

Thermochemical Properties of Mono and Di-fluorinated Ethanol's and its Radicals at Different Temperatures.

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Research Article

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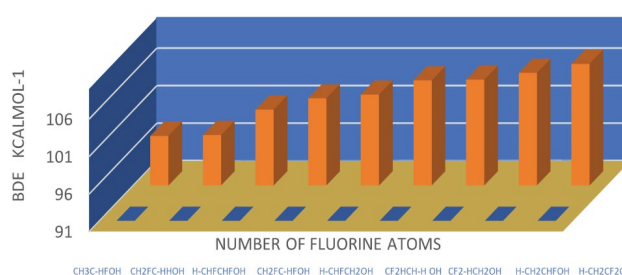
Tel: 9734622745

Keywords: Enthalpy, Entropy, Fluorinated ethanol, Heat capacity, Isodesmic reactions.

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, $S^\circ_{298^\circ\text{K}}$, and heat capacities, $C_p(T)$ 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. • Entropies ($S^\circ_{298^\circ\text{K}}$ in $\text{cal mol}^{-1} \text{K}^{-1}$) 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 $S^\circ_{298^\circ\text{K}}$ - 1500°K , and $C_p(T)$ were calculated using the rigid rotor harmonic oscillator approximation, with direct integration over energy levels of the intramolecular rotation potential energy curves.

C-H BDE Kcal mol⁻¹ VS. Number of F atoms



C—F and C—H Bond Dissociation Energies (BDEs) for mono and difluorinated ethanols and radicals.

INTRODUCTION

The aim is to calculate The enthalpy of formation, standard entropy and heat capacity of mono and di fluorinated ethanol's and its radicals 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.

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 ^[1-3]. 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^[1]. 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.

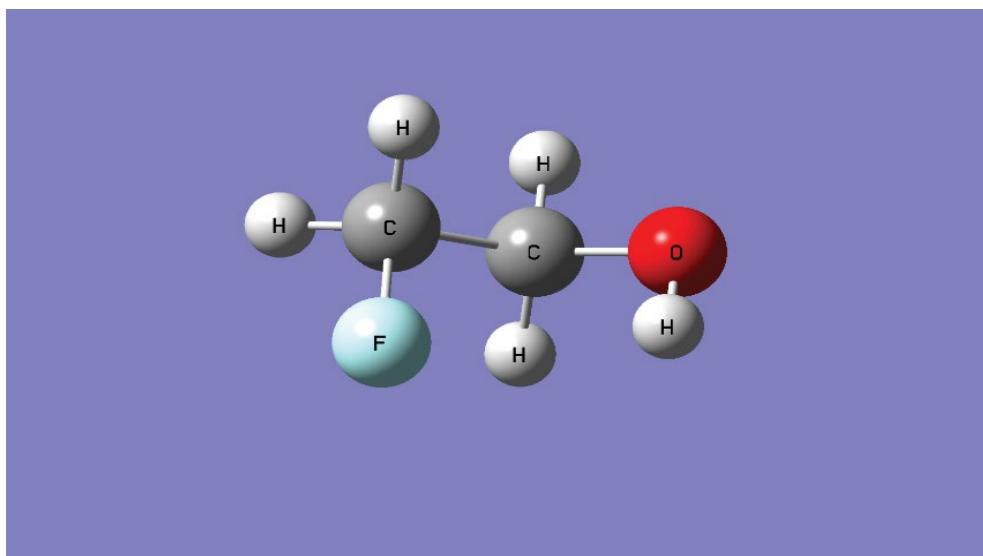


Figure 1. Optimized geometry for CH₂FCH₂OH at the m062x/6-31+g (d, p) level of theory.

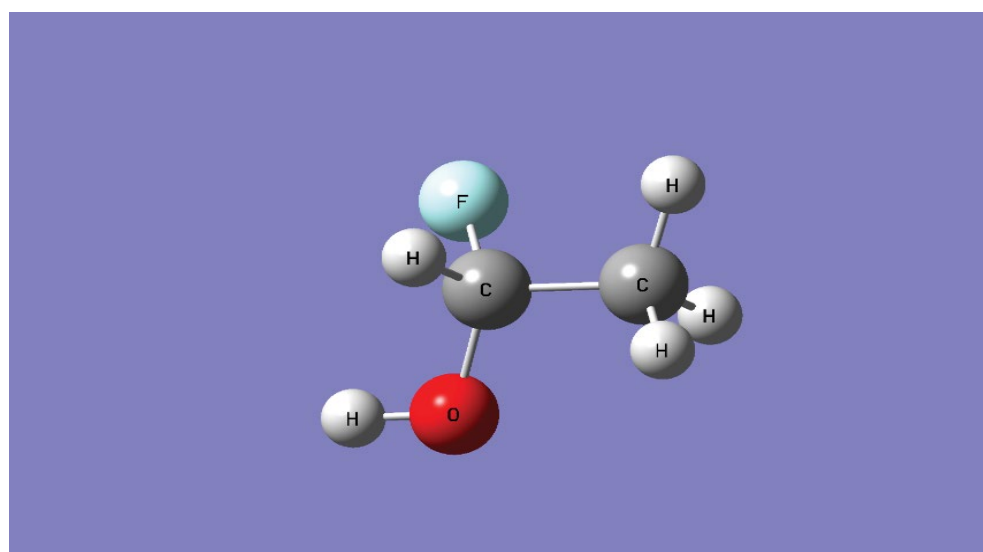


Figure 2. Optimized geometry for CH₃CHFOH at the m062x/6-31+g (d, p) level of theory.

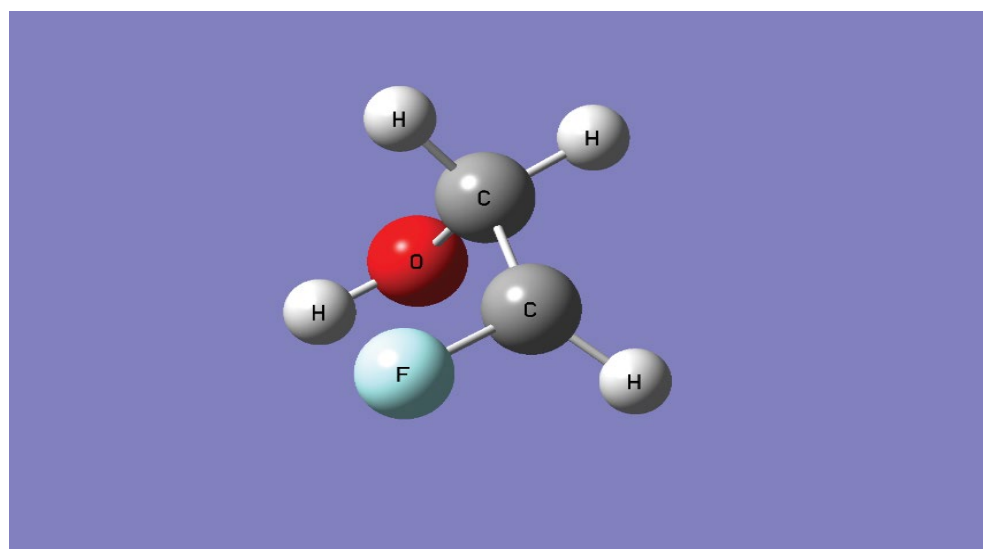


Figure 3. Optimized geometry for C•HFCH₂OH at the m062x/6-31+g(d, p) level of theory.

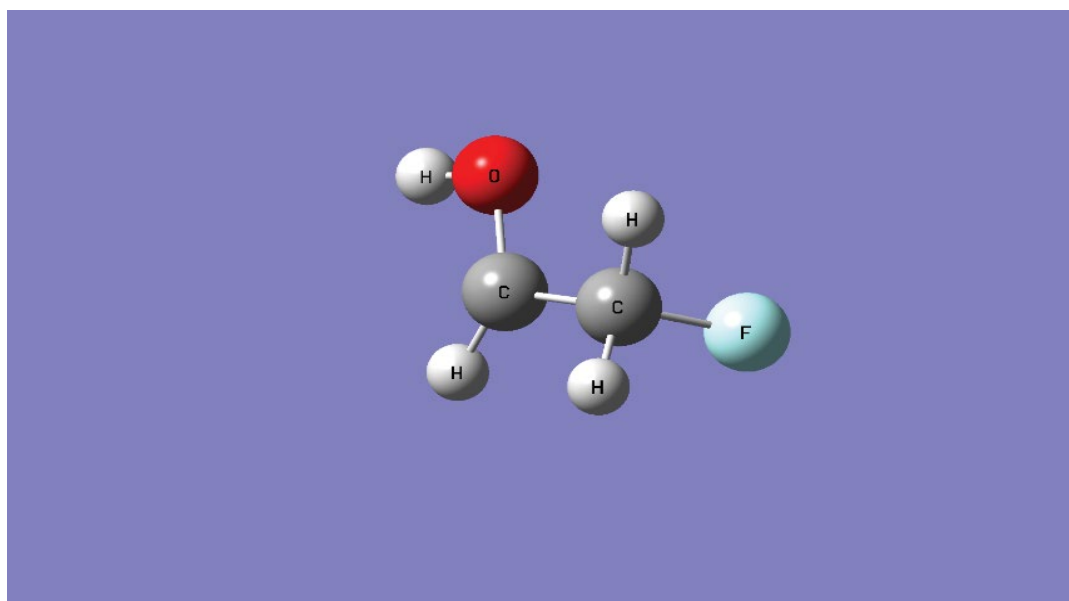


Figure 4. Optimized geometry for $\text{CH}_2\text{FCH}\cdot\text{OH}$ at the m062x/6-31+g(d, p) level of theory.

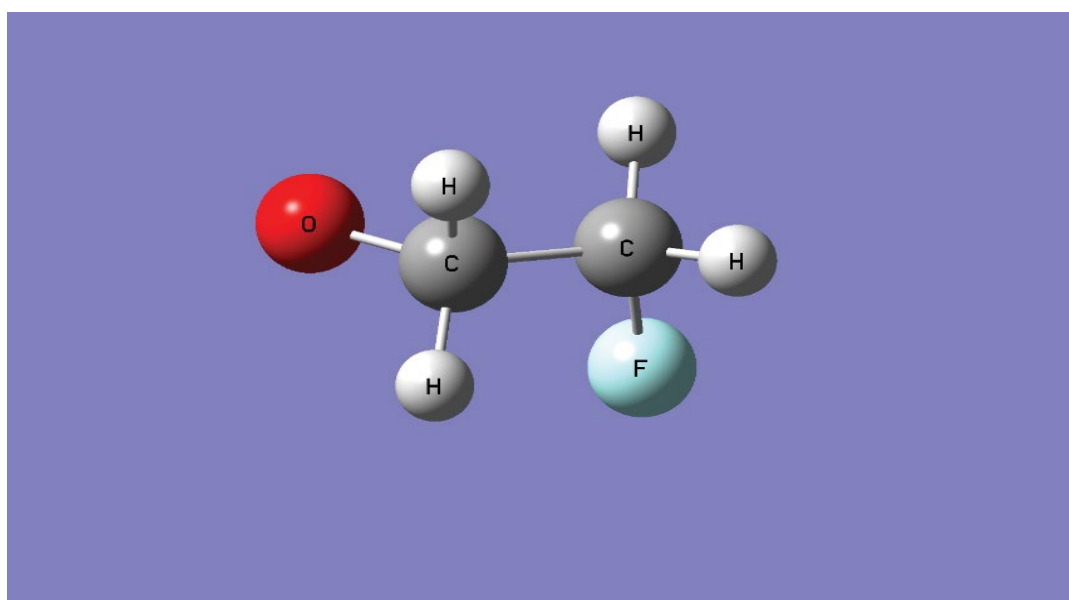


Figure 5. Optimized geometry for $\text{CH}_2\text{FCH}_2\text{O}\cdot$ at the m062x/6-31+g(d, p) level of theory.

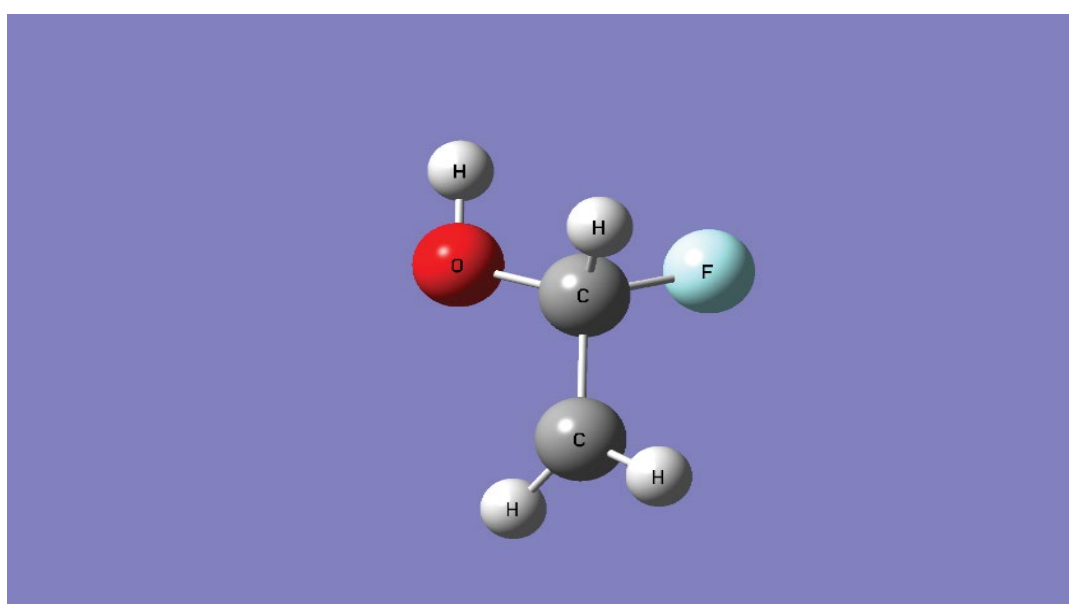


Figure 6. Optimized geometry for $\text{CH}_2\cdot\text{CHFOH}$ at the m062x/6-31+g(d, p) level of theory.

