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Gaussian M-062x/6-31+g (d,p) Calculation of Standard Enthalpy, Entropy and Heat Capacity of Some Fluorinated Alcohol's and Its Radicals at Different Temperatures

Hebah Abdel-Wahab, Joseph Bozzelli

Department of Chemistry and Environmental Science, New Jersey Institute of Technology, Newark, New Jersey, United States

Email address:

Dr.heathera@gmail.com (H. Abdel-Wahab), jbozelli@njit.edu (J. Bozzelli)

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Abstract: Thermochemical properties of fluorinated alcohols are needed for understanding their stability and reactions in the environment and in thermal process. Structures and thermochemical properties of these species were determined by the Gaussian M-062x/6-31+g (d,p) calculation. Contributions of entropy, $S°298$, and heat capacities, $Cp(T)$ due to vibration, translation, and external rotation of the molecules were calculated based on the vibration frequencies and structures obtained from the M-062x/6-31+g (d,p) density functional method. Potential barriers are calculated using M-062x/6-31+g (d,p) density functional method and are used to calculate rotor contributions to entropy and heat capacity using integration over energy levels of rotational potential. Enthalpies of formation for 19 fluorinated ethanol and some radicals were calculated with a popular ab initio and density functional theory methods: the Gaussian M-062x/6-31+g (d,p) via several series of isodesmic reactions. The recommended ideal gas phase $\Delta Hf298°$ (kcal mol^{-1}) values calculated in this study are the following: -101.74 ± 0.72 for CH_2FCH_2OH; -113.51 ±1.39 for CH_3CHFOH; -50.66 ± 0.75 for $C•HFCH_2OH$; -56.05±0.62 for $CH_2FCH•OH$; -45.00±1.31 for $CH_2FCH_2O•$; -59.61±1.20 for $CH_2•CHFOH$; -67.99± 1.29 for $CH_3CF•OH$; -58.76±1.20 for $CH_3CHFO•$; -154.12±1.72 for $CH_2FCHFOH$; -155.26±1.67 for CF_2HCH_2OH; -174.53±1.54 for CH_3CF_2OH; -104.07 ± 1.45 for $CH_2FC•FOH$; -105.63±1.74 for $C•HFCFHOH$; -99.08±1.57 for $CH_2FCHFO•$; -102.34±1.74 for $CHF_2C•HOH$; -102.23±1.57 for $C•F_2CH_2OH$; -98.86±1.57 for $CHF_2CH_2O•$; -119.41±1.74 for $CH_2•CF_2OH$; -110.56±1.62 for $CH_3CF_2O•$. Entropies ($S298°$ in cal mol^{-1} K^{-1}) were estimated using the M-062x/6-31+g (d,p) computed frequencies and geometries. Rotational barriers were determined and hindered internal rotational contributions for $S298$ °- 1500°, and $Cp(T)$ were calculated using the rigid rotor harmonic oscillator approximation, with direct integration over energy levels of the intramolecular rotation potential energy curves.

Keywords: Computation, Gaussian, Thermochemical, Enthalpy, Entropy

1. Introduction

Fluorinated hydrocarbons used as refrigerants, in polymers, heat exchange fluids, and as solvents. They are present in the atmosphere, lithosphere, and hydrosphere. Because of their less adverse effects on the stratospheric ozone layer, they are used in place of greenhouse gases. [1] Fluorinated hydrocarbons exist as compounds ranging from pure to oxidized intermediates resulting from oxidation in the environment. In order to study their reactivity in biological systems, lifetimes, and in the environment, it's critical to understand the chemical and thermodynamic properties of fluorocarbons and their breakdown intermediates.

The thermochemistry of fluorinated alcohols with one carbon atom were studied in the past and are in the literature [2]. In 2016 Hang Wang studied thermodynamic properties of fluorinated methanol using CBS-QB3, M06, M06-2X, WB97X, W1U, B3LYP, CBS-APNO and G4 Calculations. Small standard deviation suggests good error cancellation of

work reactions and accuracy. M06-2x/6-31+g (d,p) calculation have small values for standard deviations, it is an accurate method to calculate Enthalpy of fluorinated alcohols, it shows the second smallest standard deviation after CBS-QB3 method of calculation

Halogenated compounds are highly stable, have low reactivity and are valued chemicals in industry [3]. Due to its widespread use and their persistence in the environment, they are of concern to the environment. In order to understand the oxidation and reduction reactions involving such molecules, their thermochemical properties must be studied. [3]

2. Computational Method

Composite calculations and series of Isodesmic Reactions are used to calculate enthalpy of formation of fluorinated ethanols. All calculations are performed using the Gaussian 16 program. The DFT method M06-2x is used to initially analyze optimized structures, frequencies, thermo energies and internal rotors of the molecules studied. It's a Global-hybrid meta-GGA density functional approximation, GGA, generalized gradient approximation, in which the density functional depends on the up and down spin densities and their reduced gradient, meta GGA, in which the functional also depends on the up and down spin kinetic energy densities, hybrid GGA, a combination of GGA with Hartree-Fock exchange, hybrid meta GGA, a combination of meta GGA with Hartree-Fock exchange [21]. All reported values are for standard state of 298 K and 1 atm. We continue the calculation of fluorinated alcohols in this study with this method, because the M-062x/6-31+g (d,p) level of calculation have been applied to fluoro hydrocarbons [4] with small reported standard deviations

values.

3. Isodesmic and Isogyric Reaction

The enthalpy of formation of mono and di fluorinated ethanol's and its radicals has been calculated using Gaussian M-062x/6-31+g (d,p) method of calculation. In order to calculate the enthalpy of formation of fluorinated ethanols using this method, we use the calculated enthalpies of formation in work reactions along with reference species. The number of each type of bond must be conserved in the isodesmic reactions in order to cancel any systematic error in the molecular orbital calculations using this method. Calculations of enthalpies of formation is allowed to accuracies close to experimental values by the careful choice of the isodesmic reactions [5]. Taking 1-fluoroethanol as an example, two isodesmic reactions (Table 2) are selected to determine the ΔHf298 of the target molecule, 1-fluoroethanol. Since the ΔHf298 values of all species but 1-fluoroethanol in 1– 2 (Table 2) are known, the ΔHf298 of the target species 1-fluoroethanol, is obtained from this data and the calculated ΔHrxn, 298. ΔHf298 calculated using two different reference molecules are within $\pm$. 2 Kcal mol^{-1}.

