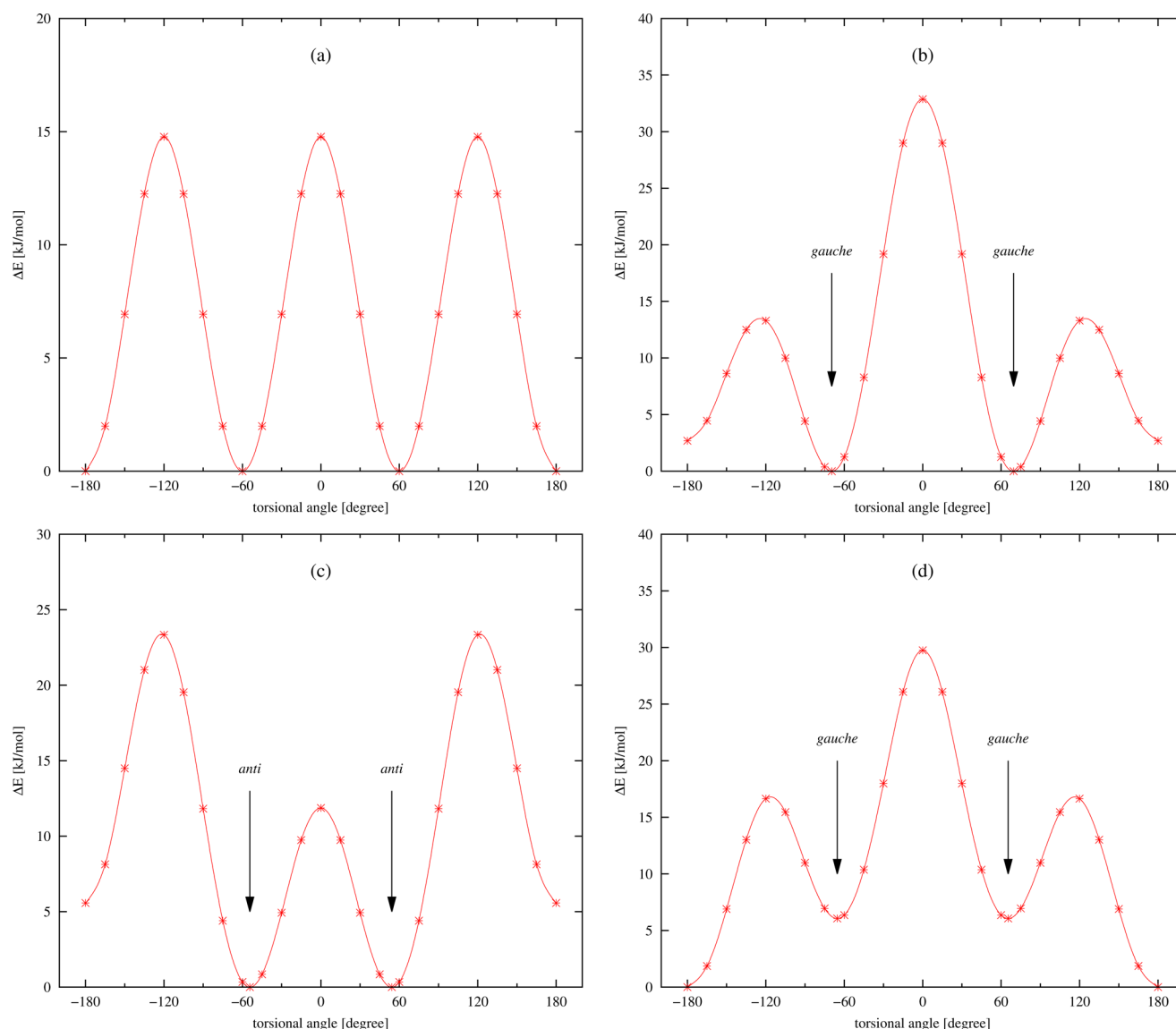


Figure 1. Potential energy curves calculated at the CCSD(T)/cc-pVTZ level. Every molecular coordinate was fully relaxed except the scanned torsional angle. Only one representative example, CH_2FCH_3 , is shown here for species where no *anti/gauche* isomerism exists. (a) CH_2FCH_3 ; (b) $\text{CH}_2\text{FCH}_2\text{F}$; (c) $\text{CHF}_2\text{CH}_2\text{F}$; (d) CHF_2CHF_2 . Potential energy curves for the other molecules are shown in the Supporting Information.

298.15 K, the thermal correction, $\Delta_f H_{298}^\circ - \Delta_f H_0^\circ$, was obtained from the NIST-JANAF tables,⁷ resulting in $\Delta_f H_{298}^\circ(\text{C}_{\text{gas}}) = 717.13 \pm 0.32$ kJ/mol.

The error bars introduced by the present protocol were investigated thoroughly in ref 22, and its validity was also proven in refs 24, 23, and 25. Briefly, based on a comparison to accurate literature data, a size- and composition-dependent error estimate was introduced; that is, to determine the 95% confidence interval of the calculated heats of formation for a given species, 0.4 kJ/mol was taken as the uncertainty for every first row atom and these contributions were summed. Therefore, for every heat of formation value calculated in this study, an associated uncertainty of ± 3.2 kJ/mol is attached. For CF_3CH_3 , where anharmonicity correction was obtained at the MP2/cc-pVTZ level, an additional error increment of 0.1 kJ/mol was also considered, resulting in a total uncertainty of ± 3.3 kJ/mol. This increment was obtained as the difference between anharmonic contributions obtained at the CCSD(T)/cc-pVTZ and MP2/cc-pVTZ levels for CHF_2CH_3 .

The uncertainty associated with the calculated entropy data is based on a statistical analysis for a benchmark data set of 15 methane derivatives including radicals. The present protocol yielded an rms deviation of 0.6 J/(K·mol) against accurate entropy values.²² Therefore, our conservative estimate is 1.5 J/(K·mol) for the 95% confidence interval of our entropy data.

This study includes three species, $\text{CH}_2\text{FCH}_2\text{F}$, $\text{CHF}_2\text{CH}_2\text{F}$, and CHF_2CHF_2 , where conformational isomerism occurs; that is, *anti* and *gauche* conformers of the species exist relative to the position of the fluorine atoms. The stereochemistry of these three HFCs is shown in terms of Newman projections in the Supporting Information. For these molecules conformationally averaged heat of formation and entropy values were also determined at 298.15 K. The statistical distribution of the conformers was calculated according to the Boltzmann distribution of the form:

$$\frac{N_{anti}}{N_{gauche}} = n \exp \left\{ - \frac{\Delta_f G_{298}^{o}(anti) - \Delta_f G_{298}^{o}(gauche)}{RT} \right\} \quad (3)$$

where $\Delta_f G_{298}^{o}(anti)$ and $\Delta_f G_{298}^{o}(gauche)$ are the Gibbs energies of formation for the *anti* and the *gauche* conformers at 298.15 K, respectively, calculated as $\Delta_f H_{298}^{o} - TS_{298}^{o}$, and n is related to the statistical weight of the conformations. That is, n equals 1/2 for $\text{CH}_2\text{FCH}_2\text{F}$ and CHF_2CHF_2 where two *gauche* rotamers exist, while it is 2 for $\text{CHF}_2\text{CH}_2\text{F}$ where a mirror-image pair of *anti* conformations can be observed.