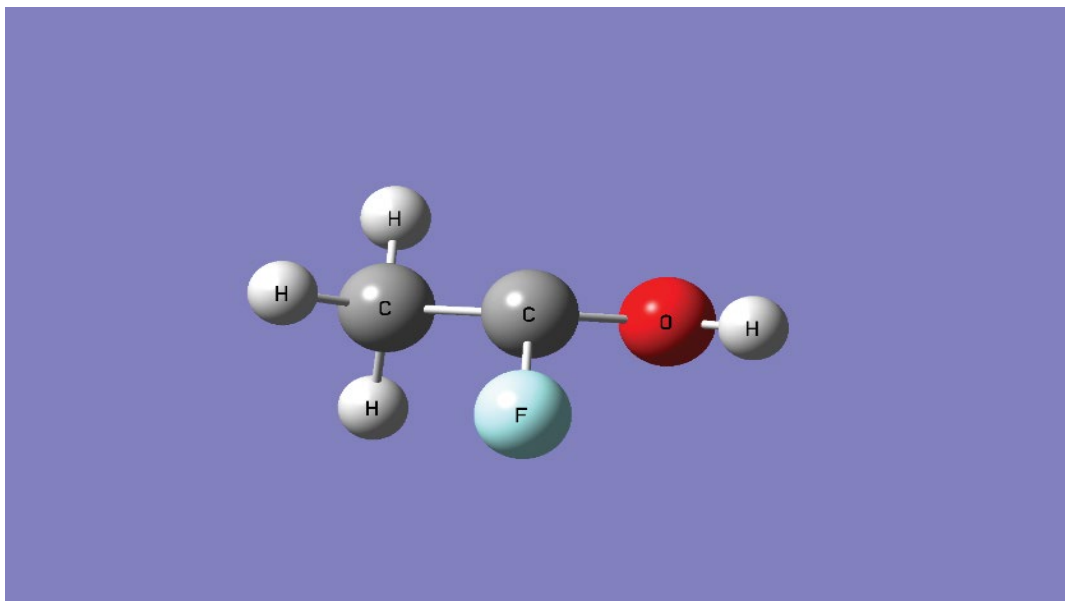


Figure 7. Optimized geometry for $\text{CH}_3\text{CF}\cdot\text{OH}$ at the m062x/6-31+g(d, p) level of theory.

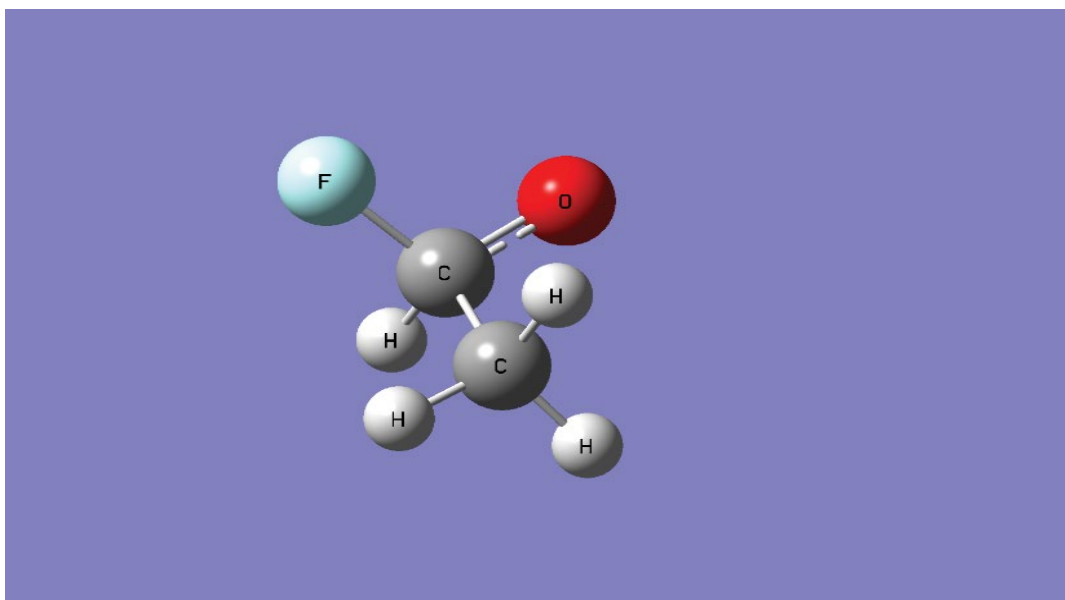


Figure 8. Optimized geometry for $\text{CH}_3\text{CHFO}\cdot$ at the m062x/6-31+g(d, p) level of theory.

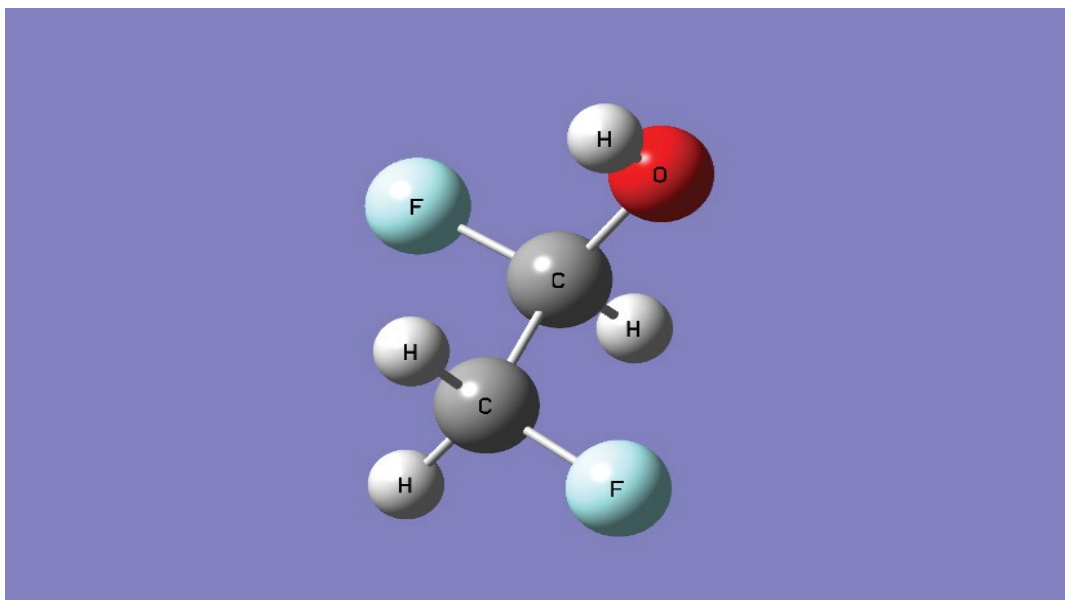


Figure 9. Optimized geometry for $\text{CH}_2\text{FCHF}\cdot\text{OH}$ at the m062x/6-31+g(d, p) level of theory.

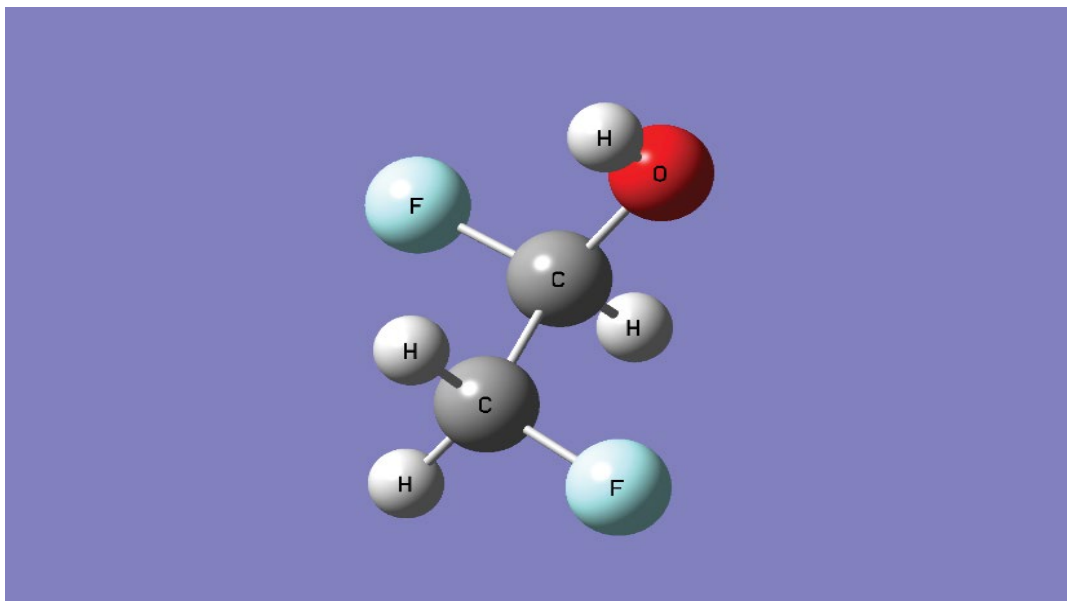


Figure 10. Optimized geometry for $\text{CF}_2\text{HCH}_2\text{OH}$ at the m062x/6-31+g(d, p) level of theory.

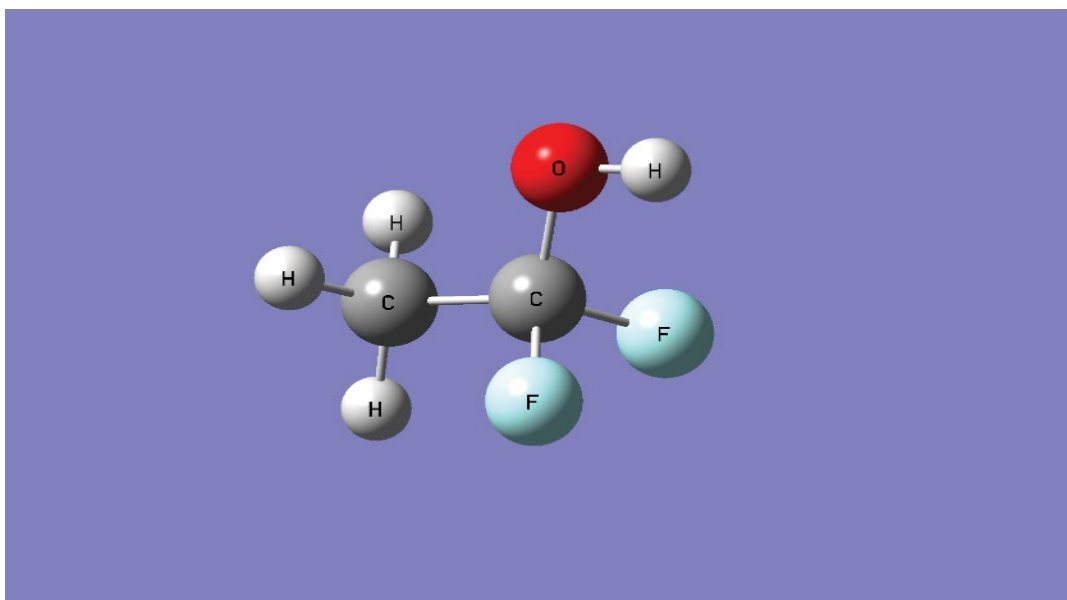


Figure 11. Optimized geometry for $\text{CH}_3\text{CF}_2\text{OH}$ at the m062x/6-31+g(d, p) level of theory.

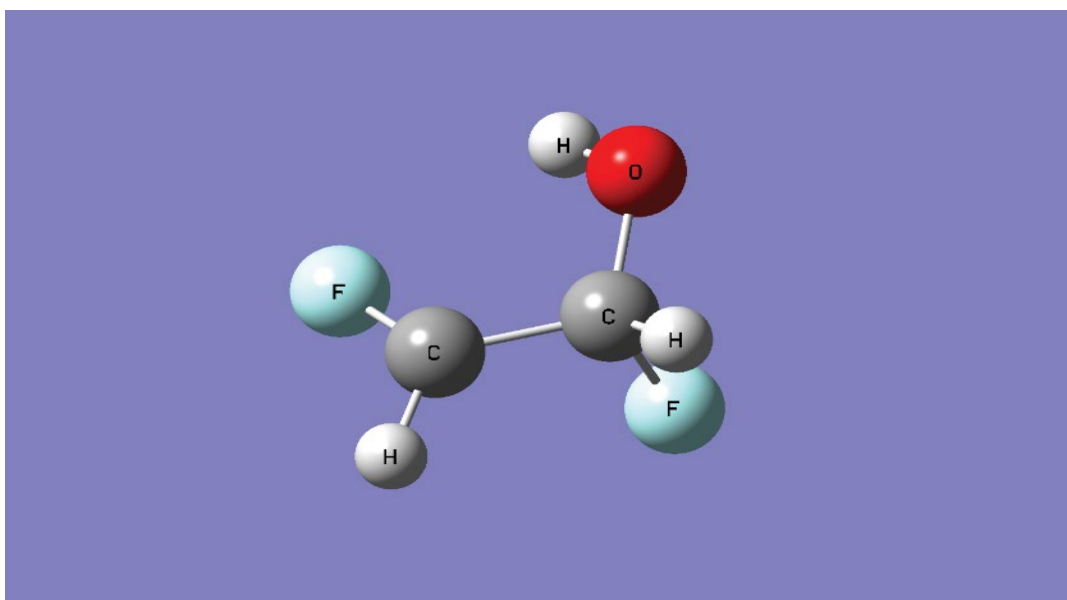


Figure 12. Optimized geometry for $\text{C}\cdot\text{HFCFHOH}$ at the m062x/6-31+g(d, p) level of theory.

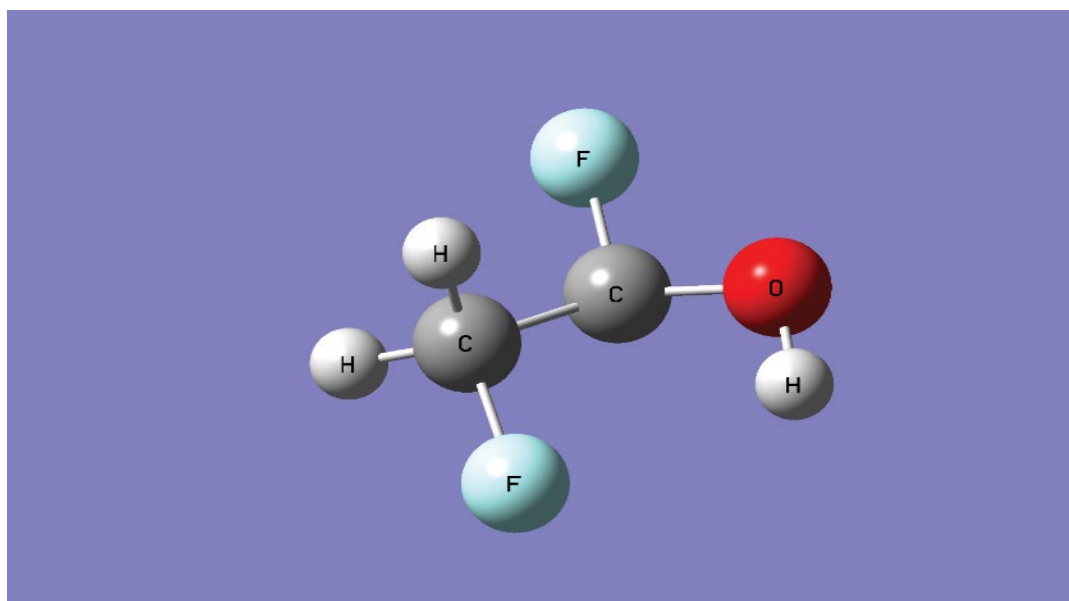


Figure 13. Optimized geometry for $\text{CH}_2\text{FC}\cdot\text{FOH}$ at the m062x/6-31+g(d, p) level of theory.