4. Reference Species

Standard enthalpy of formation for the reference species used in the isodesmic work reactions along with their uncertainties are listed, table 1. Table 2 provides one example on the method of Isodesmic Work Reactions used for the calculation of the Standard Enthalpy of Formation $\Delta_f H_2 98$ for the fluoroethanols.

Table 1. *Reference Species in the Isodesmic Reactions Standard Enthalpy of Formation Values (kcal mol^{-1} [6]).*

Species	$\Delta_f H^O_{(298)}$	Species	$\Delta_f H^O_{(298)}$
CH_3F	-56.54 $\pm$ 0.07[a] -56.62 $\pm$ 0.48[h]	CH_3OOH	-30.96 $\pm$ 0.67[b]
CH_3CH_2F	-65.42 $\pm$ 1.11[a]	CH_3CH_2OOH	-38.94 $\pm$ 0.81[b]
$CH_3CH_2CH_2F$	-70.24 $\pm$ 1.30[a]	$CH_3CH_2CH_2OOH$	-44.03 $\pm$ 0.67[b]
CH_2F_2	-108.07 $\pm$ 1.46[a] -107.67 $\pm$ 0.48[h]	$CH_3OO^{\bullet}$	2.37 $\pm$ 1.24[b]
CH_3CHF_2	-120.87 $\pm$ 1.62[a]	$CH_3CH_2OO^{\bullet}$ $CH_3CH_2CH_2OO^{\bullet}$	-6.19 $\pm$ 0.92[b] -11.35 $\pm$ 1.24[b]
$CH_3CH_2CHF_2$	-125.82 $\pm$ 1.65[a]	CH_4	-17.81 $\pm$ 0.01[c]
CHF_3	-166.71 $\pm$ 1.97[h] -166.09 $\pm$ 0.48[h]	CH_3CH_3	-20.05 $\pm$ 0.04[c]
		$CH_3CH_2CH_3$ $CH_3CH_2CH_2CH_3$	-25.01 $\pm$ 0.06[i] -30.07 $\pm$ 0.08[i]
CH_3CF_3	-180.51 $\pm$ 2.05[a]	$CH_3O^{\bullet}$	5.15 $\pm$ 0.08 [c]
$CH_3CH_2CF_3$	-185.48 $\pm$ 2.15[a]	$CH_3CH_2O^{\bullet}$	-3.01[d]
$CH_3^{\bullet}$	34.98 $\pm$ 0.02[c]	OH	8.96 $\pm$ 0.01[c]
$CH_3CH_2^{\bullet}$	28.65 $\pm$ 0.07[c]	CH_3OH	-47.97 $\pm$ 0.04[c]
$CH_3CH_2CH_2^{\bullet}$	24.21 $\pm$ 0.24[gj] 24.18[i]	CH_3CH_2OH	-56.07 $\pm$ 0.05[i]
H	52.10[c]	$HOO^{\bullet}$	2.94[cj]
O	59.57[c]	$HOOH$	-32.39 $\pm$ 0.04[fj] -32.37[i]

aWang [2], bWang [6], cRuscic [7], dBurke [8], eChase [9], fLuo [10], gBodi [11], hPedley, iATcT Tables [12], hCsontos [13]. jThe value we used in this study [6]
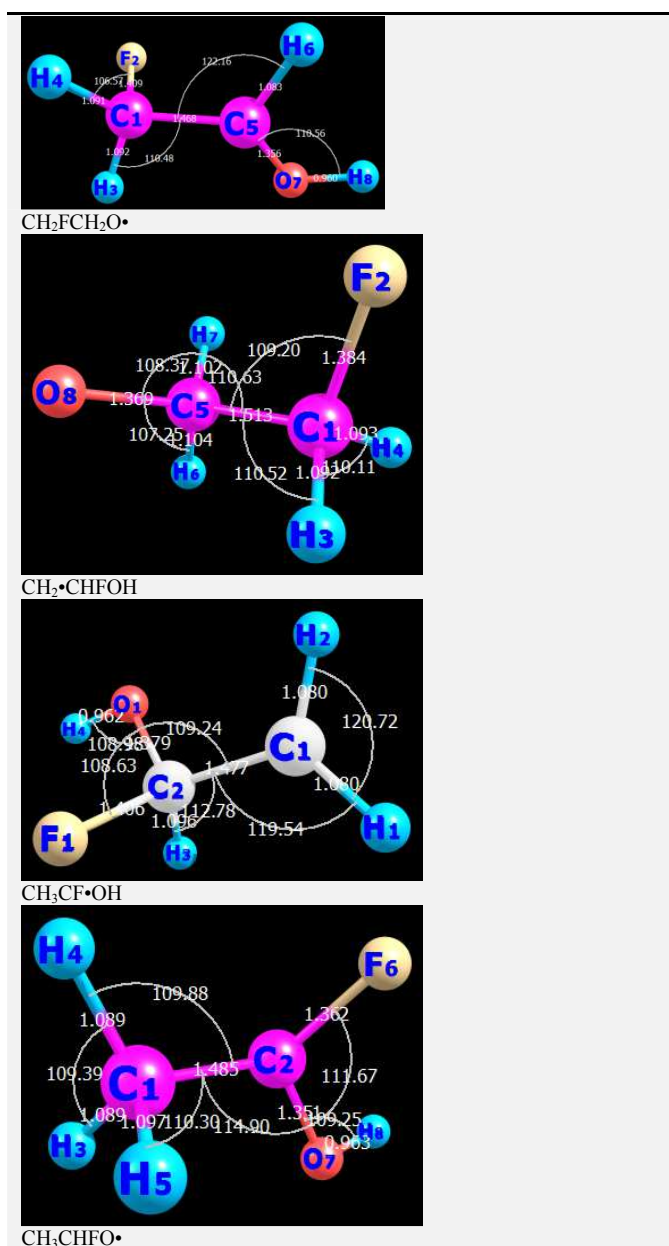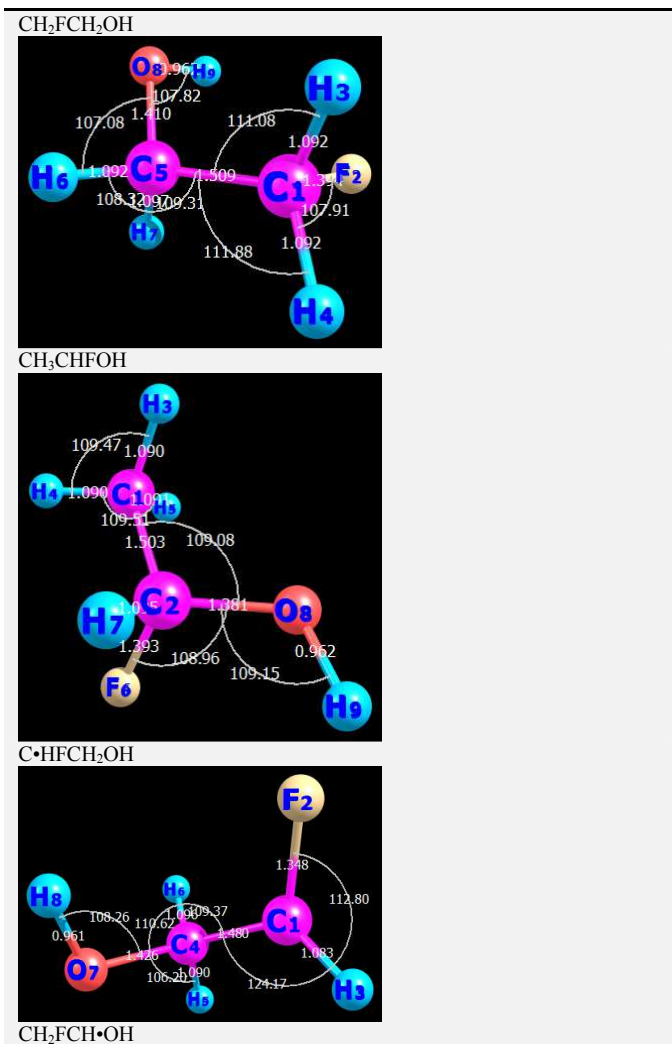
Table 2. Example for Enthalpy of Formation Calculations for 1-fluoroethanol using Isodesmic Reactions; using different reference molecules, Units in kcal mol⁻¹.