The conformationally averaged enthalpy value [$\Delta_f H_{298}^{o}(\text{c.a.})$] was derived as the weighted arithmetic mean of the individual heat of formation values for the two conformers, $\Delta_f H_{298}^{o}(anti)$ and $\Delta_f H_{298}^{o}(gauche)$, where the weights are the appropriate molar fractions calculated from eq 3:

$$\Delta_f H_{298}^{o}(\text{c.a.}) = x_{anti} \Delta_f H_{298}^{o}(anti) + (1 - x_{anti}) \Delta_f H_{298}^{o}(gauche) \quad (4)$$

In addition to the weighted mean of the individual entropies, the entropy of mixing (ΔS_{mix}) should also be considered to derive the conformationally averaged quantity, $S_{298}^{o}(\text{c.a.})$. Therefore, within the ideal gas approximation the averaged entropy can be calculated as follows:

$$S_{298}^{o}(\text{c.a.}) = x_{anti} S_{298}^{o}(anti) + (1 - x_{anti}) S_{298}^{o}(gauche) + \Delta S_{\text{mix}} \quad (5)$$

where ΔS_{mix} can be obtained from the corresponding molar fractions using the standard formula of thermodynamics.

Straightforward error bars can also be introduced to our averaged enthalpies and entropies relying on the standard formulas of error propagation:⁴⁵

$$\begin{aligned} \sigma_{\Delta_f H_{298}^{o}(\text{c.a.})} &= \left[\left(\frac{\partial \Delta_f H_{298}^{o}(\text{c.a.})}{\partial \Delta_f H_{298}^{o}(a)} \right)^2 \sigma_{\Delta_f H_{298}^{o}(a)}^2 + \left(\frac{\partial \Delta_f H_{298}^{o}(\text{c.a.})}{\partial \Delta_f H_{298}^{o}(g)} \right)^2 \sigma_{\Delta_f H_{298}^{o}(g)}^2 \right. \\ &\quad \left. + \left(\frac{\partial \Delta_f H_{298}^{o}(\text{c.a.})}{\partial S_{298}^{o}(a)} \right)^2 \sigma_{S_{298}^{o}(a)}^2 + \left(\frac{\partial \Delta_f H_{298}^{o}(\text{c.a.})}{\partial S_{298}^{o}(g)} \right)^2 \sigma_{S_{298}^{o}(g)}^2 \right]^{1/2} \end{aligned} \quad (6)$$

where $\sigma_{\Delta_f H_{298}^{o}}$ and $\sigma_{S_{298}^{o}}$ are the uncertainties of our calculated $\Delta_f H_{298}^{o}$ and S_{298}^{o} values, respectively, and the abbreviations *a* and *g* stand for *anti* and *gauche*, respectively. Similar equations can be derived for the uncertainties $\sigma_{S_{298}^{o}(\text{c.a.})}$ and $\sigma_{x_{anti}}$ associated with the conformationally averaged entropy and the molar fraction for the *anti* rotamer, respectively.

RESULTS AND DISCUSSION

Conformational Analysis. Figure 1 shows the potential energy curves for four species investigated in this study obtained at the CCSD(T)/cc-pVTZ level of theory. In all cases, three local minima exist along the rotational potential energy curve. For ethane as well as CH_2FCH_3 , CHF_2CH_3 , CF_3CH_3 , $\text{CF}_3\text{CH}_2\text{F}$, CF_3CHF_2 , and C_2F_6 , these three minima are indistinguishable. Because of the similarity of the potential energy curves for these molecules, only one representative example, CH_2FCH_3 , is considered in Figure 1. Potential energy curves for the rest of the species are shown in Figure S1 in the Supporting Information. For $\text{CH}_2\text{FCH}_2\text{F}$ and CHF_2CHF_2 an

anti and two *gauche* rotamers (mirror-image pairs) can be observed, $\text{CHF}_2\text{CH}_2\text{F}$ has a single *gauche* rotamer and a mirror-image pair of *anti* conformations. The rotational barriers between the stable structures along with the low-frequencies as well as the corrections to the zero-point energies, thermal corrections, and entropies calculated by means of the one-dimensional hindered rotor treatment are listed in Table 1. Solutions of the 1D-HR calculations, i.e., energy levels for the hindered rotations of the molecules are listed in the Supporting Information.

Table 1. Hindered-Rotor Treatment of Low-Frequency Motions^a

species	$\tilde{\nu}^b$	barrier ^c	ΔZPE^d	$\Delta(H_{298}^{o} - H_0^o)^d$	$\Delta S_{298}^{o,d}$
CH_2FCH_3	253.6	1235	−0.22	0.21	1.10
CHF_2CH_3	234.6	1198	−0.18	0.20	1.09
CF_3CH_3	231.0	1170	−0.09	0.20	1.12
<i>anti</i> - $\text{CH}_2\text{FCH}_2\text{F}$	120.6	1080	0.09	0.56	8.77
<i>gauche</i> - $\text{CH}_2\text{FCH}_2\text{F}$	152.4	2716	−0.11	0.70	10.64
<i>anti</i> - $\text{CHF}_2\text{CH}_2\text{F}$	120.8	963	0.01	0.40	7.92
<i>gauche</i> - $\text{CHF}_2\text{CH}_2\text{F}$	118.9	1923	0.02	0.39	7.79
$\text{CF}_3\text{CH}_2\text{F}$	113.6	1448	0.06	0.15	0.81
<i>anti</i> - CHF_2CHF_2	85.2	1392	−0.06	1.00	5.98
<i>gauche</i> - CHF_2CHF_2	84.3	2487	−0.05	1.00	5.89
CF_3CHF_2	78.6	1427	−0.24	0.16	0.90
C_2F_6	70.8	1564	0.00	0.13	0.75
C_2H_6	309.4	1040	−0.12	0.24	1.30

^aWavenumbers ($\tilde{\nu}$) and barrier heights are given in cm^{-1} ; ZPE and thermal correction [$\Delta(H_{298}^{o} - H_0^o)$] values are in kJ/mol, while entropy data (ΔS_{298}^{o}) are in J/(K·mol). ^bThe calculated wavenumber associated with the low-frequency rotational motion. ^cThe height of the barrier along the low-frequency motion. ^dThe difference between the results of the harmonic-oscillator and hindered rotor treatment for the given quantity.

In the case of $\text{CH}_2\text{FCH}_2\text{F}$, according to previous experimental⁴⁶ and calculated⁴⁷ results, the less symmetric polar or *gauche* rotamer (C_2 point group), due to the so-called *gauche* effect,^{48–51} is more stable by 2.5–3.4 kJ/mol than the nonpolar or *anti* rotamer (C_{2h} point group). Furthermore, at room temperature the *gauche* conformer was found to be 85–96% abundant.^{52,53} These results are in excellent agreement with our findings: at room temperature our protocol yielded 3.4 kJ/mol for the difference between the Gibbs energies of the two rotamers, and by applying eq 3, the abundance of 87⁺¹³_{−22}% was obtained for the *gauche* rotamer.

For $\text{CHF}_2\text{CH}_2\text{F}$ the *anti* rotamer belongs to the C_1 symmetry point group, whereas the *gauche* conformation has C_s symmetry. On the basis of gas phase IR and Raman experiments, Kalasinsky and co-workers⁵⁴ found the *anti* rotamer to be more stable by 4.4 ± 1.7 kJ/mol. Based on a gas phase electron diffraction investigation at 265 K, Beagley and Brown⁵⁵ reported an abundance of $92 \pm 5\%$ for the *anti* conformer. Furthermore, they predicted the *anti-gauche* energy difference to be in the range of 2.5–7.1 kJ/mol with the most likely value of 3.8 kJ/mol. The *ab initio* calculations of Chen and associates⁵⁶ at the MP4/6-311G* level of theory also found the *anti* rotamer to be more stable by 6.9 kJ/mol. Our calculations yielded 5.6 kJ/mol for the Gibbs energy difference between the two conformers at 298 K and an abundance of 95⁺⁵_{−9}% for the more stable *anti* rotamer, in good accordance with the previous findings.