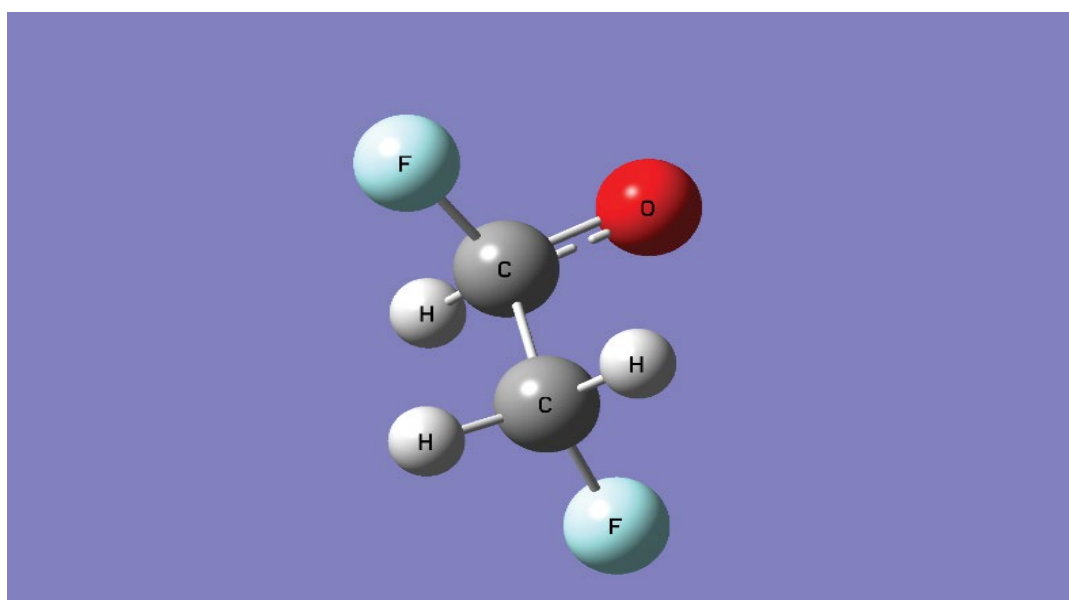


Figure 14. Optimized geometry for $\text{CH}_2\text{FCHFO}\cdot$ at the m062x/6-31+g(d, p) level of theory.

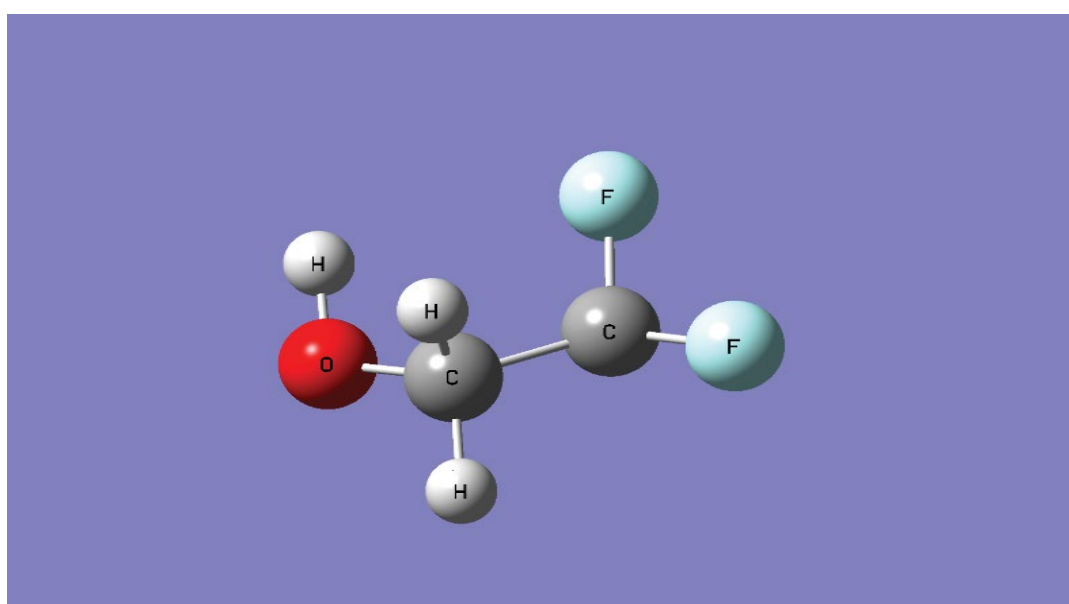


Figure 15. Optimized geometry for $\text{C}\cdot\text{F}_2\text{CH}_2\text{OH}$ at the m062x/6-31+g(d, p) level of theory.

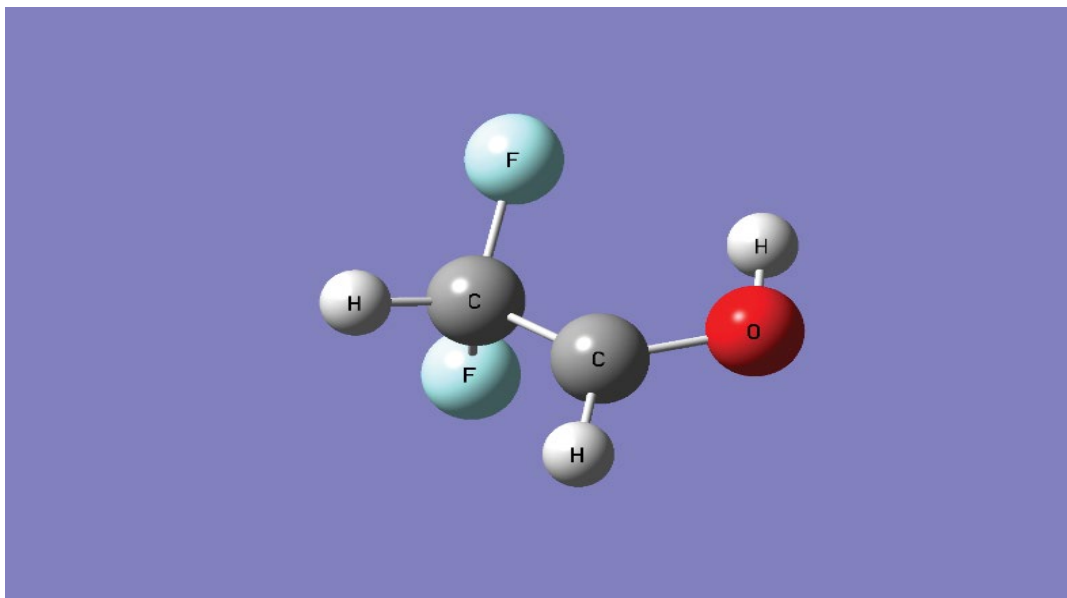


Figure 16. Optimized geometry for $\text{CHF}_2\text{C}\cdot\text{HOH}$ at the m062x/6-31+g(d, p) level of theory.

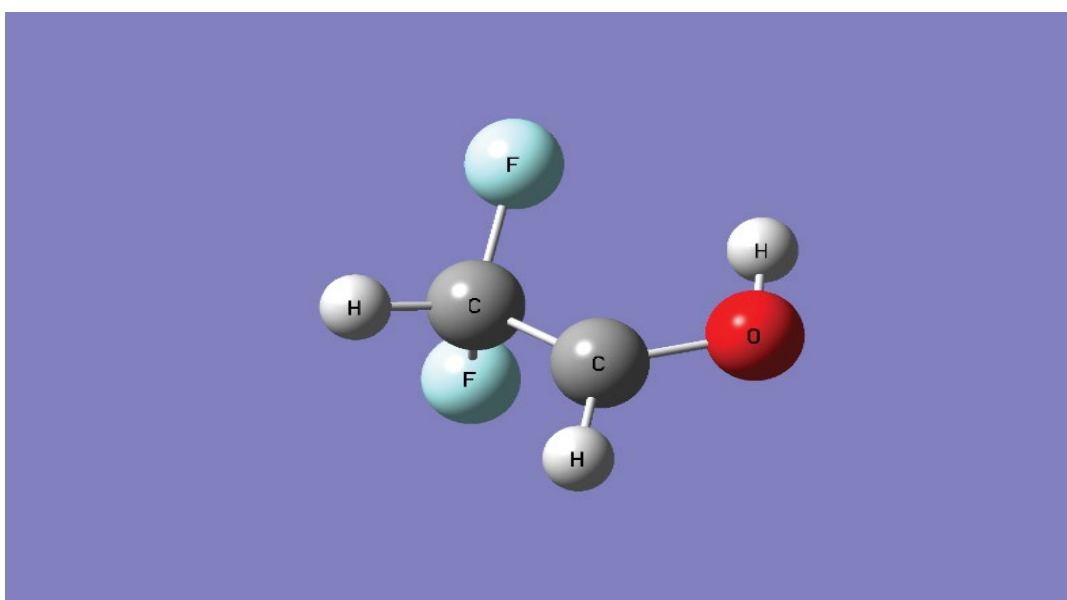


Figure 17. Optimized geometry for $\text{CHF}_2\text{CH}_2\text{O}\cdot$ at the m062x/6-31+g(d, p) level of theory.

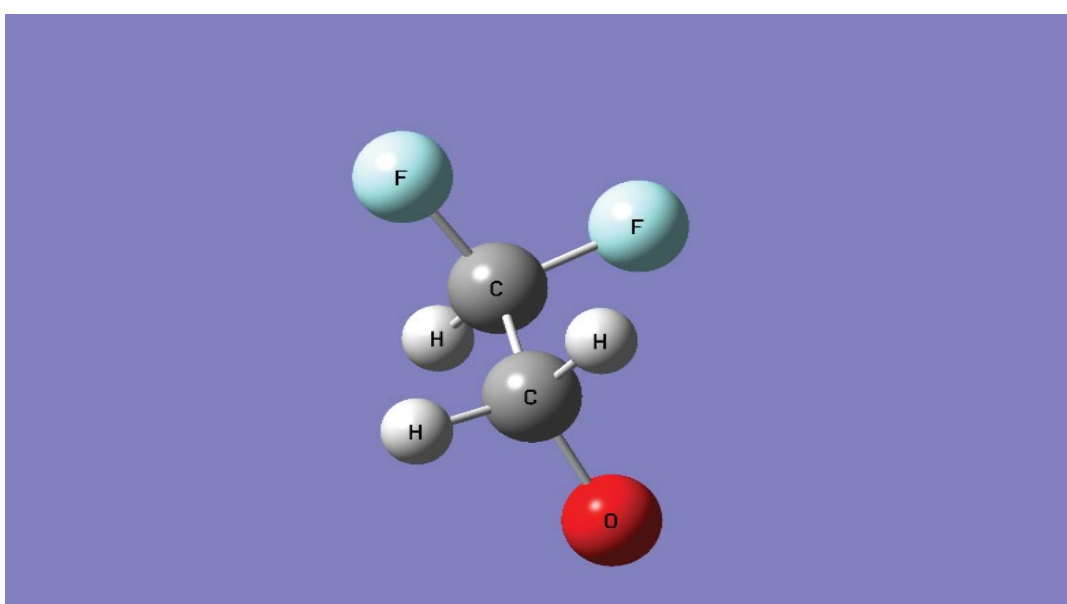


Figure 18. Optimized geometry for $\text{CH}_2\cdot\text{CF}_2\text{OH}$ at the m062x/6-31+g(d, p) level of theory.

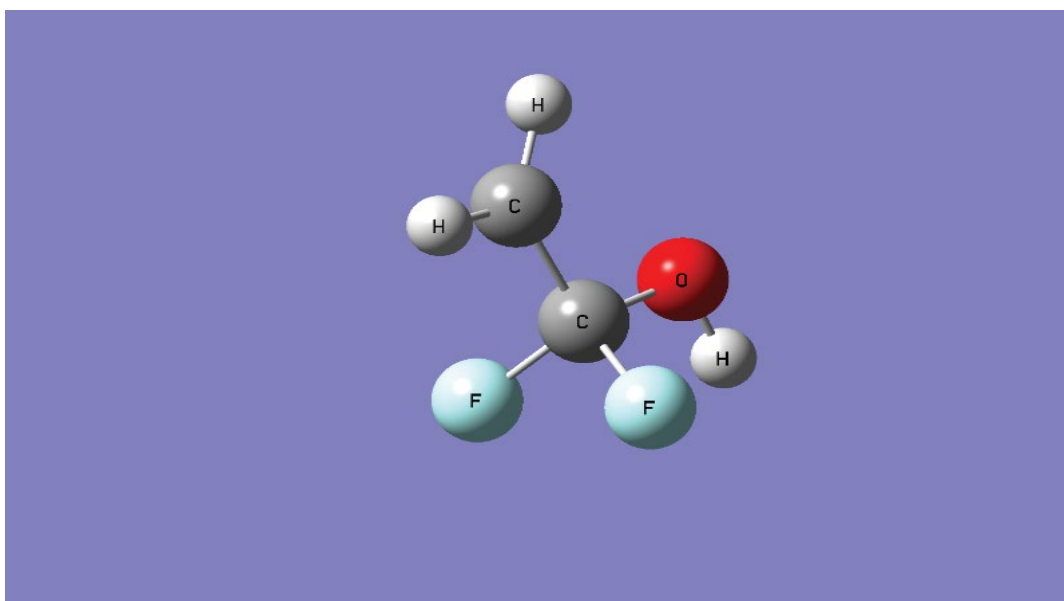


Figure 19. Optimized geometry for $\text{CHF}_2\text{C}\cdot\text{HOH}$ at the m062x/6-31+g(d, p) level of theory.

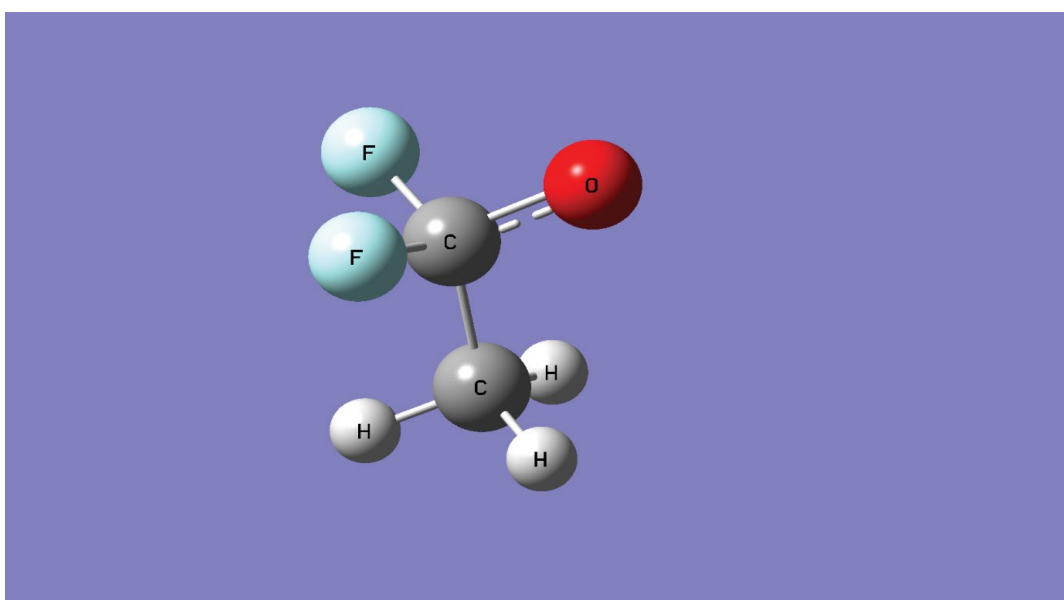


Figure 20. Optimized geometry for $\text{CHF}_2\text{CH}_2\text{O}\cdot$ at the m062x/6-31+g(d, p) level of theory.