Isodesmic Reactions	$\Delta H_{Rxn}^{(298)}$ Hartrees	$\Delta H_{Rxn\,(298)}$ kcal/mol-1	$\Delta fH^o_{(298)}$ CH₃−xCH₂FxOH, CH₃CH₂-xFxOH kcal mol⁻¹	Error kcal mole⁻¹	Equ
CH₂FCH₂OH+CH₄=CH₃CH₂OH+sCH₃F -254.173115[a] -40.447961 -154.926666 -139.683801 Reference Values -17.81 -56.21 -56.54 Kcal mol-¹	0.010609	6.657243	-101.6	±0.18	1
CH₂FCH₂OH + CH₃CH₃ = CH₃CH₂OH + CH₃CH₂F -254.173115 -79.717768 -154.926666 -178.963776 -20.05 -56.21 -65.42	0.000441	0.276731	-101.9	±1.25	2
Reported $\Delta_f H^o$ (298) kcal mol⁻¹			-101.7 ± 0.72		
Standard Deviation over rxns			±0.1		

a Hartrees, kcal mole⁻¹ *SD Standard Deviation kcal mol⁻¹ Errors reported avg of sum of uncertainties in rxn's reference species

5. Results and Discussion

Optimized Structures

Table 3. Optimized geometries showing bond angles and bond distances for target fluorinated ethanol and their related radicals calculated by M06-2x/6-31+g (d,p) level of theory. Bond lengths in A, bond angles in degree, dihedral angle in degree.