Table 2. Summary of Literature Data for Standard Enthalpies (kJ/mol) and Entropies [J/(K·mol)] for Fluoroethanes

species ^a	$\Delta_f H_0^\circ$	$\Delta_f H_{298}^\circ$ ^b	S_{298}°	notes and refs ^c
CH ₂ FCH ₃	-257.8 ± 1.0	-272.6 ± 1.0	270.6	ATcT, ref 9
	-248.3	-263.2 ± 1.7	265.0	ref 60
	-263.3 ± 1.7	-278.2 ± 1.7	265.1	MCG3//MCQCISD, refs 8, 61, 62
		-277.4 ± 4.2		ref 63
	-256.7	-272.2		W4, ref 64
		-264.0		GA, ref 65
		-272.2		ref 66
		-272.8		ATOMIC, ref 67
		[-272.4; -266.4]		BAC/AAC-MPn, refs 68, 69
		[-273.1; -268.6]		BAC/AAC-Gn, refs 69–72
		[-297.9; -270.6]		Gn, refs 69–76
		[-277.7; -268.2]		(BAC-)CBS- <i>n</i> , ref 72
	-486.8 ± 5.8	-500.5 ± 5.8	282.5	ATcT, ref 9
	-486.9 ± 6.3	-500.8 ± 6.3	282.4	refs 8, 60
CHF ₂ CH ₃		-490.8 ± 8.4		ref 77
		-494.1		GA, ref 65
		[-505.3; -499.8]		BAC/AAC-MPn, refs 68, 69, 72
		[-518.3; -499.0]		BAC/AAC-Gn, refs 69–72
		[-518.4; -500.7]		Gn, refs 69–73, 75, 76
		[-510.0; -498.3]		(BAC-)CBS- <i>n</i> , ref 72
	-742.9 ± 1.0	-755.7 ± 1.0	287.7	G3B3LYP, ref 9
	-732.8	-745.6 ± 1.7	287.3	refs 8, 60
		-749.0 ± 2.0		ref 78
		-748.7 ± 3.2		ref 77
CF ₃ CH ₃		-747.3 ± 6.3		ref 79
		-743.9		GA, ref 65
		[-757.2; -747.7]		BAC/AAC-MPn, refs 68, 69, 72
		[-773.9; -746.7]		BAC/AAC-Gn, refs 69–72
		[-775.4; -745.6]		Gn, refs 69–73, 75, 76
		[-764.4; -746.9]		(BAC-)CBS- <i>n</i> , ref 72
	-436.7 ± 4.9	-433.5 ± 4.2	286.3	GA, refs 8, 80
		-450.4 ± 4.9		ATcT, ref 9
		-433.9 ± 11.8		ref 68
		[-446.0; -432.7]		BAC/AAC-MPn, refs 68, 69, 72
<i>a/g</i> -CH ₂ FCH ₂ F		[-445.8; -440.7]		BAC/AAC-Gn, refs 69–72
		[-464.0; -429.7]		Gn, refs 69–75
		[-457.5; -442.6]		(BAC-)CBS- <i>n</i> , ref 72
		-665.0 ± 4.0		ref 8, 81
		-691.0 ± 10.0		ref 77
		-665.7		GA, ref 65
	-643.7	-656.1	309.2	MP4//HF, anti, ref 56
		[-671.5; -656.5]		BAC/AAC-MPn, refs 68, 69, 72
		[-664.0; -660.8]		BAC/AAC-Gn, refs 69–72
		[-691.7; -656.5]		Gn, refs 69–76
CF ₃ CH ₂ F		[-680.0; -661.7]		(BAC-)CBS- <i>n</i> , ref 72
	-884.5	-896.0 ± 8.0	316.2	refs 8, 60
	-902.0 ± 17.5	-913.3 ± 17.5	315.8	BAC-MP4, ref 9, 68
		[-913.3; -905.7]		BAC/AAC-MPn, refs 68, 69, 72
		[-909.8; -901.9]		BAC/AAC-Gn, refs 69–72
		[-940.2; -892.4]		Gn, refs 69–75
		[-925.0; -901.6]		(BAC-)CBS- <i>n</i> , ref 72
	-872.2 ± 5.5	-883.3 ± 5.6	313.1	BAC-MP4, ref 9
		-860.0 ± 24.0	320.3	refs 8, 82
	-864.6	-874.9	317.1	MP4//HF, anti, ref 56
<i>a/g</i> -CHF ₂ CHF ₂		[-886.1; -873.0]		BAC/AAC-MPn, refs 68, 69, 72
		[-882.7; -870.8]		BAC/AAC-Gn, refs 69–72
		[-913.2; -877.0]		Gn, refs 69–75
		[-902.2; -881.3]		(BAC-)CBS- <i>n</i> , ref 72
	-1095.0 ± 5.0	-1105.0 ± 5.0	333.7	ref 8, 60
	-1110.4 ± 8.0	-1120.0 ± 8.0	334.6	G3B3, ref 9
		[-1124.1; -1114.2]		BAC/AAC-MPn, refs 68, 69, 72
CF ₃ CHF ₂				

Table 2. continued

species ^a	$\Delta_f H_0^\circ$	$\Delta_f H_{298}^\circ$ ^b	S_{298}°	notes and refs ^c
C ₂ F ₆		[−1115.2; −1105.5]		BAC/AAC-Gn, refs 69–72
		[−1153.9; −1105.0]		Gn, refs 69–75
		[−1135.2; −1103.8]		(BAC−)CBS- <i>n</i> , ref 72
	−1342.2 ± 1.6	−1350.5 ± 1.6	341.0	ATcT, ref 9
	−1336.0 ± 3.4	−1344.3 ± 3.4		refs 8, 83
	−1324.4 ± 4.0	−1328.9 ± 4.0	334.5	CCSD(T)//B3LYP, ref
	−1335.6 ± 5.0	−1343.9 ± 5.0	332.2 ± 0.8	ref 7
	−1334.3	−1342.6 ± 6.2	331.8	ref 60
		−1345.6		GA, ref 65
	−1340.6	−1348.7	333.5	G3MP2 refs 85, 86
C ₂ H ₆		[−1357.1; −1354.9]		BAC/AAC-MPn, refs 68, 69, 72
		[−1346.3; −1335.3]		BAC/AAC-Gn, refs 69–72
		[−1392.9; −1342.1]		Gn, refs 69–73, 75
		[−1371.0; −1333.8]		(BAC−)CBS- <i>n</i> , ref 72
	−68.2 ± 0.2	−83.8 ± 0.2	229.2	ATcT, ref 9
		−83.8 ± 0.3		refs 8, 87
	−68.4 ± 0.4	−84.0 ± 0.4	229.2	ref 62
	−67.8	−84.1		W4, ref 88
	−68.2	−84.5		W4, ref 88
	−69.0	−84.7	229.1	ref 89
		[−92.9; −80.1]		BAC/AAC-MPn, refs 68, 69, 72
		[−86.0; −80.6]		BAC/AAC-Gn, refs 69–72
		[−87.4; −82.6]		Gn, refs 69–73, 75
		[−92.1; −81.5]		(BAC−)CBS- <i>n</i> , ref 72

^aThe prefix *a/g* stands for *anti/gauche*. ^bSquare brackets denote intervals for calculated results. That is, only the lowest and the highest values obtained with the corresponding method are indicated. ^cFor experimental and evaluated data only the reference is listed; otherwise, the computational method is indicated.