M06-2x/6-31+g (d,p) calculation had 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 (**Figures 1-20**), shows the optimized geometries at the m062x/6-31+g (d, p) level of theory for target molecules.

Halogenated compounds are highly stable, have low reactivity and are valued chemicals in industry^[4]. 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^[4].

EXPERIMENTAL PROCEDURE

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. All reported values are for standard state of 298 °K and 1 atm^[5]. 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 with small reported standard deviations values^[6].

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 are allowed to accuracies close to experimental values by the careful choice of the isodesmic reactions [1]. Taking 1-fluoroethanol as an example, two isodesmic reactions are selected to determine the $\Delta_f H^\circ_{(298K)}$ of the target molecule, 1-fluoroethanol (**Table 1**). Since the $\Delta_f H^\circ_{(298K)}$ values of all species but 1-fluoroethanol in **Table 1** are known, the $\Delta_f H^\circ_{(298K)}$ of the target species 1-fluoroethanol, is obtained from this data and the calculated $\Delta_{rxn} H^\circ_{(2980 K)} \cdot \Delta_f H^\circ_{(298K)}$ calculated using two different reference molecules are within ± 0.2 kcal/mol [1,2].

Reference species

Standard enthalpy of formation for the reference species used in the isodesmic work reactions along with their uncertainties are listed, (**Tables 1 and 2**) provides one example on the method of Isodesmic Work Reactions used for the calculation of the Standard Enthalpy of Formation $\Delta_f H^\circ_{(298K)}$ for the fluoroethanols.

RESULTS AND DISCUSSION

Entropy and heat capacity values

Internal rotor contributions to calculated entropy and heat capacity at 298-1500 K 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 3**). The vibrational frequencies for the calculation of heat capacity and entropy at the

Table 1. Example for enthalpy of formation calculations for 1-fluoroethanol using isodesmic reactions; using different reference molecules, Units in kcal/mol.

Isodesmic Reactions	$\Delta_{rxn} H^\circ_{(298K)}$ Hartrees	$\Delta_{rxn} H^\circ_{(298K)}$ kcal/mol	$\Delta_f H^\circ_{(298K)}$, CH3- xCH2FxOH, CH3CH2-xFxOH kcal/mol	Error kcal/mol	Equ. #
CH2FCH2OH + CH4 = CH3CH2OH + CH3F -254.173115a -40.447961 -154.926666 -139.683801 Reference Values -17.81 -56.21 -56.54 Kcal mol-1	0.010609	6.657243	-101.6	± 0.2	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	± 1.3	2
Reported $\Delta_f H^\circ_{(298)}$ kcal mol-1			-101.7 \pm 0.7		
Standard Deviation over rxns			± 0.1		

Table 2. Reference Species in the isodesmic reactions standard enthalpy of formation values (kcal/mol).

Species	$\Delta_f H^\circ_{(298K)}$	Species	$\Delta_f H^\circ_{(298K)}$
CH ₃ F	-56.54 \pm 0.07 ^a -56.62 \pm 0.48 ^h	CH ₃ OOH CH ₃ CH ₂ OOH	-30.96 \pm 0.67 ^b -38.94 \pm 0.81 ^b
CH ₃ CH ₂ F	-65.42 \pm 1.11 ^a	CH ₃ CH ₂ CH ₂ OOH	-44.03 \pm 0.67 ^b
CH ₃ CH ₂ CH ₂ F	-70.24 \pm 1.30 ^a	CH ₃ OO [*]	2.37 \pm 1.24 ^b
CH ₂ F ₂	-108.07 \pm 1.46 ^a -107.67 \pm 0.48 ^h	CH ₃ CH ₂ OO [*] CH ₃ CH ₂ CH ₂ OO [*]	-6.19 \pm 0.92 ^b -11.35 \pm 1.24 ^b
CH ₃ CHF ₂	-120.87 \pm 1.62 ^a	CH ₄	-17.81 \pm 0.01 ^c
CH ₃ CH ₂ CHF ₂	-125.82 \pm 1.65 ^a	CH ₃ CH ₃	-20.05 \pm 0.04 ^c
CHF ₃	-166.71 \pm 1.97 ^h -166.09 \pm 0.48 ^h	CH ₃ CH ₂ CH ₃ CH ₃ CH ₂ CH ₂ CH ₃	-25.01 \pm 0.06 ⁱ -30.07 \pm 0.08 ⁱ
CH ₃ CF ₃	-180.51 \pm 2.05 ^a	CH ₃ O [*]	5.15 \pm 0.08 ^c
CH ₃ CH ₂ CF ₃	-185.48 \pm 2.15 ^a	CH ₃ CH ₂ O [*]	-3.01 ^d
CH ₃ [*]	34.98 \pm 0.02 ^c	OH	8.96 \pm 0.01 ^c
CH ₃ CH ₂ [*]	28.65 \pm 0.07 ^c	CH ₃ OH	-47.97 \pm 0.04 ^c
CH ₃ CH ₂ CH ₂ [*]	24.21 \pm 0.24 ^{ej} 24.18 ^g	CH ₃ CH ₂ OH	-56.07 \pm 0.05 ⁱ
H	52.10 ^c	HOO [*]	2.94 ^{ej}
O	59.57 ^c	HOOH	-32.39 \pm 0.04 ^{fi} -32.37 ⁱ

Table 3. 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 K).

Species		S(298°K)	Cp(298°K)	Cp(298°K)	Cp(500°K)	Cp(600°K)	Cp(800°K)	Cp(1000°K)	Cp(1500°K)
CH ₂ FCH ₂ OH	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
		2.02	3.15	3.33	3.04	2.66	2.05	1.69	1.3
	Total	70.6	19.62	23.94	27.2	29.62	32.91	35.03	37.98
CH ₃ CHFOH	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
		2.67	2.17	2.21	2.18	2.09	1.89	1.71	1.4
	Total	72.32	18.35	22.21	25.5	28.16	31.96	34.42	37.75
C•HFCH ₂ OH	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
		3.09	3.16	2.52	2.04	1.74	1.41	1.25	1.11
	Total	75.58	19.01	21.38	23.7	25.76	29.06	31.55	35.56
CH ₂ FCH•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
		6	1.96	1.95	1.95	1.91	1.79	1.65	1.4
	Total	78.19	18.06	21.27	24.07	26.38	29.81	32.24	36.03
CH ₂ FCH ₂ O•	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
			81.38	22.64	25.62	28.07	30.07	33.08	35.21
	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
		2.84	1.95	2.12	2.12	2.04	1.83	1.64	1.35
	Total	74.67	18.17	21.58	24.35	26.55	29.79	32.11	35.86
CH ₃ CF•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
		1.71	2.6	3.17	3.22	3.01	2.43	1.99	1.45
	Total	73.18	18.5	22.17	24.96	27.07	30.08	32.28	35.92
CH ₃ CHFO•	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
			71.27	16.56	20.21	23.29	25.84	29.69	32.48
	Total	71.27	16.56	20.21	23.29	25.84	29.69	32.48	36.75
CH ₂ FCHFOH	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
		6.12	3.11	2.64	2.24	1.94	1.57	1.37	1.17
	Total	73.58	18.52	22.15	25.35	28	31.79	34.2	37.31
CF ₂ HCH ₂ OH	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
		2.23	3.21	3.17	2.81	2.44	1.91	1.6	1.27
	Total	70.15	18.57	21.91	24.72	27.06	30.6	33.1	36.81
CH ₃ CF ₂ OH	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
		1.58	2.45	3.09	3.28	3.14	2.6	2.14	1.53
	Total	74.52	21.11	25.91	29.44	31.93	35.01	36.8	39.08
CH ₂ FC•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
		3.15	1.91	1.96	1.91	1.83	1.65	1.5	1.27
	Total	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
		1.72	2.79	3.1	3.03	2.83	2.37	2.02	1.52
	Total	78.25	20.3	24.01	26.83	28.96	31.91	33.92	37
CH ₂ FCHFO•	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
			76.01	18.91	22.67	25.8	28.31	31.94	34.41
	Total	76.01	18.91	22.67	25.8	28.31	31.94	34.41	37.99
CHF ₂ C•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
		1.51	2.5	3.06	3.18	3.06	2.6	2.2	1.61
	Total	75.85	20.61	24.54	27.48	29.63	32.49	34.37	37.25

C•F₂CH₂OH	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
		3.46	2.45	2.04	1.75	1.55	1.32	1.21	1.09
	Total	79.21	20.29	23.15	25.66	27.76	30.94	33.19	36.65
CHF₂CH₂O•	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
CH₂•CF₂OH	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
		1.78	2.81	3.33	3.25	2.9407	2.3	1.87	1.38
	Total	76.95	21.48	25.63	28.35	27.25	32.61	34.29	37.09
CH₃CF₂O•	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
		5.78	2.51	2.41	2.26	2.1	1.83	1.63	1.34
	Total	80.75	21.44	25.08	27.94	30.2	33.47	35.73	39.11

M-062x/6-31+g (d,p) level of calculation was scaled by a factor of 0.97^[7]. 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^[8]. It employs the rigid-rotor harmonic oscillator approximation using moment of inertia from optimized structure and frequencies. The “Rotorator”^[9] program by Lay et al.^[10] 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 program is used to calculate thermodynamic functions from hindered rotations with arbitrary potentials^[11].

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

$$V(\varnothing) = a_0 + \sum_{i=1}^{10} a_i \cos(i\varnothing) + \sum_{j=1}^{10} b_j \cos(j\varnothing)$$

The coefficients a_i and b_j 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^[12]. 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 (**Table 4**)^[13-35].

Standard enthalpy values

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 5**) are listed in **Table 2** in kcal mol⁻¹. The standard deviation was calculated^[36] for all Enthalpies of formation values for all 19 fluorinated ethanol and are included in **Table 5**. Details of the method of standard deviation and example calculation(s) are shown in the supporting information table provided^[36].

The standard deviation is calculated using the following formula:

$$\sigma = \sqrt{\frac{1}{N} \sum_{i=1}^N (x_i - \mu)^2}$$

Where, X_i is the mean; the average of the numbers, μ is the actual numbers to be calculated the standard deviation of, and

$$\frac{1}{N} \sum_{i=1}^N (x_i - \mu)^2 \text{ is the variance.}$$

The standard deviation for standard enthalpy of formation for 1-fluoroethanol is calculated to be ± 0.1 . The calculation of standard deviation for this molecule is as follows:

$$N=2, \mu_1 = -101.60, \mu_2 = -101.86$$

Table 4. Bond dissociation energy (BDE's) of monofluoro and difluoro- ethanol's. ■ Bond Energies

Reactions	Bond Dissociation Energy ^a (kcal/mol) BDE (this study)	Error kcal/mol
H-CHFCH₂OH		
H-CHFCH ₂ OH = H• + •CHFCH ₂ OH -101.7 ± 0.1 52.1 -50.7 ± 0.09	103.1 ± 0.1	± 0.2
CH₂FC-HHOH		
CH ₂ FC-HHOH = H• + CH ₂ FC•HOH -101.7 ± 0.1 52.1 -56.1 ± 0.1	97.7 ± 0.1	± 0.2
CH₂FCH₂O-H		
CH ₂ FCH ₂ O-H = H• + CH ₂ FCH ₂ O• -101.7 ± 0.1 52.1 -45.0 ± 0.1	108.8 ± 0.1	± 0.2
H-CH₂CHFOH		
H-CH ₂ CHFOH = H• + •CH ₂ CHFOH -113.5 ± 0.2 52.1 -59.6 ± 0.1	106.0 ± 0.15	± 0.3
CH₃C-HFOH		
H-CH ₂ CHFOH = H• + CH ₃ C•FOH -113.5 ± 0.2 52.1 -68. ± 0.2	97.6 ± 0.2	± 0.4
CH₂FC-HFOH		
CH ₂ FC-HFOH = H• + CH ₂ FC•FOH -154.6 ± 0.6 52.1 -104.1 ± 0.1	106.8 ± 0.2	± 0.4
CH₂FCHFO-H		
CH ₂ FCHFO-H = H• + CH ₂ FCHFO• -154.6 ± 0.6 52.1 -99.1 ± 0.1	101.1 ± 0.4	± 0.8
CF₂-HCH₂OH		
CF ₂ -HCH ₂ OH = H• + •CF ₂ CH ₂ OH -155.3 ± 0.1 52.1 -102.3 ± 0.2	107.6 ± 0.35	± 0.7
CF₂HCH-HOH		
CF ₂ HCHOH-H = H• + CF ₂ HC•OH -155.3 ± 0.1 52.1 -102.4 ± 0.2	105.1 ± 0.15	± 0.7
CF₂HCH₂O-H		
CF ₂ HCH ₂ O-H = H• + CF ₂ HCH ₂ O• -155.3 ± 0.1 52.1 -98.9 ± 0.2	108.5 ± 0.15	± 0.3
H-CH₂CF₂OH		
H-CH ₂ CF ₂ OH = H• + •CH ₂ CF ₂ OH -174.5 ± 0.1 52.1 -119.4 ± 0.2	107.2 ± 0.15	± 0.3
CH₃CF₂O-H		
CH ₃ CF ₂ O-H = H• + CH ₃ CF ₂ O• -174.5 ± 0.1 52.1 -110.6 ± 0.1	116.0 ± 0.1	± 0.2

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

Table 5. 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 Target Specie	$\Delta_{\text{rxn}} H^\circ_{(298\text{K})}$	$\Delta_{\text{rxn}} H^\circ_{(298\text{K})}$ kcal/mol	$\Delta_{\text{rxn}} H^\circ_{(298\text{K})}$ kcal/mol	Error kcal/mol
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	± 0.2
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	± 1.3
Reported $\Delta_f H^\circ_{(298\text{K})}$ kcal mol⁻¹			-101.7 ± 0.7	
Standard Deviation over rxns			± 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	± 1.5
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	± 1.3