CH₂FCH₂OH

CH₃CHFOH

C•HFCH₂OH

CH₂FCH•OH

CH₂FCH₂O•

CH₂•CHFOH

CH₃CF•OH

CH₃CHFO•

CH₂FCHFOH

CH₂FCHFO•

CF₂HCH₂OH

C•F₂CH₂OH

CH₃CF₂OH

CHF₂C•HOH

C•HFCFHOH

CHF₂CH₂O•

CH₂•CF₂OH

CH₂FC•FOH

CH₃CF₂O•
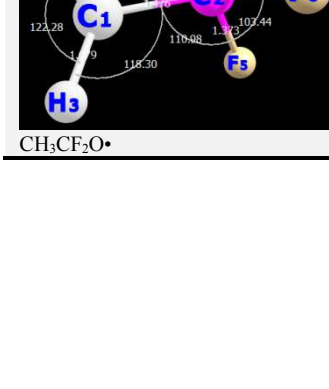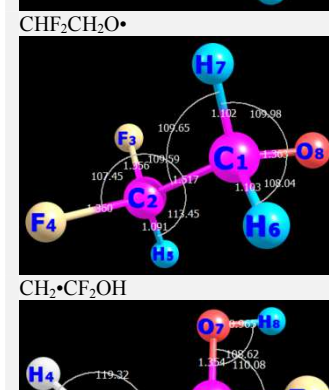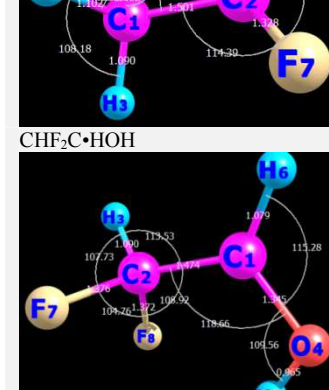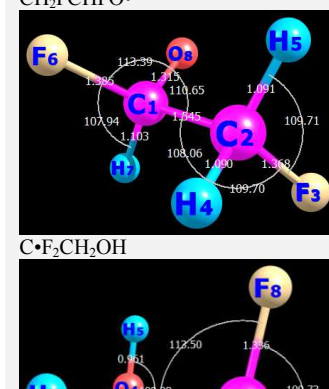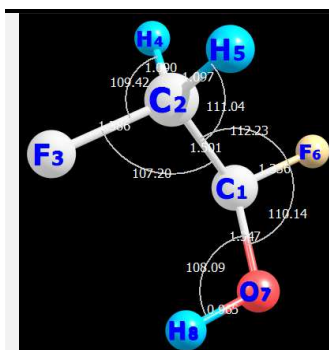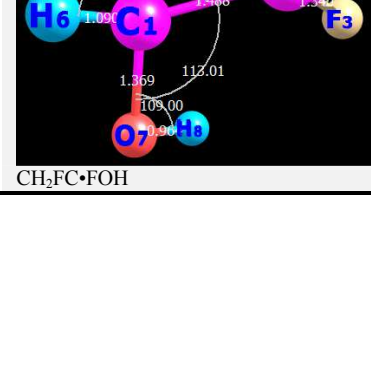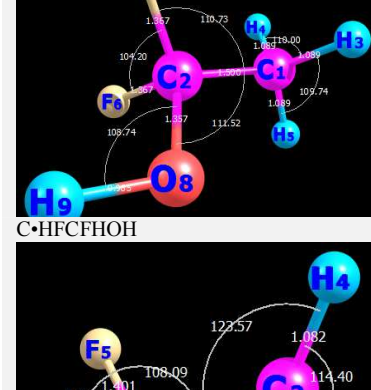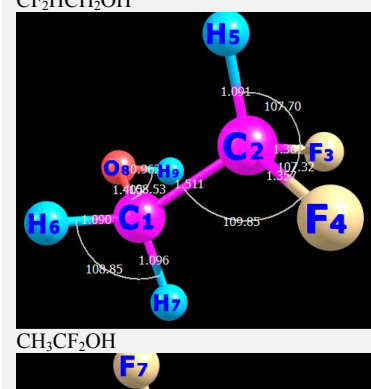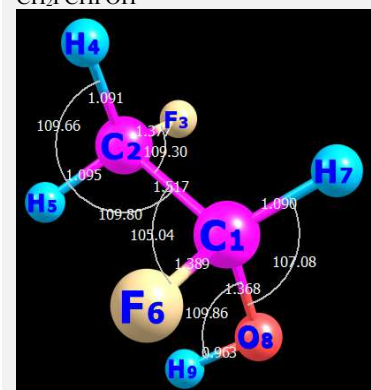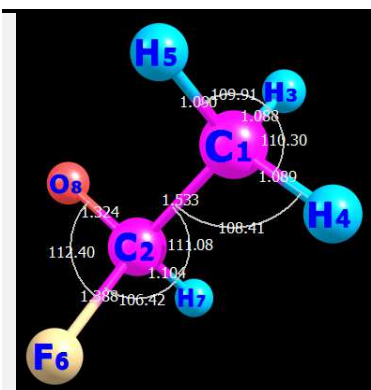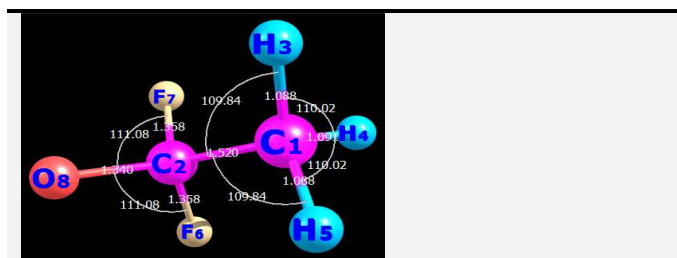
Enthalpies of formation were determined from isodesmic work reactions from M-062x/6-31+g (d,p) method of calculation. The standard enthalpy of formation for the reference species along with their uncertainties, which are used the isodesmic work reactions, table 4, are listed in table 1 in kcal mol^{-1}. The standard deviation was calculated [14] for all Enthalpies of formation values for all 19 fluorinated ethanol and are included in table 4. Details of the method of standard deviation [14] and example calculation(s) are shown in the *Supporting Information table provided.

6. Standard Enthalpy Values

Table 4. *Standard Enthalpy of Formation using isodesmic reactions: Monofluoro and Difluoro- Ethanols using the M06-2x/6-31+g (d,p) Level of Theory. Errors reported as sum of avg uncertainty in rxn's reference specie.*

Isodesmic Reactions arget Specie	$\Delta H_{Rxn\,(298)}$ Hartrees	$\Delta H_{Rxn\,(298)}$ Kcal/mole[1]	$\Delta_f H_{(298)}$ kcal mol^{-1}	Error kcal mol^{-1}
CH$_2$FCH$_2$OH + CH$_4$ = CH$_3$CH$_2$OH + CH$_3$F -254.173115 -40.447961 -154.926666 -139.683801 -17.81 -56.21 -56.54	0.010609	6.657243	-101.6	±0.18
CH$_2$FCH$_2$OH + CH$_3$CH$_3$ = CH$_3$CH$_2$OH + CH$_3$CH$_2$F -254.173115 -79.717768 -154.926666 -178.963776 -20.05 -56.21 -65.42	0.000441	0.276731	-101.9	±1.25
Reported $\Delta_f H^o$ (298) kcal mol^{-1} Standard Deviation over rxns			-101.7 ± 0.72 ±0.1	
CH$_3$CHFOH + CH$_3$CH$_2$CH$_3$ = CH$_3$CH$_2$OH + CH$_3$CH$_2$CH$_2$F -254.19203 -118.990915 -154.926666 -218.237381 -25.02 -56.21 -70.24	0.018898	11.85867	-113.3	±1.52
CH$_3$CHFOH + CH$_3$CH$_3$ = CH$_3$CH$_2$OH + CH$_3$CH$_2$F -254.19203 -79.717768 -154.926666 -178.963776 -20.05 -56.21 -65.42	0.019356	12.14606	-113.7	±1.25
Reported $\Delta_f H^o$ (298) kcal mol^{-1} Standard Deviation over rxns			-113.5 ±1.39 ±0.2	
C•HFCH$_2$OH + CH$_3$CH$_2$CH$_3$ = CH$_3$CH$_2$O• + CH$_3$CH$_2$CH$_2$F -253.518298 -118.990915 -154.268107 -218.237381 -25.02 -3.01 -70.24	0.003725	2.337471	-50.6	±1.42
C•HFCH$_2$OH + CH$_4$ = CH$_3$CH$_2$O• + CH$_3$F -253.518298 -40.447961 -154.268107 -139.683801 -17.81 -3.01 -56.54	0.014351	9.005382	-50.8	±0.08
Reported $\Delta_f H^o$ (298) kcal mol^{-1} Standard Deviation over rxns			-50.7 ± 0.75 ±0.09	
CH$_2$FCH•OH + CH$_3$CH$_3$ = CH$_3$CH$_2$O• + CH$_3$CH$_2$F -253.518298 -79.717768 -154.268107 -178.963776 -20.05 -3.01 -65.42	0.012436	7.803702	-56.2	±1.15
CH$_2$FCH•OH + CH$_4$ = CH$_3$CH$_2$O• + CH$_3$F -253.518298 -40.447961 -154.268107 -139.683801 -17.81 -3.01 -56.54	0.022604	14.18421	-55.9	±0.08
Reported $\Delta_f H^o$ (298) kcal mol^{-1} Standard Deviation over rxns			-56.1±0.62 ±0.1	
CH$_2$FCH$_2$O• + CH$_3$CH$_2$CH$_3$ = CH$_3$CHO• + CH$_3$CH$_2$CH$_2$F -253.509195 -118.990915 -154.268107 -218.237381 -25.02 -3.01 -70.24	-0.00538	-3.37474	-44.9	±1.42
CH$_2$FCH$_2$O• + CH$_4$ = CH$_3$O• + CH$_3$CH$_2$F -253.509195 -40.447961 -114.989112 -178.963776 -17.81 5.15 -65.42	0.004268	2.678208	-45.1	±1.20
Reported $\Delta_f H^o$ (298) kcal mol^{-1} Standard Deviation over rxns			-45.0±1.31 ±0.1	
CH$_2$•CHFOH + CH$_4$ =CH$_3$O• + CH$_3$CH$_2$F -253.532134 -40.447961 -114.989112 -178.963776 -17.81 5.15 -65.42	0.027207	17.07264	-59.5	±1.2
CH$_2$•CHFOH + CH$_3$CH$_3$ = CH$_3$CH$_2$O• + CH$_3$CH$_2$F -253.532134 -79.717768 -154.268107 -178.963776 -20.05 -3.01 -65.42	0.018019	11.30708	-59.7	±1.15
Reported $\Delta_f H^o$ (298) kcal mol^{-1} Standard Deviation over rxns			-59.6±1.20 ±0.1	