Table 3. Calculated Thermochemical Quantities for Fluoroethanes^a

species	$H_{298}^\circ - H_0^\circ$	$\Delta_f H_0^\circ$	$\Delta_f H_{298}^\circ$	$\Delta_f H_{298}^\circ(\text{c.a.})^b$	S_{298}°	$S_{298}^\circ(\text{c.a.})^b$
CH ₂ FCH ₃	12.7	−257.0 ± 3.2	−272.5 ± 3.2		264.6 ± 1.5	
CHF ₂ CH ₃	13.9	−488.6 ± 3.2	−503.0 ± 3.2		282.0 ± 1.5	
CF ₃ CH ₃	15.2	−738.3 ± 3.3	−751.5 ± 3.3		286.8 ± 1.5	
<i>anti</i> -CH ₂ FCH ₂ F	14.7	−429.8 ± 3.2	−443.4 ± 3.2	−446.9 ± 3.4	289.5 ± 1.5	296.8 ± 2.8
<i>gauche</i> -CH ₂ FCH ₂ F	14.5	−433.5 ± 3.2	−447.3 ± 3.2		288.8 ± 1.5	
<i>anti</i> -CHF ₂ CH ₂ F	15.7	−653.7 ± 3.2	−666.4 ± 3.2	−666.1 ± 3.4	309.8 ± 1.5	316.9 ± 2.0
<i>gauche</i> -CHF ₂ CH ₂ F	15.6	−648.3 ± 3.2	−661.0 ± 3.2		309.2 ± 1.5	
CF ₃ CH ₂ F	16.8	−894.6 ± 3.2	−906.2 ± 3.2		316.0 ± 1.5	
<i>anti</i> -CHF ₂ CHF ₂	17.8	−867.9 ± 3.2	−878.4 ± 3.2	−877.6 ± 3.8	319.0 ± 1.5	323.2 ± 4.7
<i>gauche</i> -CHF ₂ CHF ₂	17.8	−861.7 ± 3.2	−872.2 ± 3.2		318.9 ± 1.5	
CF ₃ CHF ₂	18.5	−1100.6 ± 3.2	−1110.6 ± 3.2		332.9 ± 1.5	
C ₂ F ₆	20.0	−1331.3 ± 3.2	−1339.8 ± 3.2		331.0 ± 1.5	
C ₂ H ₆	11.9	−68.2 ± 3.2	−84.5 ± 3.2		228.9 ± 1.5	

^aHeats of formation and thermal corrections are in kJ/mol and standard entropies are in J/(K·mol). ^bConformationally averaged value. See text for details.

According to the spectroscopic study of Kalasinsky et al.⁵⁴ and that of Klaboe and Nielsen,⁵⁷ the *anti* conformation of CHF₂CHF₂ with the C_{2h} molecular symmetry is more stable than the less symmetric (C₂) *gauche* rotamer in the gas phase by 4.9 ± 0.4 kJ/mol. The same energy difference with a higher uncertainty, 4.9 ± 0.8 kJ/mol, was measured earlier⁵⁸ by means of gas phase electron diffraction at 253 K along with the *anti* abundance of 84 ± 6%. The NMR study of Cavalli and Abraham⁵⁹ predicted a somewhat higher value, 10 kJ/mol, for the energy difference. The MP4/6-311G** calculations of Chen and associates⁵⁶ resulted in an *anti-gauche* difference of 6.2 kJ/mol, which lies approximately in the middle of the previous experimental results. Our protocol also favors the *anti* rotamer to be more stable than the *gauche* one by 6.2 kJ/mol at

room temperature, and the calculated abundance of the former is 86⁺¹⁴_{−22}%. Consequently, our values agree well with previous experimental and computational results.

Thermodynamic Functions. An extensive summary of available literature data for the heat of formation and entropy values for ethane and its fluorinated derivatives is given in Table 2. Our calculated results including temperature corrections as well as enthalpies and entropies along with their conformationally averaged values are summarized in Table 3. In the following, after a short general discussion, the most relevant thermodynamic data for each molecule will be briefly reviewed.

Considering the computational results listed in Table 2, it can be seen that the most widely used methods are the earlier composite approaches augmented with empirical atom (AAs)

or bond (BACs) additivity corrections. Zachariah and co-workers⁶⁸ applied the BAC-MP4 method^{90,91} to study the thermodynamic properties of a large number of C₁ and C₂ HFCs. Very briefly, this method is based on MP4/6-31G(d,p) single point calculations using HF/6-31G(d) geometries and harmonic frequencies.

Kondo et al.⁶⁹ performed BAC-MP2 as well as BAC-MP4 calculations with the 6-31G(d,p) basis set. They also carried out some calculations at the MP2/6-31G(d,p), G2, and G2MP2 levels of theory and then applied atom additivity corrections.

Zhang and associates⁷⁰ performed a large number of calculations on C₁ and C₂ CFCs, HCFCs, and HFCs using the G3, G3MP2, G3MP2B3, and G3B3 methods. Heat of formation values were calculated on the basis of the atomization energy approach as well as isodesmic reaction schemes. In order to improve the accuracy of their results, BACs were also taken into consideration; that is, the BAC-G3, BAC-G3MP2, BAC-G3MP2B3, and BAC-G3B3 approaches were also used.

Berry et al.^{71,72} applied various composite protocols and also the BAC-MP4 method to calculate heats of formation for fluoroethanes. The G2, G2(MP2), CBS-4, and CBS-Q model chemistries along with their bond additivity counterparts were invoked in these studies. Yamada and co-workers⁷⁴ used the G2(MP2) method as well; however, their calculations were based on isodesmic reaction schemes.

Haworth and associates⁷⁵ calculated the thermodynamic properties for a number of C₁ and C₂ HFCs and their oxidized derivatives applying the G3, G3[MP2(full)], G3(MP4SDQ), G2, and G2MP2 approaches.

Bond⁷⁶ used a bond separation method relying on G3 and G3MP2 calculations along with the experimental heat of formation for fluoromethane as a basis to calculate enthalpies and free energies of formation for fluoromethanes and fluoroethanes.

Recently, Rayne and Forest⁷³ studied the performance of the G3 and G4 model chemistries in calculating enthalpies for small CFCs, HCFCs, and HFCs within the atomization energy approach.

Comparing our protocol with the above-described methods, it is fair to say that our model chemistry is much more advanced. Consequently, our thermochemical results supersede all data in accuracy calculated with the earlier composite approaches.

A limited number of experimentally derived data points are also available for the species studied here. Most of these results are discussed and, in some cases, corrected and re-evaluated in the reviews of Chen and co-workers⁶⁰ as well as Kolesov and Papina.⁷⁷ As can be seen in Tables 2 and 3, the experimental values are more or less consistent with the theoretical ones; however, notable exceptions do exist.

In the following subsections the most relevant experimental and theoretical thermochemical data for each fluoroethane compound studied in this paper are briefly discussed. The best available thermochemical quantities are collected in Table 4.