Reported $\Delta_f H^\circ$ (298K) kcal mol⁻¹			-113.5 ± 1.4	
Standard Deviation over rxns			± 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	± 1.4
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	± 0.1
Reported $\Delta_f H^\circ$ (298K) kcal mol⁻¹			-50.7 ± 0.8	
Standard Deviation over rxns			± 0.1	
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	± 1.2
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	± 0.1
Reported $\Delta_f H^\circ$ (298K) kcal mol⁻¹			-56.1 ± 0.6	
Standard Deviation over rxns			± 0.1	
CH ₂ FCH ₂ O• + CH ₃ CH ₂ CH ₃ = CH ₃ CHO• + CH ₂ 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	± 1.4
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	± 1.2
Reported $\Delta_f H^\circ$ (298K) kcal mol⁻¹			-45.0 ± 1.3	
Standard Deviation over rxns			± 0.1	
CH ₂ •CHFOH + CH ₄ = CH ₃ O• + CH ₂ 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	± 1.2
Reported $\Delta_f H^\circ$ (298K) kcal mol⁻¹			-59.6 ± 1.2	
Standard Deviation over rxns			± 0.1	
CH ₃ CF•OH + CH ₃ CH ₃ = CH ₃ CH ₂ O• + CH ₃ CH ₂ F -253.542527 -79.717768 -154.268107 -178.963776 -20.05 -5.01 -65.42	0.028412	17.82879	-68.2	± 1.2
CH ₃ CF•OH + CH ₃ CH ₂ CH ₃ = CH ₃ CH ₂ O• + CH ₃ CH ₂ CH ₂ F -253.542527 -118.990915 -154.268107 -218.237381 -25.02 -5.01 -70.24	0.027954	17.54139	-67.8	± 1.4
Reported $\Delta_f H^\circ$ (298K) kcal mol⁻¹			-68.0 ± 1.3	
Standard Deviation over rxns			± 0.2	
CH ₃ CHFO• + CH ₄ = CH ₃ O• + CH ₃ CH ₂ F -253.530783 -40.447961 -114.989112 -178.963776 -17.81 5.15 -65.42	0.025856	16.22487	-58.7	± 1.2
CH ₃ CHFO• + CH ₃ CH ₃ = CH ₃ CH ₂ O• + CH ₃ CH ₂ F -253.530783 -79.717768 -154.268107 -178.963776 -20.05 -3.01 -65.42	0.016668	10.45932	-58.8	± 1.2
Reported $\Delta_f H^\circ$ (298K) kcal mol⁻¹			-58.8 ± 1.2	
Standard Deviation over rxns			± 0.2	

$\text{CH}_2\text{FCHFOH} + \text{CH}_4 = \text{CH}_3\text{CH}_2\text{OH} + \text{CH}_2\text{F}_2$ -353.429924 -40.447961 -154.926666 -238.938973 -17.81 -56.21 -108.07	0.012246	7.684475	-154.2	± 1.6
$\text{CH}_2\text{FCHFOH} + \text{CH}_3\text{CH}_2\text{CH}_3 = \text{CH}_3\text{CH}_2\text{OH} + \text{CH}_3\text{CH}_2\text{CHF}_2$ -353.429924 -118.990915 -154.926666 -317.498882 -25.02 -56.21 -125.82	-0.00471	-2.95494	-154.1	± 1.9
Reported $\Delta_f H^\circ$ (298K) kcal mol⁻¹			-154.2 ± 1.7	
Standard Deviation over rxns			± 0.6	
$\text{CF}_2\text{HCH}_2\text{OH} + \text{CH}_4 = \text{CH}_3\text{CH}_2\text{OH} + \text{CH}_2\text{F}_2$ -353.431533 -40.447961 -154.926666 -238.938973 -17.81 -56.21 -108.07	0.013855	8.694137	-155.2	± 1.6
$\text{CF}_2\text{HCH}_2\text{OH} + \text{CH}_3\text{CH}_3 = \text{CH}_3\text{CH}_2\text{OH} + \text{CH}_3\text{CHF}_2$ -353.431533 -79.717768 -154.926666 -278.225303 -20.05 -56.21 -120.87	-0.00267	-1.67419	-155.4	± 1.8
Reported $\Delta_f H^\circ$ (298K) kcal mol⁻¹			-155.3 ± 1.7	
Standard Deviation over rxns			± 0.1	
$\text{CH}_3\text{CF}_2\text{OH} + \text{CH}_4 = \text{CH}_3\text{CH}_2\text{OH} + \text{CH}_2\text{F}_2$ -353.462472 -40.447961 -154.926666 -238.938973 -17.81 -56.21 -108.07	0.044794	28.10864	-174.6	± 1.6
$\text{CH}_3\text{CF}_2\text{OH} + \text{CH}_3\text{CH}_2\text{CH}_3 = \text{CH}_3\text{CH}_2\text{OH} + \text{CH}_3\text{CH}_2\text{CHF}_2$ -353.462472 -118.990915 -154.926666 -317.498882 -25.02 -56.21 -125.82	0.027839	17.46922	-174.5	± 1.5
Reported $\Delta_f H^\circ$ (298K) kcal mol⁻¹			-174.5 ± 1.5	
Standard Deviation over rxns			± 0.1	
$\text{CH}_2\text{FC}\cdot\text{FOH} + \text{CH}_4 = \text{CH}_3\text{CH}_2\text{O}\cdot + \text{CH}_2\text{F}_2$ -352.776406 -40.447961 -154.268107 -238.938973 -17.81 -3.01 -108.07	0.017287	10.84775	-104.1	± 1.5
$\text{CH}_2\text{FC}\cdot\text{FOH} + \text{CH}_3\text{CH}_2\text{CH}_3 = \text{CH}_3\text{CH}_2\text{O}\cdot + \text{CH}_3\text{CH}_2\text{CHF}_2$ -352.776406 -118.990915 -154.268107 -317.498882 -25.02 -3.01 -125.82	0.000332	0.208333	-104.0	± 1.4
Reported $\Delta_f H^\circ$ (298K) kcal mol⁻¹			-104.1 ± 1.5	
Standard Deviation over rxns			± 0.1	
$\text{C}\cdot\text{HFCFHOH} + \text{CH}_4 = \text{CH}_3\text{O}\cdot + \text{CH}_3\text{CHF}_2$ -352.778474 -40.447961 -114.989112 -278.225303 -17.81 5.15 -120.87	0.01202	7.542658	-105.5	± 1.7
$\text{C}\cdot\text{HFCFHOH} + \text{CH}_3\text{CH}_3 = \text{CH}_3\text{O}\cdot + \text{CH}_3\text{CH}_2\text{CHF}_2$ -352.778474 -79.717768 -114.989112 -317.498882 -20.05 5.15 -125.82	0.008248	5.175694	-105.8	± 1.8
Reported $\Delta_f H^\circ$ (298K) kcal mol⁻¹			-105.6 ± 1.7	
Standard Deviation over rxns			± 0.2	
$\text{CHF}_2\text{C}\cdot\text{HOH} + \text{CH}_4 = \text{CH}_3\text{O}\cdot + \text{CH}_3\text{CHF}_2$ -352.773245 -40.447961 -114.989112 -278.225303 -17.81 5.15 -120.87	0.006791	4.261414	-102.5	± 1.7
$\text{CHF}_2\text{C}\cdot\text{HOH} + \text{CH}_3\text{CH}_3 = \text{CH}_3\text{O}\cdot + \text{CH}_3\text{CH}_2\text{CHF}_2$ -352.773245 -79.717768 -114.989112 -317.498882 -20.05 5.15 -125.82	0.003019	1.89445	-102.2	± 1.8
Reported $\Delta_f H^\circ$ (298K) kcal mol⁻¹			-102.3 ± 1.7	
Standard Deviation over rxns			± 0.2	
$\text{CH}_2\text{FCHFO}\cdot + \text{CH}_4 = \text{CH}_3\text{CH}_2\text{O}\cdot + \text{CH}_2\text{F}_2$ -352.768218 -40.447961 -154.268107 -238.938973 -17.81 -3.01 -108.07	0.009099	5.709704	-99.0	± 1.5
$\text{CH}_2\text{FCHFO}\cdot + \text{CH}_3\text{CH}_3 = \text{CH}_3\text{CH}_2\text{O}\cdot + \text{CH}_3\text{CHF}_2$ -352.768218 -79.717768 -154.268107 -278.225303 -20.05 -3.01 -120.87	-0.00742	-4.65863	-99.2	± 1.7
Reported $\Delta_f H^\circ$ (298K) kcal mol⁻¹			-99.1 ± 1.6	
Standard Deviation over rxns			± 0.1	

$C \cdot F_2CH_2OH + CH_4 = CH_3CH_2O \cdot + CH_2F_2$ -352.773245 -40.447961 -154.268107 -238.938973 -17.81 -3.01 -108.07	0.014126	8.864192	-102.1	± 1.5
$C \cdot F_2CH_2OH + CH_3CH_3 = CH_3CH_2O \cdot + CH_3CHF_2$ -352.773245 -79.717768 -154.268107 -278.225303 -20.05 -3.01 -120.87	-0.0024	-1.50414	-102.3	± 1.7
Reported $\Delta_f H^\circ_{(298K)}$ kcal mol⁻¹			-102.2 ± 1.6	
Standard Deviation over rxns			± 0.2	
$CHF_2CH_2O \cdot + CH_4 = CH_3CH_2O \cdot + CH_2F_2$ -352.767873 -40.447961 -154.268107 -238.938973 -17.81 -3.01 -108.07	0.008754	5.493214	-98.8	± 1.5
$CHF_2CH_2O \cdot + CH_3CH_3 = CH_3CH_2O \cdot + CH_3CHF_2$ -352.767873 -79.717768 -154.268107 -278.225303 -20.05 -3.01 -120.87	-0.00777	-4.87512	-99.0	1.7
Reported $\Delta_f H^\circ_{(298K)}$ kcal mol⁻¹			-98.9 ± 1.6	
Standard Deviation over rxns			± 0.2	
$CH_2 \cdot CF_2OH + CH_4 = CH_3O \cdot + CH_3CHF_2$ -352.800434 -40.447961 -114.989112 -278.225303 -17.81 5.15 -120.87	0.03398	21.32276	-119.2	± 1.7
$CH_2 \cdot CF_2OH + CH_3CH_3 = CH_3O \cdot + CH_3CH_2CHF_2$ -352.800434 -79.717768 -114.989112 -317.498882 -20.05 5.15 -125.82	0.030208	18.95579	-119.6	± 1.8
Reported $\Delta_f H^\circ_{(298K)}$ kcal mol⁻¹			-119.4 ± 1.7	
Standard Deviation over rxns			± 0.2	
$CH_3CF_2O \cdot + CH_4 = CH_3CH_2O \cdot + CH_2F_2$ -352.786755 -40.447961 -154.268107 -238.938973 -17.81 5.15 -108.07	0.027636	17.34184	-110.6	± 1.5
$CH_3CF_2O \cdot + CH_3CH_2CH_3 = CH_3CH_2O \cdot + CH_3CH_2CHF_2$ -352.786755 -118.990915 -154.268107 -317.498882 -25.02 5.15 -125.82	0.010681	6.702424	-110.5	± 1.8
Reported $\Delta_f H^\circ_{(298K)}$ kcal mol⁻¹			-110.6 ± 1.6	
Standard Deviation over rxns			± 0.1	

Step 1, $X_1 = (-101.60-101.86)/2 = -101.73$

Step 2, $(X_1 - \mu_1) = (-101.73+ 101.60)^2 = 0.0169$

$(X_1 - \mu_2) = (-101.73+ 101.86)^2 = 0.0169$

Step 3, $\frac{1}{2} (0.0169 + 0.0169) = 0.0169$

Step 4, square root of 0.0169 = 0.13 = ± 0.1

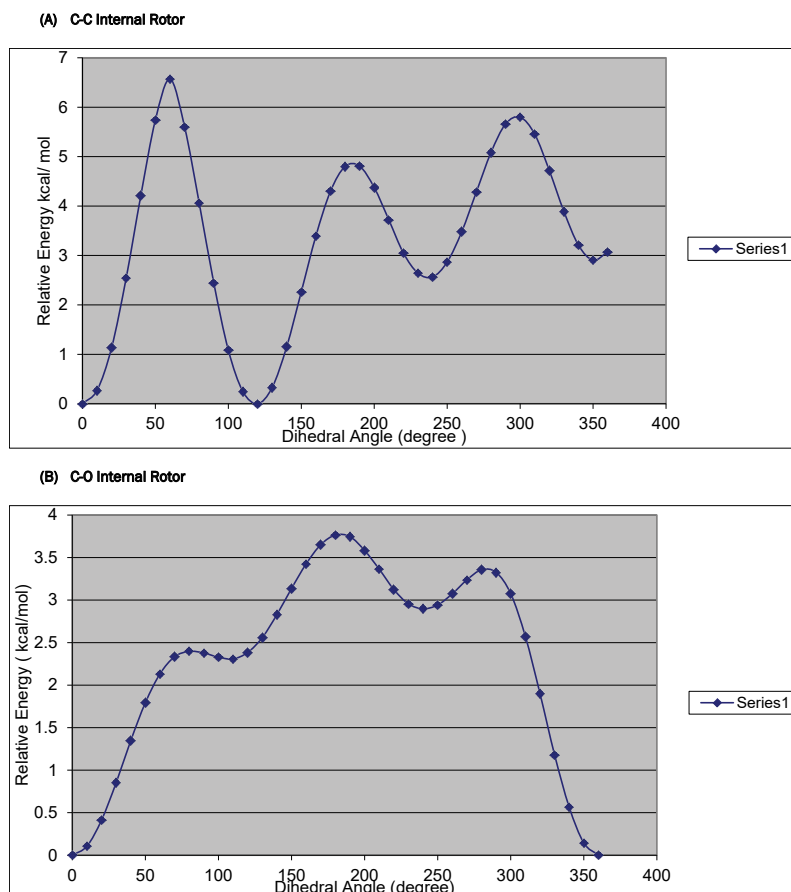


Figure 21. Potential energy profile of C-C and C-O internal rotors for $\text{CH}_2\text{FCH}_2\text{OH}$. The solid lines indicate Fourier series expansion.