Isodesmic Reactions arget Specie	$\Delta H_{Rxn (298)}$ Hartrees	$\Delta H_{Rxn (298)}$ Kcal/mole[1]	$\Delta_f H_{(298)}$ kcal mol^{-1}	Error kcal mol^{-1}
$CH_3CF\bullet OH + CH_3CH_3 = CH_3CH_2O\bullet + CH_3CH_2F$				
-253.542527 -79.717768 -154.268107 -178.963776	0.028412	17.82879	-68.2	±1.15
-20.05 -5.01 -65.42				
$CH_3CF\bullet OH + CH_3CH_2CH_3 = CH_3CH_2O\bullet + CH_3CH_2CH_2F$				
-253.542527 -118.990915 -154.268107 -218.237381	0.027954	17.54139	-67.8	±1.42
-25.02 -5.01 -70.24				
Reported $\Delta_f H^o$ (298) kcal mol^{-1}			-68.0± 1.29	
Standard Deviation over rxns			±0.2	
$CH_3CHFO\bullet + CH_4 = CH_3O\bullet + CH_3CH_2F$				
-253.530783 -40.447961 -114.989112 -178.963776	0.025856	16.22487	-58.7	±1.2
-17.81 5.15 -65.42				
$CH_3CHFO\bullet + CH_3CH_3 = CH_3CH_2O\bullet + CH_3CH_2F$				
-253.530783 -79.717768 -154.268107 -178.963776	0.016668	10.45932	-58.8	±1.15
-20.05 -3.01 -65.42				
Reported $\Delta_f H^o$ (298) kcal mol^{-1}			-58.8±1.20	
Standard Deviation over rxns			±0.2	
$CH_2FCHFOH + CH_4 = CH_3CH_2OH + CH_2F_2$				
-353.429924 -40.447961 -154.926666 -238.938973	0.012246	7.684475	-154.2	±1.57
-17.81 -56.21 -108.07				
$CH_2FCHFOH + CH_3CH_2CH_3 = CH_3CH_2OH + CH_3CH_2CHF_2$				
-353.429924 -118.990915 -154.926666 -317.498882	-0.00471	-2.95494	-154.1	±1.87
-25.02 -56.21 -125.82				
Reported $\Delta_f H^o$ (298) kcal mol^{-1}			-154.2±1.72	
Standard Deviation over rxns			±0.6	
$CF_2HCH_2OH + CH_4 = CH_3CH_2OH + CH_2F_2$				
-353.431533 -40.447961 -154.926666 -238.938973	0.013855	8.694137	-155.2	±1.57
-17.81 -56.21 -108.07				
$CF_2HCH_2OH + CH_3CH_3 = CH_3CH_2OH + CH_3CHF_2$				
-353.431533 -79.717768 -154.926666 -278.225303	-0.00267	-1.67419	-155.4	±1.76
-20.05 -56.21 -120.87				
Reported $\Delta_f H^o$ (298) kcal mol^{-1}			-155.3±1.67	
Standard Deviation over rxns			±0.1	
$CH_3CF_2OH + CH_4 = CH_3CH_2OH + CH_2F_2$				
-353.462472 -40.447961 --154.926666 -238.938973	0.044794	28.10864	-174.6	±1.57
-17.81 -56.21 -108.07				
$CH_3CF_2OH + CH_3CH_2CH_3 = CH_3CH_2OH + CH_3CH_2CHF_2$		17.46922		
-353.462472 -118.990915 -154.926666 -317.498882	0.027839		-174.5	±1.52
-25.02 -56.21 -125.82				
Reported $\Delta_f H^o$ (298) kcal mol^{-1}			-174.5±1.54	
Standard Deviation over rxns			±0.1	
$CH_2FC\bullet FOH + CH_4 = CH_3CH_2O\bullet + CH_2F_2$				
-352.776406 -40.447961 -154.268107 -238.938973	0.017287	10.84775	-104.1	±1.47
-17.81 -3.01 -108.07				
$CH_2FC\bullet FOH + CH_3CH_2CH_3 = CH_3CH_2O\bullet + CH_3CH_2CHF_2$				
-352.776406 -118.990915 -154.268107 -317.498882	0.000332	0.208333	-104.0	±1.42
-25.02 -3.01 -125.82				
Reported $\Delta_f H^o$ (298) kcal mol^{-1}			-104.1 ± 1.45	
Standard Deviation over rxns			±0.1	
$C\bullet HFCFHOH + CH_4 = CH_3O\bullet + CH_3CHF_2$				
-352.778474 -40.447961 -114.989112 -278.225303	0.01202	7.542658	-105.5	±1.71
-17.81 5.15 -120.87				
$C\bullet HFCFHOH + CH_3CH_3 = CH_3O\bullet + CH_3CH_2CHF_2$				
-352.778474 - 79.717768 -114.989112 -317.498882	0.008248	5.175694	-105.8	±1.77
-20.05 5.15 -125.82				
Reported $\Delta_f H^o$ (298) kcal mol^{-1}			-105.6±1.74	
Standard Deviation over rxns			±0.2	
$CHF_2C\bullet HOH + CH_4 = CH_3O\bullet + CH_3CHF_2$				
-352.773245 -40.447961 -114.989112 -278.225303	0.006791	4.261414	-102.5	±1.71
-17.81 5.15 -120.87				
$CHF_2C\bullet HOH + CH_3CH_3 = CH_3O\bullet + CH_3CH_2CHF_2$				
-352.773245 -79.717768 -114.989112 -317.498882	0.003019	1.89445	-102.2	±1.77
-20.05 5.15 -125.82				
Reported $\Delta_f H^o$ (298) kcal mol^{-1}			-102.3±1.74	
Standard Deviation over rxns			±0.2	
$CH_2FCHFO\bullet + CH_4 = CH_3CH_2O\bullet + CH_2F_2$				
-352.768218 - 40.447961 -154.268107 -238.938973	0.009099	5.709704	-99.0	±1.47
-17.81 -3.01 -108.07				