CH₂FCH₃. Kormos and co-workers⁶¹ calculated enthalpies of formation for several monofluorinated alkanes using the multicoefficient (MC) G3 method on equilibrium structures obtained at the MCQCISD level of theory. For CH₂FCH₃, the 298 K heat of formation value of -278.2 ± 1.7 kJ/mol was recommended.

Bakowies⁶⁷ also investigated the heat of formation of CH₂FCH₃ using another composite approach termed ATOMIC,⁹² which applies simple precomputed isodesmic

Table 4. Best Available Enthalpies of Formation at 0 and 298.15 K (in kJ/mol) as Well as Standard Molar Entropies at 298.15 K [J/(K·mol)] for Fluoroethanes^a

species	$\Delta_f H_0^\circ$	$\Delta_f H_{298}^\circ$	S_{298}°
CH ₂ FCH ₃	-257.8 ± 1.0^b	-272.6 ± 1.0^b	264.6 ± 1.5
CHF ₂ CH ₃	-488.6 ± 3.2	-503.0 ± 3.2	282.0 ± 1.5
CF ₃ CH ₃	-737.2 ± 3.3^c	-750.3 ± 3.3^c	286.8 ± 1.5
<i>anti</i> -CH ₂ FCH ₂ F	-429.8 ± 3.2	-443.4 ± 3.2	289.5 ± 1.5
<i>gauche</i> -CH ₂ FCH ₂ F	-433.5 ± 3.2	-447.3 ± 3.2	288.8 ± 1.5
		-446.9 ± 3.4^d	296.8 ± 2.8^d
<i>anti</i> -CHF ₂ CH ₂ F	-653.7 ± 3.2	-666.4 ± 3.2	309.8 ± 1.5
<i>gauche</i> -CHF ₂ CH ₂ F	-648.3 ± 3.2	-661.0 ± 3.2	309.2 ± 1.5
		-666.1 ± 3.4^d	316.9 ± 2.0^d
CF ₃ CH ₂ F	-894.6 ± 3.2	-906.2 ± 3.2	316.0 ± 1.5
<i>anti</i> -CHF ₂ CHF ₂	-867.9 ± 3.2	-878.4 ± 3.2	319.0 ± 1.5
<i>gauche</i> -CHF ₂ CHF ₂	-861.7 ± 3.2	-872.2 ± 3.2	318.9 ± 1.5
		-877.6 ± 3.8^d	323.2 ± 4.7^d
CF ₃ CHF ₂	-1100.6 ± 3.2	-1110.6 ± 3.2	332.9 ± 1.5
C ₂ F ₆	-1334.3 ± 4.0^c	-1342.6 ± 4.0^c	332.2 ± 0.8^e

^aPreviously established values are set as italic. ^bReference 9. ^cAveraged value. See text for details. ^dConformationally averaged value. See text for details. ^eReference 7.

corrections to estimate contributions beyond the CCSD(T) level. The most accurate version of this protocol yielded -272.8 kJ/mol for CH₂FCH₃.

The W4 model chemistry of Martin and co-workers¹² yielded 2837.7 kJ/mol⁶⁴ for the atomization energy of CH₂FCH₃ at 0 K, which can be converted to an enthalpy of formation $\Delta_f H_0^\circ(\text{CH}_2\text{FCH}_3) = -256.7$ kJ/mol using literature data for $\Delta_f H_0^\circ(\text{H})$,⁷ $\Delta_f H_0^\circ(\text{C})$,⁴⁴ and $\Delta_f H_0^\circ(\text{F})$.⁹³ Furthermore, $\Delta_f H_0^\circ(\text{CH}_2\text{FCH}_3) = -272.2$ kJ/mol can be obtained using the thermal correction calculated in this study.

Based on a quantitative relationship between heats of formation and covalent potential⁹⁴—a scale of electronegativity (EN), which was derived from Yuan's EN scale⁹⁵—Luo and Benson⁶³ estimated $\Delta_f H_{298}^\circ(\text{CH}_2\text{FCH}_3)$ to be -277.4 ± 4.2 kJ/mol. A year later, using the concept of electronegativity equilibration, Smith⁶⁶ obtained $\Delta_f H_{298}^\circ(\text{CH}_2\text{FCH}_3) = -272.2$ kJ/mol with a bond energy scheme based on the traditional Pauling electronegativities.

Burcat's compendium⁹ using the data from the most recent version of ATcT¹⁰ lists $\Delta_f H_0^\circ(\text{CH}_2\text{FCH}_3) = -257.8 \pm 1.0$ kJ/mol and $\Delta_f H_{298}^\circ(\text{CH}_2\text{FCH}_3) = -272.6 \pm 1.0$ kJ/mol.

Our protocol yielded $\Delta_f H_0^\circ(\text{CH}_2\text{FCH}_3) = -257.0 \pm 3.2$ kJ/mol and $\Delta_f H_{298}^\circ(\text{CH}_2\text{FCH}_3) = -272.5 \pm 3.2$ kJ/mol, in excellent agreement with both the most recent ATcT data and the W4 results of Martin and associates.⁶⁴ Because our results are associated with a considerably higher uncertainty, we suggest the ATcT values, $\Delta_f H_0^\circ(\text{CH}_2\text{FCH}_3) = -257.8 \pm 1.0$ kJ/mol and $\Delta_f H_{298}^\circ(\text{CH}_2\text{FCH}_3) = -272.6 \pm 1.0$ kJ/mol, as the best available benchmark data for the heat of formation of this species.

The JPL database⁸ lists the entropy data of $S_{298}^\circ(\text{CH}_2\text{FCH}_3) = 265.1$ J/(K·mol) published by Gurvich et al.⁶² In a reasonable agreement with this latter result, Chen and associates⁶⁰ estimated $S_{298}^\circ(\text{CH}_2\text{FCH}_3)$ to be 265.0 J/(K·mol). An entropy value of 270.6 J/(K·mol) is listed in Burcat's database;⁹ it is calculated using frequencies from ref 96 and auxiliary data from B3LYP calculations. Our entropy, $S_{298}^\circ(\text{CH}_2\text{FCH}_3) = 264.6 \pm 1.5$ J/(K·mol), is in a reasonable agreement with those obtained by Gurvich and Chen. Nevertheless, due to the lack of well-

defined error bars attached to their estimates, we suggest our calculated data as a new reference for $S_{298}^{\circ}(\text{CH}_2\text{FCH}_3)$.

CHF_2CH_3 . Kolesov and co-workers⁹⁷ measured the heat of combustion for 1,1-difluoroethane in a bomb calorimeter. Based on the reaction enthalpy, -1219.6 ± 8.4 kJ/mol, $\Delta_f H_0^{\circ}(\text{CHF}_2\text{CH}_3) = -497.0 \pm 8.5$ kJ/mol was obtained.⁷⁷ Chen et al.⁶⁰ recommended a revised value, -1216.3 ± 6.3 kJ/mol, for the above combustion process and obtained $\Delta_f H_{298}^{\circ}(\text{CH}_2\text{FCH}_3) = -500.1 \pm 6.3$ kJ/mol.

The most recent version of Burcat's database⁹ uses the ATcT values¹⁰ and recommends $\Delta_f H_0^{\circ}(\text{CHF}_2\text{CH}_3) = -486.8 \pm 5.8$ kJ/mol and $\Delta_f H_{298}^{\circ}(\text{CHF}_2\text{CH}_3) = -500.5 \pm 5.8$ kJ/mol.