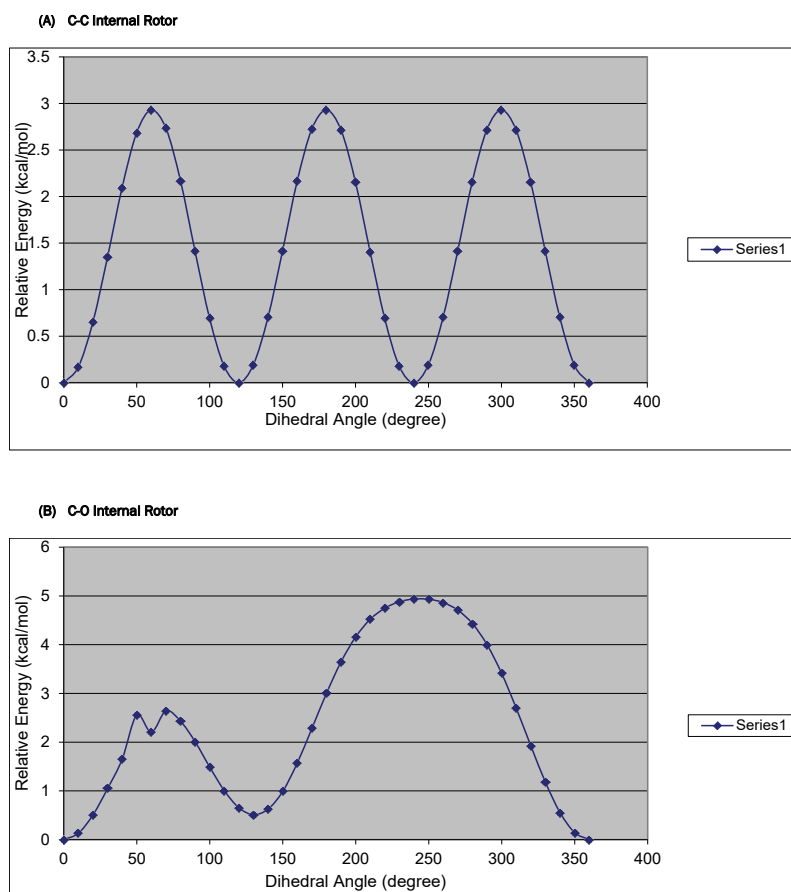


Figure 22. Potential energy profile of C-C and C-O internal rotors for CH_3CHOH . The solid lines indicate Fourier series expansion.

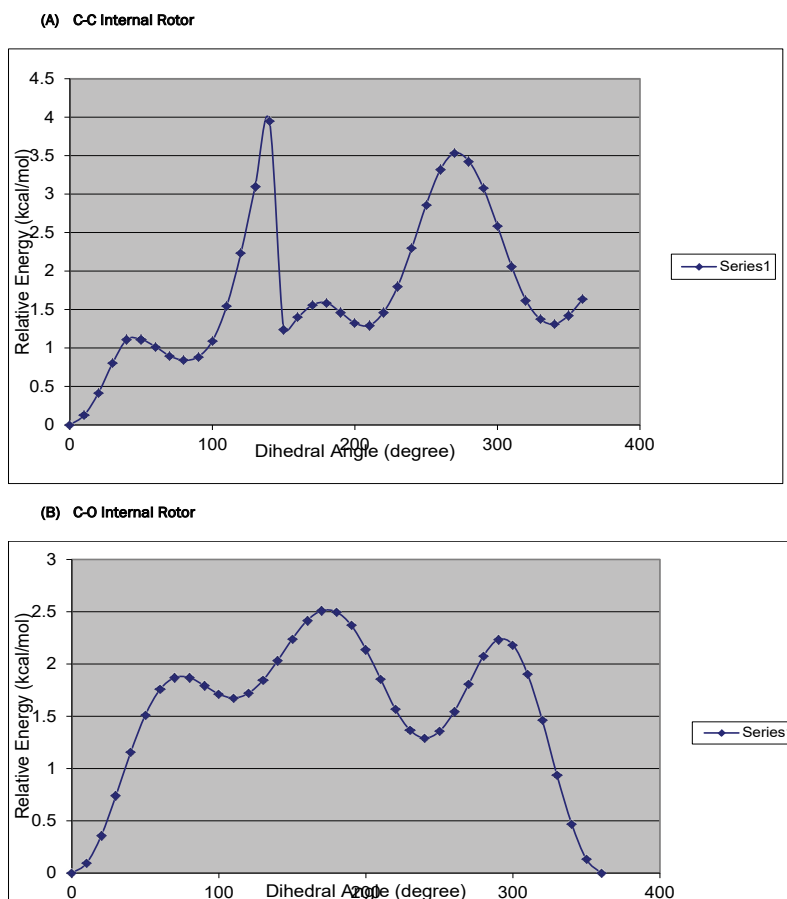


Figure 23. Potential energy profile of C-C and C-O internal rotors for C•HFCH₂OH. The solid lines indicate Fourier series expansion.

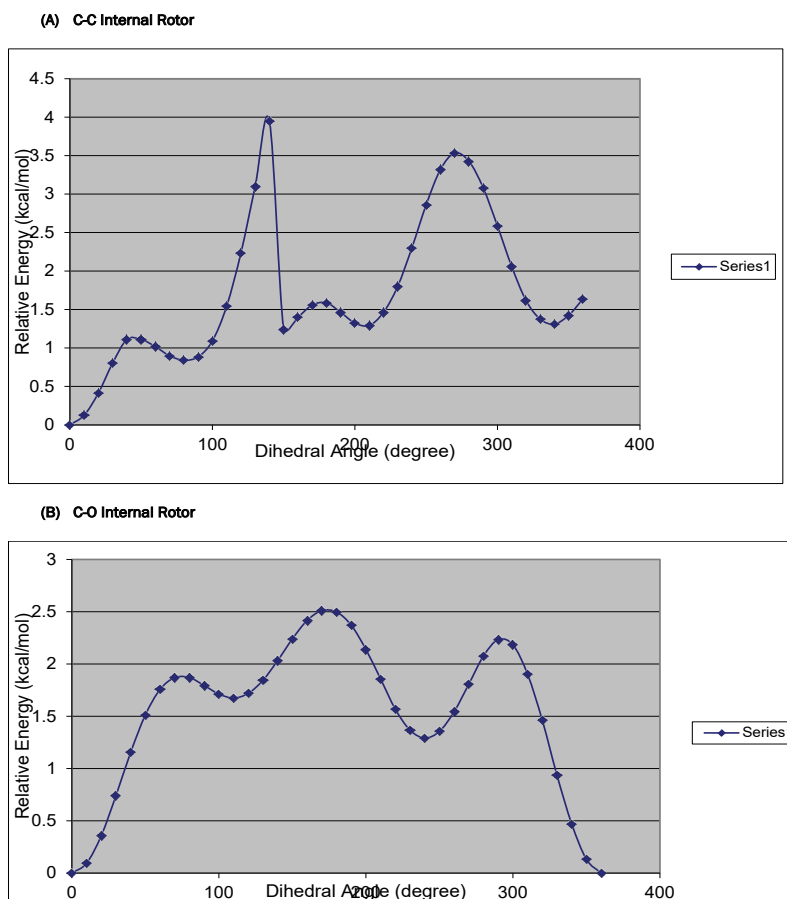
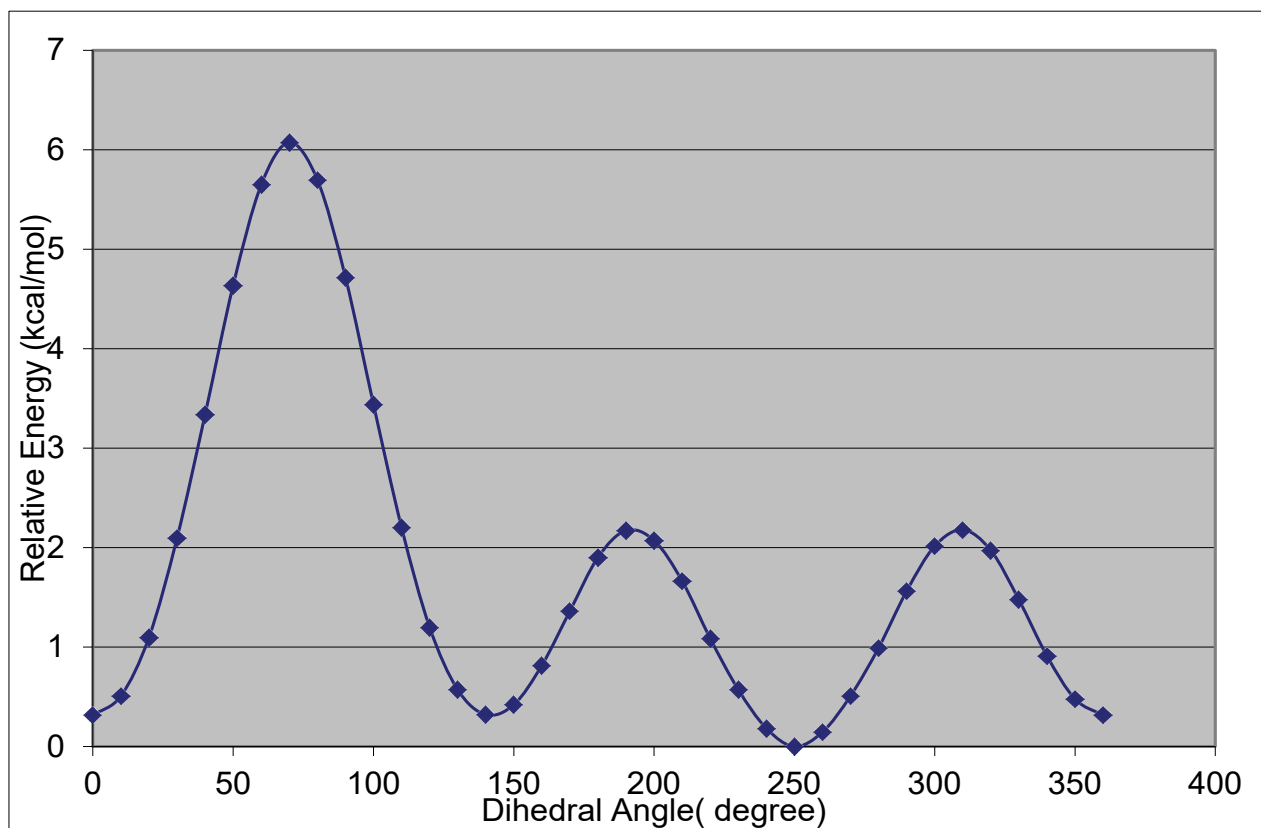


Figure 24. Potential energy profile of C-C and C-O internal rotors for C•HFCH₂OH. The solid lines indicate Fourier series expansion.

(A) C-C Internal Rotor



(B) C-O Internal Rotor

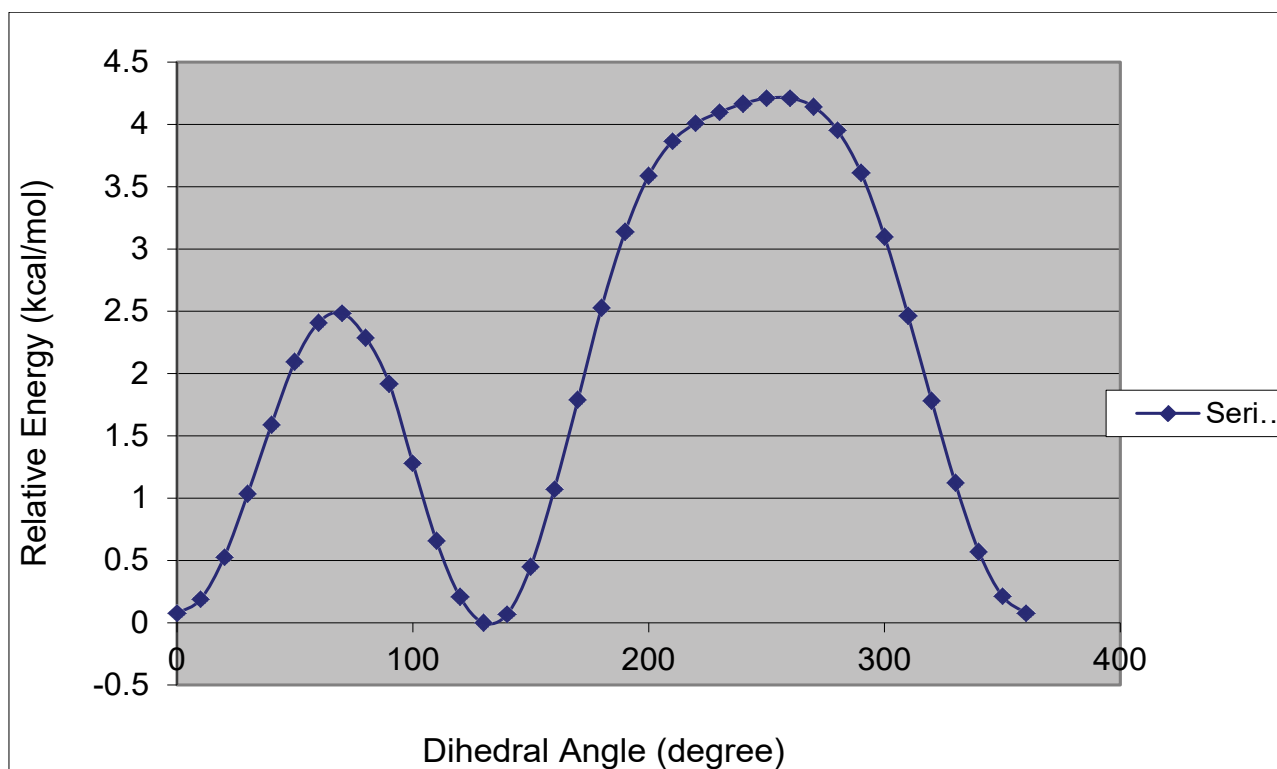


Figure 25. Potential energy profile of C-C and C-O internal rotors for $\text{CH}_2\text{FCH}_2\text{O}\cdot$. The solid lines indicate Fourier series expansion.

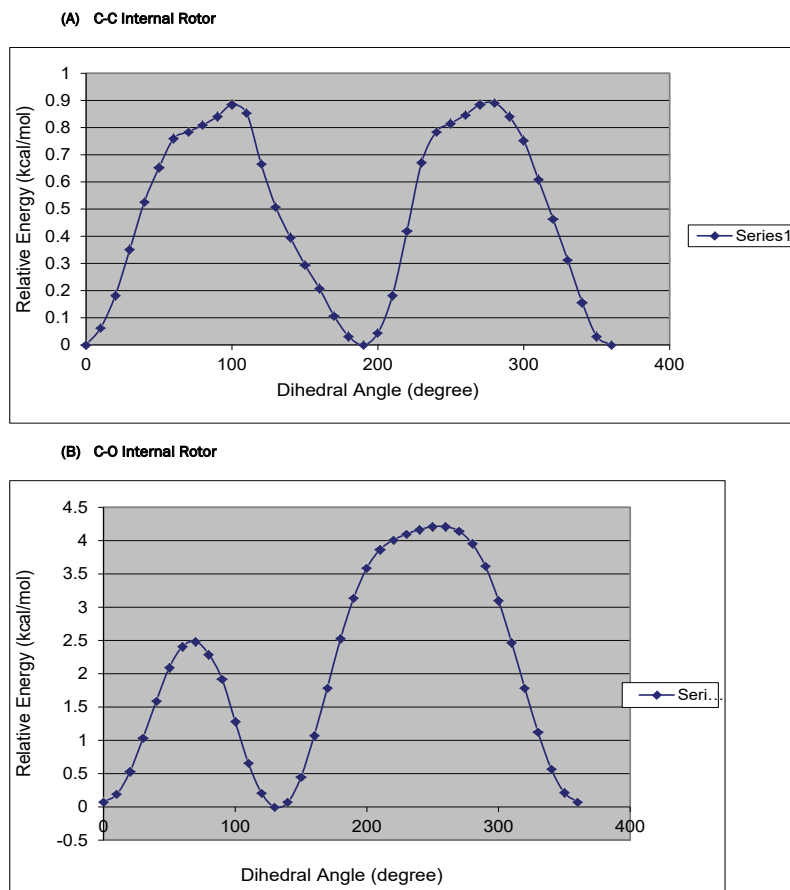


Figure 26. Potential energy profile of C-C and C-O internal rotors for $\text{CH}_2 \bullet \text{CHFOH}$. The solid lines indicate Fourier series expansion.