Isodesmic Reactions arget Specie	$\Delta H_{Rxn (298)}$ Hartrees	$\Delta H_{Rxn (298)}$ Kcal/mole[1]	$\Delta_f H_{(298)}$ kcal mol^{-1}	Error kcal mol^{-1}
$CH_2FCHFO\bullet + CH_3CH_3 = CH_3CH_2O\bullet + CH_3CHF_2$				
-352.768218 -79.717768 -154.268107 -278.225303	-0.00742	-4.65863	-99.2	±1.66
-20.05 -3.01 -120.87				
Reported $\Delta_f H^o$ (298) kcal mol^{-1}			-99.1±1.57	
Standard Deviation over rxns			±0.1	
$C\bullet F_2CH_2OH + CH_4 = CH_3CH_2O\bullet + CH_2F_2$				
-352.773245 -40.447961 -154.268107 -238.938973	0.014126	8.864192	-102.1	±1.47
-17.81 -3.01 -108.07				
$C\bullet F_2CH_2OH + CH_3CH_3 = CH_3CH_2O\bullet + CH_3CHF_2$				
-352.773245 -79.717768 -154.268107 -278.225303	-0.0024	-1.50414	-102.3	±1.66
-20.05 -3.01 -120.87				
Reported $\Delta_f H^o$ (298) kcal mol^{-1}			-102.2±1.57	
Standard Deviation over rxns			±0.2	
$CHF_2CH_2O\bullet + CH_4 = CH_3CH_2O\bullet + CH_2F_2$				
-352.767873 -40.447961 -154.268107 -238.938973	0.008754	5.493214	-98.8	±1.47
-17.81 -3.01 -108.07				
$CHF_2CH_2O\bullet + CH_3CH_3 = CH_3CH_2O\bullet + CH_3CHF_2$				
-352.767873 -79.717768 -154.268107 -278.225303	-0.00777	-4.87512	-99.0	1.66
-20.05 -3.01 -120.87				
Reported $\Delta_f H^o$ (298) kcal mol^{-1}			-98.9±1.57	
Standard Deviation over rxns			±0.2	
$CH_2\bullet CF_2OH + CH_4 = CH_3O\bullet + CH_3CHF_2$				
-352.800434 -40.447961 -114.989112 -278.225303	0.03398	21.32276	-119.2	±1.71
-17.81 5.15 -120.87				
$CH_2\bullet CF_2OH + CH_3CH_3 = CH_3O\bullet + CH_3CH_2CHF_2$				
-352.800434 -79.717768 -114.989112 -317.498882	0.030208	18.95579	-119.6	±1.77
-20.05 5.15 -125.82				
Reported $\Delta_f H^o$ (298) kcal mol^{-1}			-119.4±1.74	
Standard Deviation over rxns			±0.2	
$CH_3CF_2O\bullet + CH_4 = CH_3CH_2O\bullet + CH_2F_2$				
-352.786755 -40.447961 -154.268107 -238.938973	0.027636	17.34184	-110.6	±1.47
-17.81 5.15 -108.07				
$CH_3CF_2O\bullet + CH_3CH_2CH_3 = CH_3CH_2O\bullet + CH_3CH_2CHF_2$				
-352.786755 -118.990915 -154.268107 -317.498882	0.010681	6.702424	-110.5	±1.77
-25.02 5.15 -125.82				
Reported $\Delta_f H^o$ (298) kcal mol^{-1}			-110.6±1.62	
Standard Deviation over rxns			±0.1	

Hartrees, kcal mole[-1] *SD Standard Deviation kcal mol^{-1} Errors reported avg of sum of uncertainties in rxn's reference species

7. Entropy and Heat Capacity Values

Internal rotor contributions to calculated entropy and heat capacity at 298-1500K were determined using the molecular mass of each molecule, number of optical isomers, symmetry of the molecule, electron degeneracy, moment of inertia, and vibrational frequencies values (table 5). The vibrational frequencies for the calculation of heat capacity and entropy at the M-062x/6-31+g (d,p) level of calculation was scaled by a factor of 0.97. The moment of inertia values is shown in the Supporting Information Table provided. To calculate the contributions of external rotor, vibration and transition to the calculated entropy and heat capacity, the "SMCPS" program is used. It employs the rigid-rotor harmonic oscillator approximation using moment of inertia from optimized structure and frequencies. The "Rotator" program by Lay et al. is used to calculate internal rotor contributions from the corresponding internal rotor torsion frequencies. In this paper, a torsional potential curve presenting a ten-parameter Fourier series function is used to calculate the contribution of internal rotor. Parameters and detailed functions are shown in the Supporting Information Table provided. Rotor [15-18] program is used to calculate thermodynamic functions from hindered rotations with arbitrary potentials.

Calculation of the Hamiltonian matrix of the internal rotor, and subsequent calculation of energy levels by direct diagonalization of the matrix are employed by this technique. Rotational barriers versus dihedral angle is presented as a potential curve. In this paper, the calculated torsional potential at discrete torsional angles

$$V(\Phi)= a_0 + \Sigma\, a_i \cos(i\Phi) + \Sigma\, b_j \cos(j\Phi) \qquad i,j= 1\text{-}10 \qquad (1)$$

The coefficients ai and bj are calculated to present the maxima and minima of the torsional potentials with a possibility to shift from the extreme angular positions.

Calculations of heat capacity and standard entropy based on benchmark database and the computational chemistry comparison for the M-062x/6-31+g (d,p) calculation method, the vibrational frequencies were scaled by a factor of 0.987 [19]. Potential Energy profiles for mono and di fluorinated ethanol and their related radicals are listed in the Supporting Information Table provided., the solid lines are the fit of

Fourier series expansion, rotator contribution for barriers below 7 kcal mol^{-1} were added to the SMCPS calculated entropy and heat capacity. Energies are in kcal mol^{-1}. Table 6.