With our present protocol, -488.6 ± 3.2 and -503.0 ± 3.2 kJ/mol were obtained for $\Delta_f H_0^{\circ}(\text{CH}_2\text{FCH}_3)$ and $\Delta_f H_{298}^{\circ}(\text{CH}_2\text{FCH}_3)$, respectively. These results are in line with the previously established experimental as well as theoretical values. Since our enthalpies are associated with the tightest error bars, we suggest our results as theoretical benchmarks for $\Delta_f H_0^{\circ}(\text{CHF}_2\text{CH}_3)$ and $\Delta_f H_{298}^{\circ}(\text{CHF}_2\text{CH}_3)$.

Chen et al.⁶⁰ estimated $S_{298}^{\circ}(\text{CHF}_2\text{CH}_3)$ to be 282.4 J/(K·mol), which is consistent with Burcat's value of 282.5 J/(K·mol). The latter data is based on B3LYP calculations and the IR spectrum of the molecule. Because no well-defined error estimates are available for the results published previously, our entropy value, $S_{298}^{\circ}(\text{CHF}_2\text{CH}_3) = 282.0 \pm 1.5$ J/(K·mol) is proposed as a new benchmark.

CF_3CH_3 . Kolesov and co-workers⁷⁸ measured the heat of combustion for 1,1,1-trifluoroethane in a bomb calorimeter and recommended -749.0 ± 2.0 kJ/mol for $\Delta_f H_{298}^{\circ}(\text{CF}_3\text{CH}_3)$. Later, the experimental data for the combustion process was reanalyzed and corrected by Kolesov and Papina,⁷⁷ and an updated value of -748.7 ± 3.2 kJ/mol was reported for this quantity.

Combining the above heat of combustion taken from ref 78 with auxiliary literature data for $\Delta_f H_{298}^{\circ}(\text{CO}_2)$ and $\Delta_f H_{298}^{\circ}(\text{HF} \cdot 4.5\text{H}_2\text{O})$, Chen and associates⁶⁰ recommended $\Delta_f H_{298}^{\circ}(\text{CF}_3\text{CH}_3) = -745.6 \pm 1.7$ kJ/mol. This value was also adopted by the JPL database.⁸

Based on the bond dissociation energy of $D_{298}^{\circ}(\text{CH}_3 - \text{CF}_3) = 423.4 \pm 4.6$ kJ/mol derived by Rodgers and Ford⁷⁹ in a kinetic data analysis, $\Delta_f H_{298}^{\circ}(\text{CF}_3\text{CH}_3) = -747.3 \pm 6.3$ kJ/mol was reported.

Burcat's database⁹ lists the values of $\Delta_f H_0^{\circ}(\text{CF}_3\text{CH}_3) = -742.9 \pm 1.0$ kJ/mol and $\Delta_f H_{298}^{\circ}(\text{CF}_3\text{CH}_3) = -755.7 \pm 1.0$ kJ/mol as the results of G3B3LYP calculations.

Our results for $\Delta_f H_0^{\circ}(\text{CF}_3\text{CH}_3)$ and $\Delta_f H_{298}^{\circ}(\text{CF}_3\text{CH}_3)$, -738.3 ± 3.3 and -751.5 ± 3.3 kJ/mol, respectively, are between the values obtained from the experiments and the calculations of Burcat and Ruscic. Although the accuracy of the computational method applied here surpasses that of all previous studies, including the G3B3LYP calculations of Burcat and Ruscic, our associated error bars are still larger than those listed in Burcat's compendium. The error bar of ± 1.0 kJ/mol for the G3B3LYP results is most likely a typo in Burcat's table, since all other data calculated with this method is uniformly attached with an estimated uncertainty of ± 8.0 kJ/mol.

In order to establish a reasonable estimate to the quantity $\Delta_f H_{298}^{\circ}(\text{CF}_3\text{CH}_3)$, the experimental result of ref 77 and the calculated data from this work were averaged. The value presented in ref 60 is considered to be too high and inconsistent with our data; therefore, it was omitted from the averaging. In this manner, $\Delta_f H_{298}^{\circ}(\text{CF}_3\text{CH}_3) = 750.3 \pm 3.3$ kJ/mol was obtained, and this average value is proposed as

reference for $\Delta_f H_{298}^{\circ}(\text{CF}_3\text{CH}_3)$. The corresponding 0 K enthalpy, -737.2 ± 3.3 kJ/mol, was obtained from the averaged 298 K value using the thermal correction, $\Delta_f H_{298}^{\circ} - \Delta_f H_0^{\circ}$, calculated from our results. This data is considered as the best available result for $\Delta_f H_0^{\circ}(\text{CF}_3\text{CH}_3)$.

Based on a calorimetric study, Russell and associates⁹⁸ derived 279.8 ± 0.6 J/(K·mol) for $S_{298}^{\circ}(\text{CF}_3\text{CH}_3)$. Chen and associates⁶⁰ calculated the value of 287.3 J/(K·mol), which is in line with Burcat's data⁹ of 287.7 J/(K·mol). Our calculated entropy value, $S_{298}^{\circ}(\text{CF}_3\text{CH}_3) = 286.8 \pm 1.5$ J/(K·mol), is in excellent agreement with the estimates of both Chen et al. and Burcat. Furthermore, due to its well-defined error bar, we suggest our result as a theoretical benchmark for this quantity.

$\text{CH}_2\text{FCH}_2\text{F}$. To the best of our knowledge, there is no experimental study which directly deals with the heat of formation of 1,2-difluoroethane, $\text{CH}_2\text{FCH}_2\text{F}$. Nevertheless, by combining the dissociation energy $D_{298}^{\circ}(\text{CH}_2\text{F} - \text{CH}_2\text{F})$ from the kinetic study of Kerr and Timlin⁸⁰ with the heat of formation value $\Delta_f H_{298}^{\circ}(\text{CH}_2\text{F}) = 32.6 \pm 8.4$ kJ/mol from ref 99, Zachariah and co-workers⁶⁸ estimated -433.9 ± 11.8 kJ/mol for $\Delta_f H_{298}^{\circ}(\text{CH}_2\text{FCH}_2\text{F})$.

Burcat's compendium⁹ using the data from the most recent version of ATcT¹⁰ lists $\Delta_f H_0^{\circ}(\text{CH}_2\text{FCH}_2\text{F}) = -436.7 \pm 4.9$ kJ/mol and $\Delta_f H_{298}^{\circ}(\text{CH}_2\text{FCH}_2\text{F}) = -450.4 \pm 4.9$ kJ/mol.

Our calculations resulted in $\Delta_f H_0^{\circ}(\text{anti-CH}_2\text{FCH}_2\text{F}) = -429.8 \pm 3.2$ kJ/mol and $\Delta_f H_{298}^{\circ}(\text{anti-CH}_2\text{FCH}_2\text{F}) = -443.4 \pm 3.2$ kJ/mol as well as $\Delta_f H_{298}^{\circ}(\text{gauche-CH}_2\text{FCH}_2\text{F}) = -433.5 \pm 3.2$ kJ/mol and $\Delta_f H_{298}^{\circ}(\text{gauche-CH}_2\text{FCH}_2\text{F}) = -447.3 \pm 3.2$ kJ/mol, while conformational averaging yielded $\Delta_f H_{298}^{\circ}(\text{c.a., CH}_2\text{FCH}_2\text{F}) = -446.9 \pm 3.4$ kJ/mol. Our values for $\Delta_f H_0^{\circ}(\text{gauche-CH}_2\text{FCH}_2\text{F})$, as well as $\Delta_f H_{298}^{\circ}(\text{c.a., CH}_2\text{FCH}_2\text{F})$ agree well with the ATcT enthalpies listed in Burcat's tables. However, our present investigation is more detailed and provides more accurate values than previous studies; therefore, our results are proposed as new benchmark values.