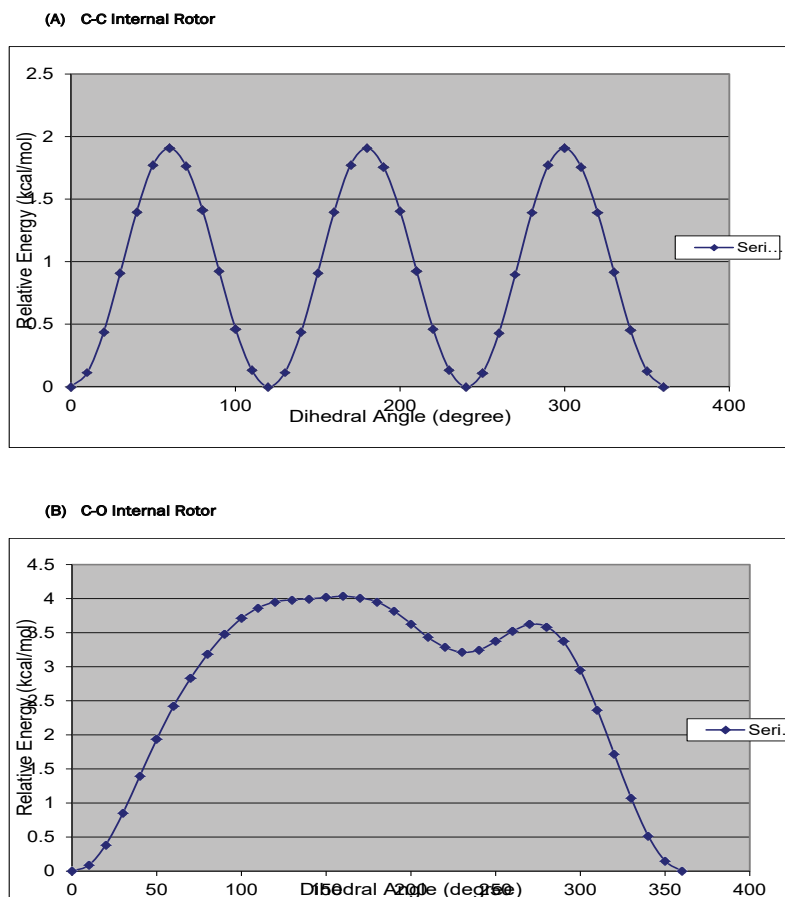


Figure 27. Potential energy profile of C-C and C-O internal rotors for $\text{CH}_3\text{CF} \bullet \text{OH}$. The solid lines indicate Fourier series expansion.

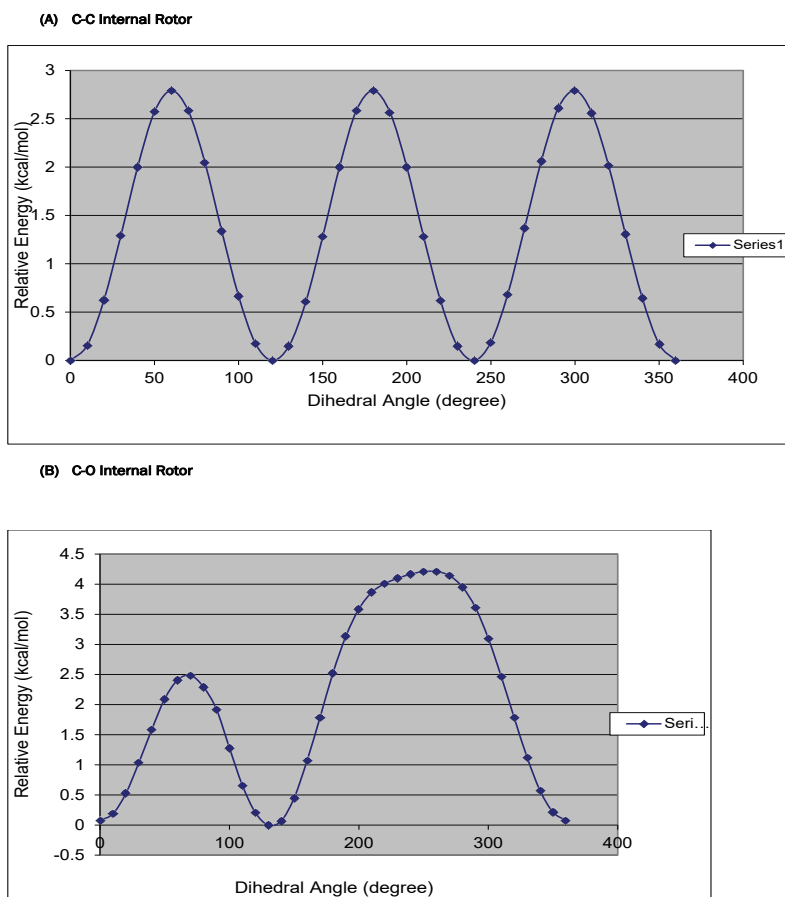


Figure 28. Potential energy profile of C-C and C-O internal rotors for $\text{CH}_3\text{CHFO}\cdot$. The solid lines indicate Fourier series expansion.

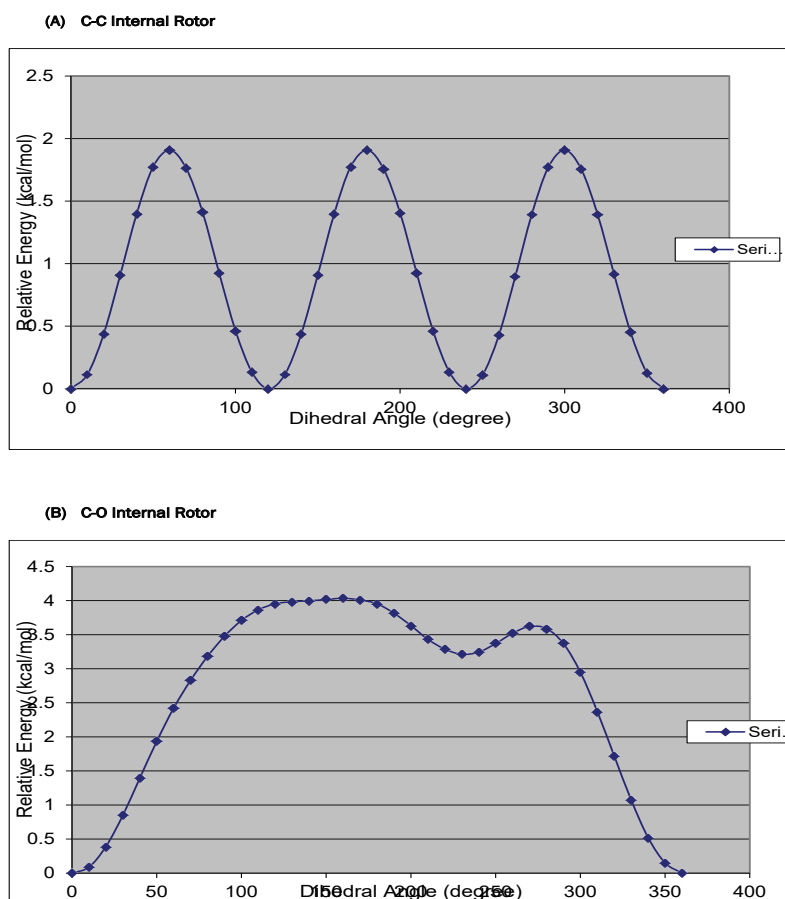


Figure 29. Potential energy profile of C-C and C-O internal rotors for CH_2FCHFOH . The solid lines indicate Fourier series expansion.

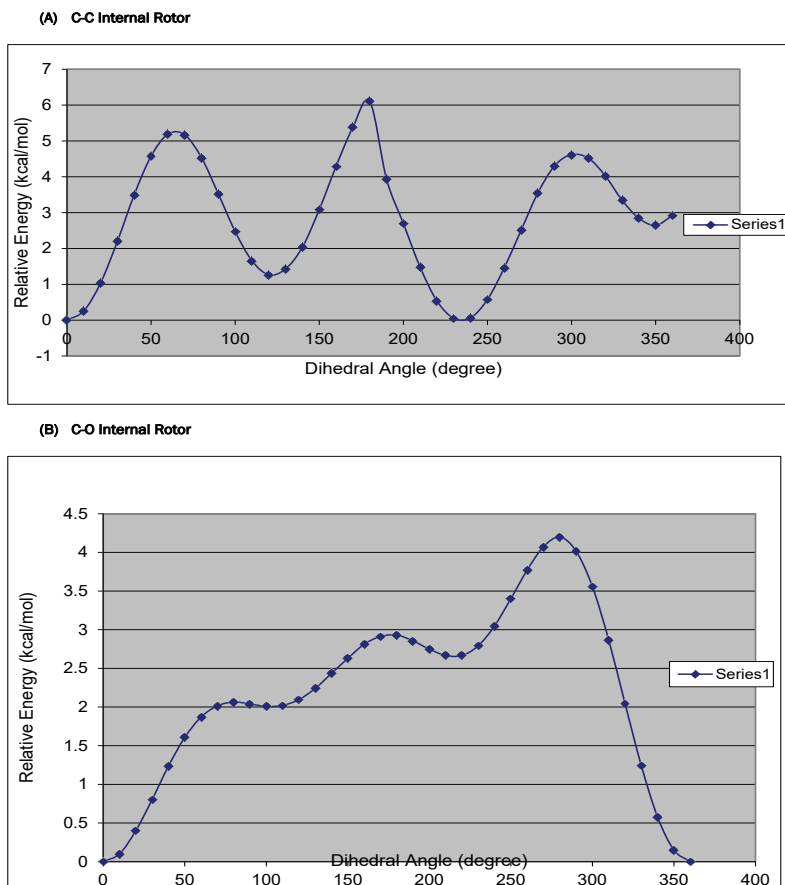


Figure 30. Potential energy profile of C-C and C-O internal rotors for $\text{CH}_3\text{CHFO}\cdot$. The solid lines indicate Fourier series expansion.

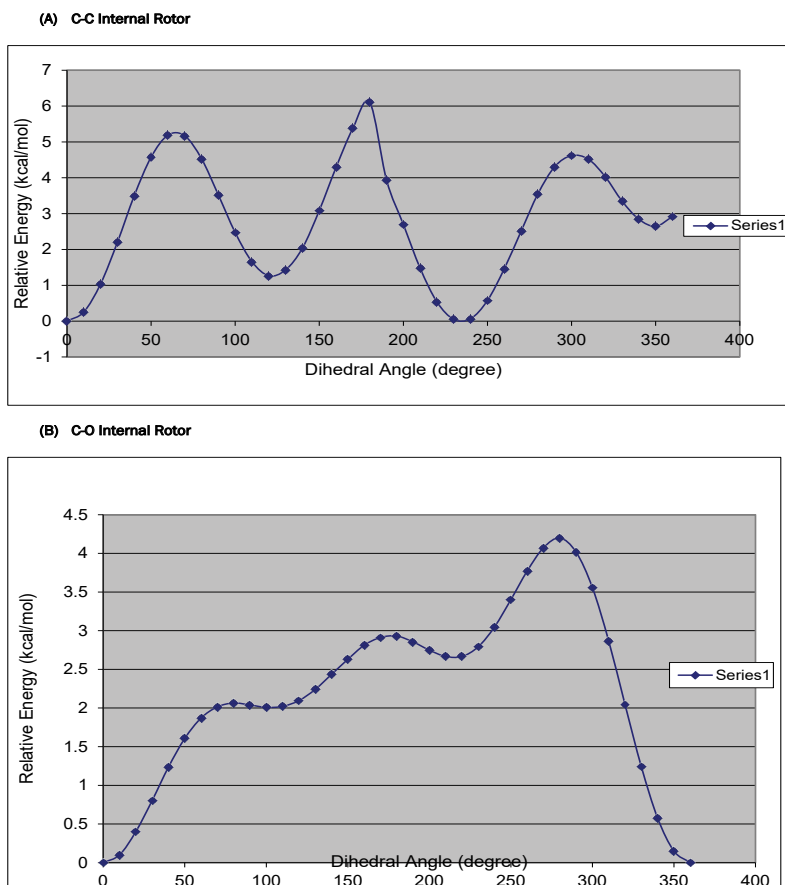


Figure 31. Potential energy profile of C-C and C-O internal rotors for CH_2FCHFOH . The solid lines indicate Fourier series expansion.

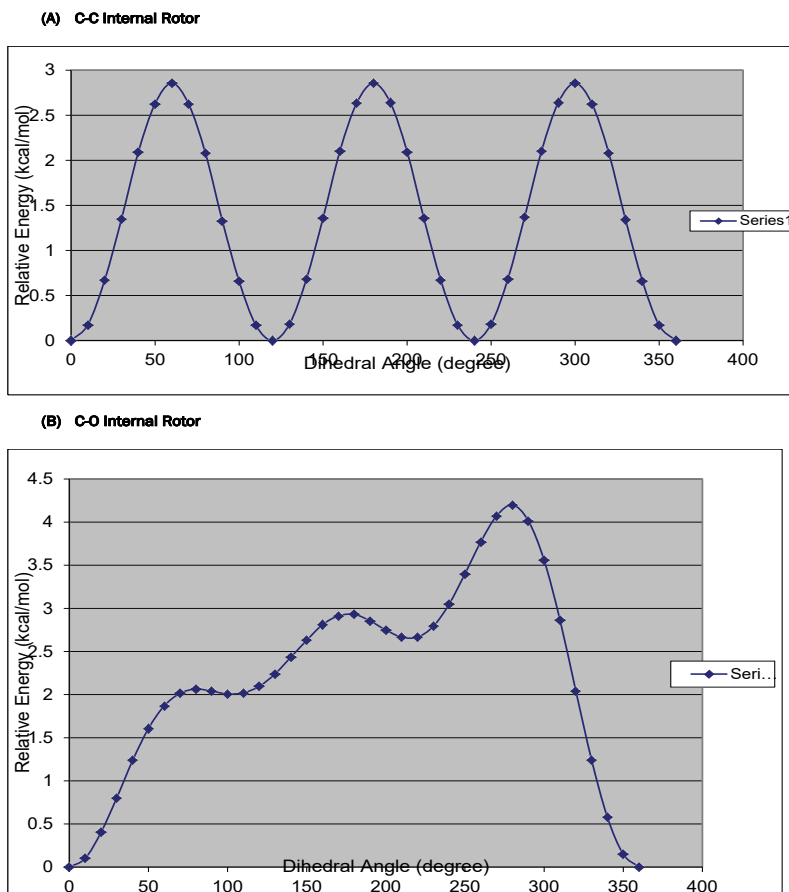


Figure 32. Potential energy profile of C-C and C-O internal rotors for $\text{CH}_2\text{FC}\cdot\text{FOH}$. The solid lines indicate Fourier series expansion.