Table 5. *Monofluoro and Difluoro- Ethanol's Ideal Gas phase Entropy and Heat Capacity obtained using M-062x/6-31+g (d,p) level of theory (Cal mol^{-1} K^{-1}).*

Species		S(298)	Cp(298)	Cp(400)	Cp(500)	Cp(600)	Cp(800)	Cp(1000)	Cp(1500)
CH_2FCH_2OH	TVR	64.74	13.23	17.12	20.72	23.75	28.18	31.11	35.06
	Internal Rotor	3.84	3.24	3.48	3.43	3.22	2.68	2.23	1.62
	Total	2.02	3.15	3.33	3.04	2.66	2.05	1.69	1.3
		70.6	19.62	23.94	27.2	29.62	32.91	35.03	37.98
CH_3CHFOH	TVR	65.17	14.06	17.9	21.37	24.26	28.51	31.32	35.15
	Internal Rotor	4.48	2.13	2.09	1.95	1.8	1.56	1.4	1.19
	Total	2.67	2.17	2.21	2.18	2.09	1.89	1.71	1.4
		72.32	18.35	22.21	25.5	28.16	31.96	34.42	37.75
$C•HFCH_2OH$	TVR	66.3	13.54	16.96	19.97	22.48	26.29	29.04	33.33
	Internal Rotor	6.19	2.31	1.91	1.69	1.54	1.36	1.25	1.13
	Total	3.09	3.16	2.52	2.04	1.74	1.41	1.25	1.11
		75.58	19.01	21.38	23.7	25.76	29.06	31.55	35.56
$CH_2FCH•OH$	TVR	66.47	13.76	17.09	20.04	22.52	26.29	29.02	33.31
	Internal Rotor	5.72	2.34	2.22	2.09	1.95	1.73	1.56	1.32
	Total	6	1.96	1.95	1.95	1.91	1.79	1.65	1.4
		78.19	18.06	21.27	24.07	26.38	29.81	32.24	36.03
CH_2FCH_2O	TVR	75.3	20.44	23.66	26.27	28.39	31.55	33.79	37.16
	Internal Rotor	6.08	2.2	1.96	1.7982	1.68	1.53	1.43	1.27
	Total	81.38	22.64	25.62	28.07	30.07	33.08	35.21	38.42
$CH_2•CHFOH$	TVR	66.89	14.8	18.21	21.07	23.4	26.9	29.44	33.49
	Internal Rotor	4.94	1.42	1.25	1.17	1.12	1.06	1.04	1.01
	Total	2.84	1.95	2.12	2.12	2.04	1.83	1.64	1.35
		74.67	18.17	21.58	24.35	26.55	29.79	32.11	35.86
$CH_3CF•OH$	TVR	66.56	13.94	17.25	20.17	22.62	26.38	29.11	33.38
	Internal Rotor	4.91	1.97	1.75	1.57	1.44	1.27	1.18	1.08
	Total	1.71	2.6	3.17	3.22	3.01	2.43	1.99	1.45
		73.18	18.5	22.17	24.96	27.07	30.08	32.28	35.92
CH_3CHFO	TVR	66.73	14.44	18.16	21.39	24.09	28.18	31.12	35.58
	Internal Rotor	4.55	2.12	2.05	1.9	1.75	1.51	1.36	1.18
	Total	71.27	16.56	20.21	23.29	25.84	29.69	32.48	36.75
$CH_2FCHFOH$	TVR	67.46	15.41	19.51	23.12	26.07	30.23	32.83	36.15
	Internal Rotor	0	0	0	0	0	0	0	0
	Total	6.12	3.11	2.64	2.24	1.94	1.57	1.37	1.17
		73.58	18.52	22.15	25.35	28	31.79	34.2	37.31
CF_2HCH_2OH	TVR	62.94	12	15.54	18.95	21.9	26.43	29.57	34.06
	Internal Rotor	4.98	3.36	3.2	2.97	2.72	2.26	1.93	1.48
	Total	2.23	3.21	3.17	2.81	2.44	1.91	1.6	1.27
		70.15	18.57	21.91	24.72	27.06	30.6	33.1	36.81
CH_3CF_2OH	TVR	68.41	16.53	20.74	24.23	27.01	30.87	33.29	36.37
	Internal Rotor	4.53	2.13	2.08	1.93	1.77	1.53	1.38	1.18
	Total	1.58	2.45	3.09	3.28	3.14	2.6	2.14	1.53
		74.52	21.11	25.91	29.44	31.93	35.01	36.8	39.08
$CH_2FC•FOH$	TVR	69.58	15.15	18.76	21.84	24.36	28.05	30.59	34.38
	Internal Rotor	6.18	3.28	2.51	2.07	1.8	1.5	1.34	1.16
	Total	3.15	1.91	1.96	1.91	1.83	1.65	1.5	1.27
		78.9	20.34	23.22	25.82	27.99	31.19	33.43	36.81
$C•HFCFHOH$	TVR	69.6	15.48	19.22	22.3	24.76	28.32	30.75	34.41
	Internal Rotor	6.92	2.03	1.69	1.49	1.37	1.22	1.15	1.07
	Total	1.72	2.79	3.1	3.03	2.83	2.37	2.02	1.52
		78.25	20.3	24.01	26.83	28.96	31.91	33.92	37
CH_2FCHFO	TVR	70.53	15.99	19.88	23.22	25.94	29.93	32.65	36.59
	Internal Rotor	5.48	2.92	2.79	2.58	2.37	2.01	1.76	1.4
	Total	76.01	18.91	22.67	25.8	28.31	31.94	34.41	37.99
$CHF_2C•HOH$	TVR	68.27	15.46	19.18	22.25	24.71	28.28	30.72	34.4
	Internal Rotor	6.07	2.65	2.3	2.05	1.86	1.61	1.45	1.24
	Total	1.51	2.5	3.06	3.18	3.06	2.6	2.2	1.61
		75.85	20.61	24.54	27.48	29.63	32.49	34.37	37.25