For $S_{298}^{\circ}(\text{CH}_2\text{FCH}_2\text{F})$ Burcat's database⁹ lists 286.3 J/(K·mol) taken from G3B3 calculations. Our computational approach yielded 288.8 ± 1.5 and 289.5 ± 1.5 J/(K·mol) for $S_{298}^{\circ}(\text{gauche-CH}_2\text{FCH}_2\text{F})$ and $S_{298}^{\circ}(\text{anti-CH}_2\text{FCH}_2\text{F})$, respectively. Conformational averaging resulted in $S_{298}^{\circ}(\text{c.a., CH}_2\text{FCH}_2\text{F}) = 296.8 \pm 2.8$ J/(K·mol). Since our values are presented with rigorous error bars, they are preferred over previous data.

$\text{CHF}_2\text{CH}_2\text{F}$. Lacher and co-workers⁸¹ reported -664.8 ± 4.2 kJ/mol for $\Delta_f H_{298}^{\circ}(\text{CHF}_2\text{CH}_2\text{F})$ based on the heat of hydrogenation measured earlier¹⁰⁰ for $\text{CF}_2=\text{CFCl}$. Citing ref 81, the JPL database⁸ adopts a somewhat revised value of -665.0 ± 4.0 kJ/mol.

On the basis of the above heat of hydrogenation experiment (ref 100), Kolesov and Papina⁷⁷ recommended a significantly lower value of -691.0 ± 10.0 kJ/mol for $\Delta_f H_{298}^{\circ}(\text{CHF}_2\text{CH}_2\text{F})$.

For the more stable *anti* rotamer our protocol yielded -653.7 ± 3.2 and -666.4 ± 3.2 kJ/mol at 0 and 298 K, respectively, while -648.3 ± 3.2 and -661.0 ± 3.2 kJ/mol were obtained for $\Delta_f H_0^{\circ}(\text{gauche-CHF}_2\text{CH}_2\text{F})$ and $\Delta_f H_{298}^{\circ}(\text{gauche-CHF}_2\text{CH}_2\text{F})$, respectively. Conformational averaging resulted in $\Delta_f H_{298}^{\circ}(\text{c.a., CHF}_2\text{CH}_2\text{F}) = -666.1 \pm 3.4$ kJ/mol. Because of their highest accuracy, our values are recommended as new theoretical benchmark enthalpies for this species.

The only available entropy data, $S_{298}^{\circ}(\text{CHF}_2\text{CH}_2\text{F})$ 309.2 J/(K·mol), was calculated by Chen and co-workers⁵⁶ at the MP4/6-311G(d,p) level of theory. This value agrees well with our results for the *anti* and *gauche* rotamers, 309.8 ± 1.5 and 309.2

± 1.5 J/(K·mol), respectively. For the conformationally averaged entropy, 316.9 ± 2.0 J/(K·mol) was derived. Our entropy values are suggested as new theoretical benchmarks.

CF₃CH₂F. No experimental heat of formation data has been found for CF₃CH₂F. Chen et al.⁶⁰ published $\Delta_f H_0^\circ(\text{CF}_3\text{CH}_2\text{F}) = -884.5$ kJ/mol and $\Delta_f H_{298}^\circ(\text{CF}_3\text{CH}_2\text{F}) = -895.8 \pm 8.4$ kJ/mol, which were derived from three estimated empirical reaction enthalpies. These values are also adopted by the JPL database.⁸

Citing the BAC-MP4 study of Zachariah and co-workers,⁶⁸ Burcat's database⁹ adopts the significantly lower values of -902.0 ± 17.5 kJ/mol and -913.3 ± 17.5 kJ/mol for $\Delta_f H_0^\circ(\text{CF}_3\text{CH}_2\text{F})$ and $\Delta_f H_{298}^\circ(\text{CF}_3\text{CH}_2\text{F})$, respectively.

Enthalpies obtained by the present protocol, $\Delta_f H_0^\circ(\text{CF}_3\text{CH}_2\text{F}) = -894.6 \pm 3.2$ kJ/mol and $\Delta_f H_{298}^\circ(\text{CF}_3\text{CH}_2\text{F}) = -906.2 \pm 3.2$ kJ/mol, lie in the middle of the above empirical and calculated results. Nevertheless, because our computational procedure supersedes the BAC-MP4 method in accuracy, and the associated uncertainties of our enthalpies are tighter than those of the previous results, we recommend our values as new references for $\Delta_f H_0^\circ(\text{CF}_3\text{CH}_2\text{F})$ and $\Delta_f H_{298}^\circ(\text{CF}_3\text{CH}_2\text{F})$.

For $S_{298}^\circ(\text{CF}_3\text{CH}_2\text{F})$ Chen et al.⁶⁰ derived 316.2 J/(K·mol), which was calculated using a selection of experimental vibrational frequencies. The BAC-MP4 study of Zachariah and co-workers⁶⁸ yielded $S_{298}^\circ(\text{CF}_3\text{CH}_2\text{F}) = 315.8$ J/(K·mol), which is also listed in Burcat's database.⁹ Our result, $S_{298}^\circ(\text{CF}_3\text{CH}_2\text{F}) = 316.0 \pm 1.5$ J/(K·mol), lies exactly between the two former values and is preferred over them.

CHF₂CHF₂. Millward and co-workers⁸² measured the C–C bond strength in CHF₂CHF₂ to be 382.4 ± 15.5 kJ/mol. Based on this result, the heat of formation for CHF₂CHF₂ was estimated to be -860.0 ± 24.0 kJ/mol, as listed in the JPL database.⁸ Using the same experimental result of ref 82, Zachariah and associates⁶⁸ calculated $\Delta_f H_{298}^\circ(\text{CHF}_2\text{CHF}_2) = -877.8 \pm 17.5$ kJ/mol in line with their BAC-MP4 value of -883.3 ± 5.6 kJ/mol.

The present protocol yielded -867.9 ± 3.2 and -878.4 ± 3.2 kJ/mol for $\Delta_f H_0^\circ(\text{anti-CHF}_2\text{CHF}_2)$ and $\Delta_f H_{298}^\circ(\text{anti-CHF}_2\text{CHF}_2)$, respectively, and -861.7 ± 3.2 and -872.2 ± 3.2 kJ/mol for $\Delta_f H_0^\circ(\text{gauche-CHF}_2\text{CHF}_2)$ and $\Delta_f H_{298}^\circ(\text{gauche-CHF}_2\text{CHF}_2)$, respectively. For the conformationally averaged enthalpy at 298.15 K, -877.6 ± 3.8 kJ/mol was obtained. Because, on one hand, the experimentally derived heats of formation are associated with significant uncertainties and, on the other hand, the present protocol supersedes all previous computational studies in accuracy, we suggest our results as new theoretical benchmark values.

For $S_{298}^\circ(\text{CHF}_2\text{CHF}_2)$ Burcat's compendium⁹ lists 313.1 J/(K·mol). The JPL database⁸ adopts 320.3 J/(K·mol) taken from the review of Frenkel and associates.¹⁰¹ In their MP4/6-311G(d,p) study, Chen and co-workers⁵⁶ calculated $S_{298}^\circ(\text{CHF}_2\text{CHF}_2) = 317.1$ J/(K·mol) via a direct summation over energy levels using a fitted potential energy function to treat the internal rotational motion properly. Our entropy values for the *anti* and *gauche* rotamers of CHF₂CHF₂ are 319.0 ± 1.5 and 318.9 ± 1.5 J/(K·mol), respectively, while conformational averaging yielded $S_{298}^\circ(\text{c.a.}) = 323.2 \pm 4.7$ J/(K·mol). Because of the accuracy of our protocol as well as the well-defined error bars of our results, we suggest these latter values as new benchmarks for the entropy data of this species.

CF₃CHF₂. Chen and associates⁶⁰ obtained $\Delta_f H_0^\circ(\text{CF}_3\text{CHF}_2) = -1095.0 \pm 5.0$ kJ/mol and $\Delta_f H_{298}^\circ(\text{CF}_3\text{CHF}_2) = -1105.0 \pm$

5.0 kJ/mol by averaging two heat of formation data calculated on the basis of three experimental reaction enthalpies. A large discrepancy can be observed between these values and the G3B3 results listed in Burcat's database;⁹ that is, the latter tabulated enthalpies are lower by 15.0 kJ/mol.

Our results, $\Delta_f H_0^\circ(\text{CF}_3\text{CHF}_2) = -1100.6 \pm 3.2$ kJ/mol and $\Delta_f H_{298}^\circ(\text{CF}_3\text{CHF}_2) = -1110.6 \pm 3.2$ kJ/mol, lie approximately in the middle of the above two values, however, they are more consistent with the data of Chen et al.⁶⁰

Since the uncertainties associated with our enthalpies are smaller, these values are preferred over previous data.

On the basis of G3B3 calculations, Burcat⁹ lists 334.6 J/(K·mol) for $S_{298}^\circ(\text{CF}_3\text{CHF}_2)$. This entropy agrees well with the result of 333.7 J/(K·mol) obtained by Chen and associates⁵⁶ and adopted by the JPL database.⁸ In line with these previous findings, our calculations yielded $S_{298}^\circ(\text{CF}_3\text{CHF}_2) = 332.9 \pm 1.5$ J/(K·mol), and our value is suggested as a new theoretical benchmark for $S_{298}^\circ(\text{CF}_3\text{CHF}_2)$.

C₂F₆. As can be seen in Table 2, a notable discrepancy exists among the available enthalpy values of hexafluoroethane. Adopting the ATcT values, the most recent version of Burcat's compendium⁹ lists -1342.2 ± 1.6 and -1350.5 ± 1.6 kJ/mol for $\Delta_f H_0^\circ(\text{C}_2\text{F}_6)$ and $\Delta_f H_{298}^\circ(\text{C}_2\text{F}_6)$, respectively. In a preceding investigation, Ruscic and co-workers⁸³ applied the thermochemical network approach to obtain reliable estimates for the thermochemistry of several CF₃X compounds. For C₂F₆ the somewhat higher values of -1336.0 ± 3.4 and -1344.3 ± 3.4 kJ/mol were obtained at 0 and 298 K, respectively. The JPL database⁸ adopts these values as well. Compared to the values listed in Burcat's tables,⁹ these results show a much better agreement with other experimental and computational findings, including our values as well. The tabulated enthalpies of the NIST-JANAF database⁷ are $\Delta_f H_0^\circ(\text{C}_2\text{F}_6) = -1335.6 \pm 5.0$ kJ/mol and $\Delta_f H_{298}^\circ(\text{C}_2\text{F}_6) = -1343.9 \pm 5.0$ kJ/mol, and they are based on a least-squares fit on five experimentally derived heat of formation values. The data reported in ref 83 also supports these results. The present protocol yielded $\Delta_f H_0^\circ(\text{C}_2\text{F}_6) = -1331.3 \pm 3.2$ kJ/mol and $\Delta_f H_{298}^\circ(\text{C}_2\text{F}_6) = -1339.8 \pm 3.2$ kJ/mol. Obviously, the results of refs 83 and 7 as well as the present study are fairly consistent since the error bars are overlapping. However, the comparison of the values computed here and those obtained previously suggests that the former ones are probably too high, while the latter ones are most likely too low.

Therefore, in order to deliver a reliable estimate to the enthalpy of formation for C₂F₆, the results obtained in refs 83 and 7 as well as in this work were averaged. The resulting mean values, -1334.3 ± 4.0 and -1342.6 ± 4.0 kJ/mol, are proposed as new references for $\Delta_f H_0^\circ(\text{C}_2\text{F}_6)$ and $\Delta_f H_{298}^\circ(\text{C}_2\text{F}_6)$, respectively.

For $S_{298}^\circ(\text{C}_2\text{F}_6)$, Burcat⁹ lists 341.0 J/(K·mol). This result is considerably larger than the experimentally derived values, 332.2 ± 0.8 and 331.8 J/(K·mol), suggested in the NIST-JANAF tables⁷ and in the review of Chen and associates,⁶⁰ respectively. Our calculated entropy data 331.0 ± 1.5 J/(K·mol) also supports the latter two results. Due to its small uncertainty, the NIST-JANAF value, 332.2 ± 0.8 J/(K·mol), is suggested to be retained as a reference for $S_{298}^\circ(\text{C}_2\text{F}_6)$.

C₂H₆. Although highly accurate and consistent heats of formation as well as entropy values are available in the literature for ethane, these quantities were also calculated in this study to further prove the accuracy of our protocol. Considering the most accurate results for $\Delta_f H_0^\circ(\text{C}_2\text{H}_6)$ and $\Delta_f H_{298}^\circ(\text{C}_2\text{H}_6)$ (the

first three rows for ethane in Table 2), a very good agreement can be observed with our data, -68.2 ± 3.2 and -84.5 ± 3.2 kJ/mol, respectively. This agreement also confirms the accuracy of our computational method and the reliability of the attached error bars.

The same conclusion can be drawn if one compares previous entropy and thermal correction data with those obtained in this study. For $S_{298}^{\circ}(\text{C}_2\text{H}_6)$, our calculations resulted in 228.9 ± 1.5 J/(K·mol). This is in line with the previously established values of 229.1 and 229.2 J/(K·mol) by Chao and co-workers⁸⁹ and Gurvich et al.,⁶² respectively. Our result for $H_{298}^{\circ} - H_0^{\circ}$, 11.9 kJ/mol, exactly coincides with the value published by Chao and associates in ref 89.

CONCLUDING REMARKS

In this study, molar thermochemical properties, including enthalpies of formation at 0 and 298.15 K as well as standard entropies for a series of fluorinated ethane derivatives, have been calculated using an *ab initio* model chemistry. The vibrational frequency-dependent contributions, e.g., zero-point vibrational energies as well as thermal enthalpy and entropy corrections, are corrected for the hindered rotation around the C–C bond via solving a one-dimensional Schrödinger equation for this motion. In three cases, conformational flexibility was also considered, and by means of the Boltzmann distribution, conformationally averaged enthalpies and entropies were also derived. The available results from previous experimental and theoretical studies were briefly discussed, and in all cases except the enthalpies of CH_2FCH_3 and the entropy value of C_2F_6 , new theoretical benchmark values were suggested.

ASSOCIATED CONTENT

Supporting Information

Total energies and their contributions in atomic units, 0 K heats of formation and their contributions in kJ/mol, optimized equilibrium structures in terms of Cartesian coordinates, rotational constants, harmonic vibrational frequencies, along with anharmonicity constants as well as solutions of the 1D-HR calculations. This material is available free of charge via the Internet at <http://pubs.acs.org/>.

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Notes

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