Species		S(298)	Cp(298)	Cp(400)	Cp(500)	Cp(600)	Cp(800)	Cp(1000)	Cp(1500)
C•F$_2$CH$_2$OH	TVR	69.57	15.16	18.73	21.81	24.32	28.03	30.58	34.37
	Internal Rotor	6.18	2.68	2.38	2.11	1.89	1.5848	1.41	1.19
	Total	3.46	2.45	2.04	1.75	1.55	1.32	1.21	1.09
		79.21	20.29	23.15	25.66	27.76	30.94	33.19	36.65
CHF$_2$CH$_2$O	TVR	70.02	15.31	18.91	22.14	24.87	29.03	31.94	36.19
	Internal Rotor	5.78	2.51	2.41	2.26	2.1	1.83	1.63	1.34
	Total	75.79	17.82	21.32	24.4	26.97	30.86	33.57	37.53
CH$_2$•CF$_2$OH	TVR	70.2	17.3	21.07	23.93	26.13	29.24	31.38	34.69
	Internal Rotor	4.97	1.37	1.23	1.16	1.11	1.06	1.04	1.01
	Total	1.78	2.81	3.33	3.25	2.9407	2.3	1.87	1.38
		76.95	21.48	25.63	28.35	27.25	32.61	34.29	37.09
CH$_3$CF$_2$O•	TVR	70.14	16.85	20.78	23.99	26.55	30.3	32.87	36.66
	Internal Rotor	4.84	2.08	1.89	1.7	1.54	1.35	1.23	1.11
	Total	5.78	2.51	2.41	2.26	2.1	1.83	1.63	1.34
		80.75	21.44	25.08	27.94	30.2	33.47	35.73	39.11

***Table 6.** Bond Dissociation Energy (BDE's) of Monofluoro and Difluoro- Ethanol's.*

Bond Energies

Reactions	Bond Dissociation Energy[a] (Kcal mol^{-1})	Error Kcal mol^{-1}
	BDE (this study)	
H-CHFCH$_2$OH		
H-CHFCH$_2$OH = H• + •CHFCH$_2$OH	103.1± 0.1	±0.2
-101.7 ±0.1 52.1 -50.7±0.09		
CH$_2$FC-HHOH		
CH$_2$FC-HHOH = H• + CH$_2$FC•HOH	97.7±0.1	±0.2
-101.7±0.1 52.1 -56.1±0.1		
CH$_2$FCH$_2$O-H		
CH$_2$FCH$_2$O-H = H• + CH$_2$FCH$_2$O•	108.8±0.1	±0.2
-101.7±0.1 52.1 -45.0±0.1		
H-CH$_2$CHFOH		
H-CH$_2$CHFOH = H• + •CH$_2$CHFOH	106.0±0.15	±0.3
-113.5±0.2 52.1 -59.6±0.1		
CH$_3$C-HFOH		
H-CH$_2$CHFOH = H• + CH$_3$C•FOH	97.6±0.2	±0.4
-113.5±0.2 52.1 -68. ±0.2		
CH$_3$CHFO-H		
CH$_3$CHFO-H = H• + CH$_3$CHFO•	106.8±0.2	±0.4
-113.5±0.2 52.1 -58.8±0.2		
H-CHFCHFOH		
H-CHFCHFOH = H• + • CHFCHFOH	101.1±0.4	±0.8
-154.6±0.6 52.1 -105.6±0.2		
CH$_2$FC-HFOH	102.6±0.35	±0.7
CH$_2$FC-HFOH = H• + CH$_2$FC• FOH		
-154.6±0.6 52.1 -104.1 ±0.1		
CH$_2$FCHFO-H	107.6±0.35	
CH$_2$FCHFO-H = H• + CH$_2$FCHFO•	105.1±0.15	±0.3
154.6±0.6 52.1 -99.1±0.1		
CF$_2$-HCH$_2$OH		
CF$_2$-HCH$_2$OH = H• + • CF$_2$CH$_2$OH	105.0±0.15	±0.3
-155.3±0.1 52.1 -102.3±0.2		
CF$_2$HCH-HOH		
CF$_2$HCHOH-H = H• + CF$_2$HC•OH		
-155.3±0.1 52.1 -102.4±0.2		
CF$_2$HCH$_2$O-H		
CF$_2$HCH$_2$O-H = H• + CF$_2$HCH$_2$O•	108.5±0.15	±0.3
-155.3±0.1 52.1 -98.9±0.2		
H-CH$_2$CF$_2$OH		
H-CH$_2$CF$_2$OH = H• + •CH$_2$CF$_2$OH	107.2±0.15	±0.3
-174.5±0.1 52.1 -119.4±0.2		
CH$_3$CF$_2$O-H		
CH$_3$CF$_2$O-H = H• + CH$_3$CF$_2$O•	116.0±0.1	±0.2
-174.5±0.1 52.1 -110.6±0.1		

a standard deviation among the work reactions.

8. Conclusions

Thermodynamic properties of 19 mono and di-fluoro ethanols and their related radicals are calculated using the ab initio and Global-hybrid meta-GGA density function methods. Isodesmic work reactions are employed for cancellation of calculation errors. Multiple work reactions are utilized to calculate standard enthalpy of formation at the Gaussian M06-2X calculation level. Optimized geometries and frequencies are used to determine entropy and heat capacity with M06-2x/6-31+g (d,p) level of calculation. Intermolecular torsion potential curves at the M-06-2x/6-31+g (d,p) level of calculation are used to calculate hindered internal rotation contributions to heat capacity and entropy with a correction to the calculated heat capacity and entropy. The Thermochemical properties: Entropy, Heat Capacities at (298 – 1500K), Standard Enthalpy of formation (298K), and the C—F and C—H Bond Dissociation Energies (BDEs) for Mono and Difluorinated Ethanols and Radicals: $CH_3−xCHFxOH$, CH_3CH_2-xFxOH have been calculated. The C-H bond energies range from 102.2 to 107.2 Kcal mol^{-1} on the methyl carbons, and from 97.3 to 105.2 Kcal mol^{-1} on the secondary ethyl carbons. The calculated values for C-H bond energies for fluorinated methyl carbons are higher than those of the fluorinated ethyl carbons. Calculated values for the O-H bond energies for 2-fluoroethanol are higher than those of O-H bond energies for 1-fluoroethanol and an intermediate calculated value for O-H bond energies for 1, 2-difluoroethanol. Introducing a fluorine atom to either methyl or ethyl carbon increases O-H bond energy [20].

Supporting Information

Supporting information is available, Cartesian Coordinates; Z-matrixes, vibration frequencies, moments of inertia, the method of standard deviation, Optimized Geometries, and C-C and C-O internal rotors potential energy profile for target fluorinated ethanol and their related radicals are included.

Acknowledgements

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