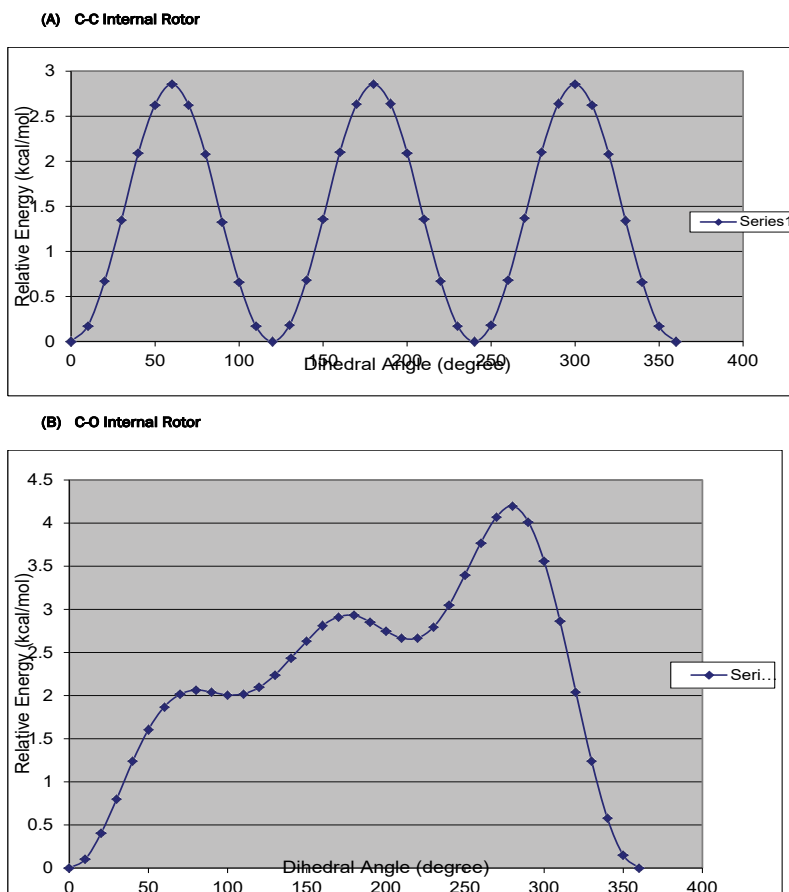


Figure 33. Potential energy profile of C-C and C-O internal rotors for $\text{C}\cdot\text{HFCFHOH}$. The solid lines indicate Fourier series expansion.

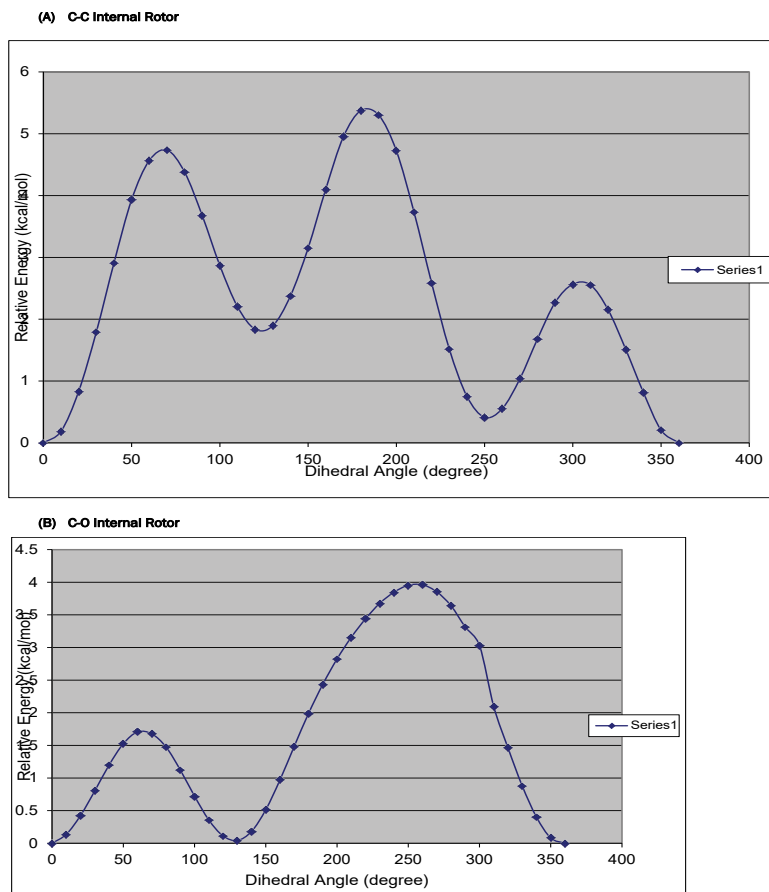


Figure 34. Potential energy profile of C-C and C-O internal rotors for $\text{CH}_2\text{FCHFO}\cdot$. The solid lines indicate Fourier series expansion.

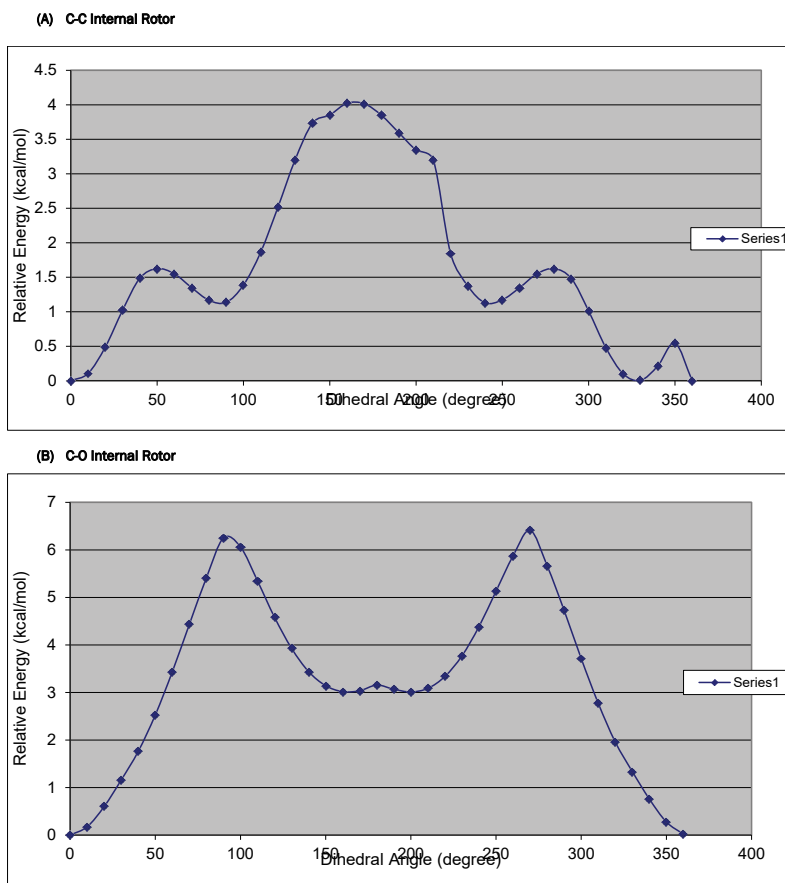


Figure 35. Potential energy profile of C-C and C-O internal rotors for $\text{CHF}_2\text{C}\cdot\text{HOH}$. The solid lines indicate Fourier series expansion.

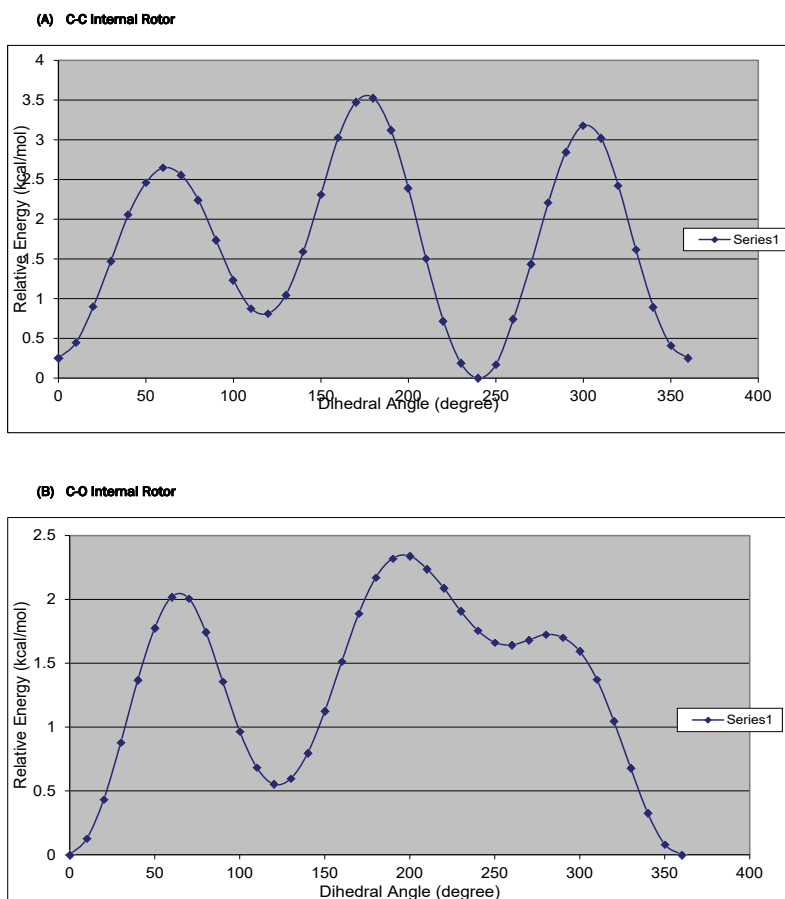


Figure 36. Potential energy profile of C-C and C-O internal rotors for $C\bullet F_2CH_2OH$. The solid lines indicate Fourier series expansion.

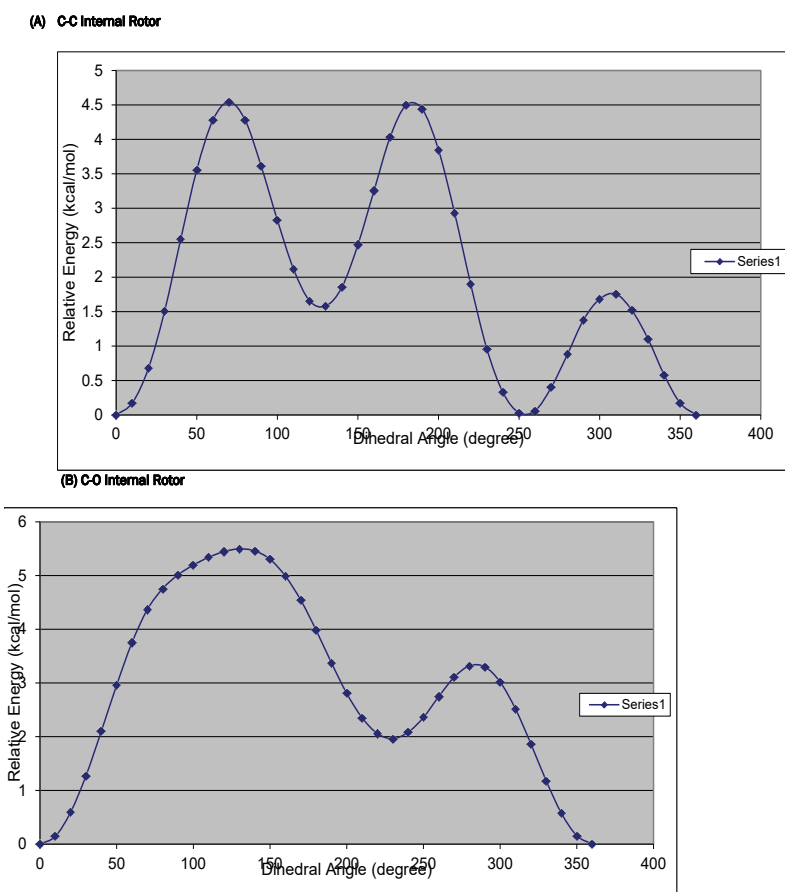


Figure 37. Potential energy profile of C-C and C-O internal rotors for $CHF_2CH_2O\bullet$. The solid lines indicate Fourier series expansion.

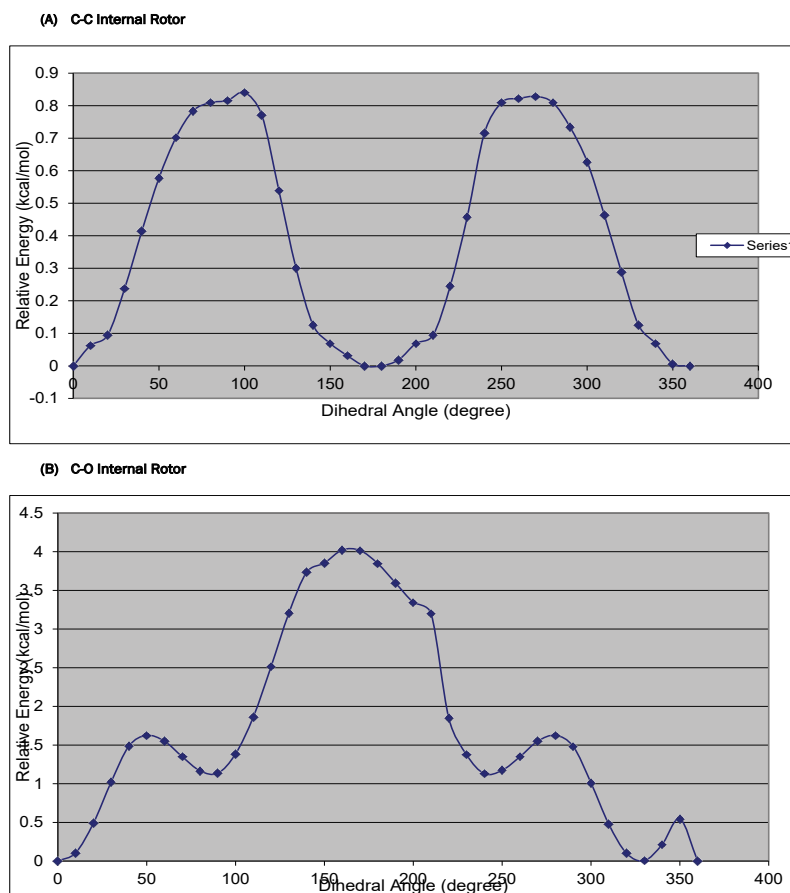


Figure 38. Potential energy profile of C-C and C-O internal rotors for $\text{CH}_2 \cdot \text{CF}_2\text{OH}$. The solid lines indicate Fourier series expansion.

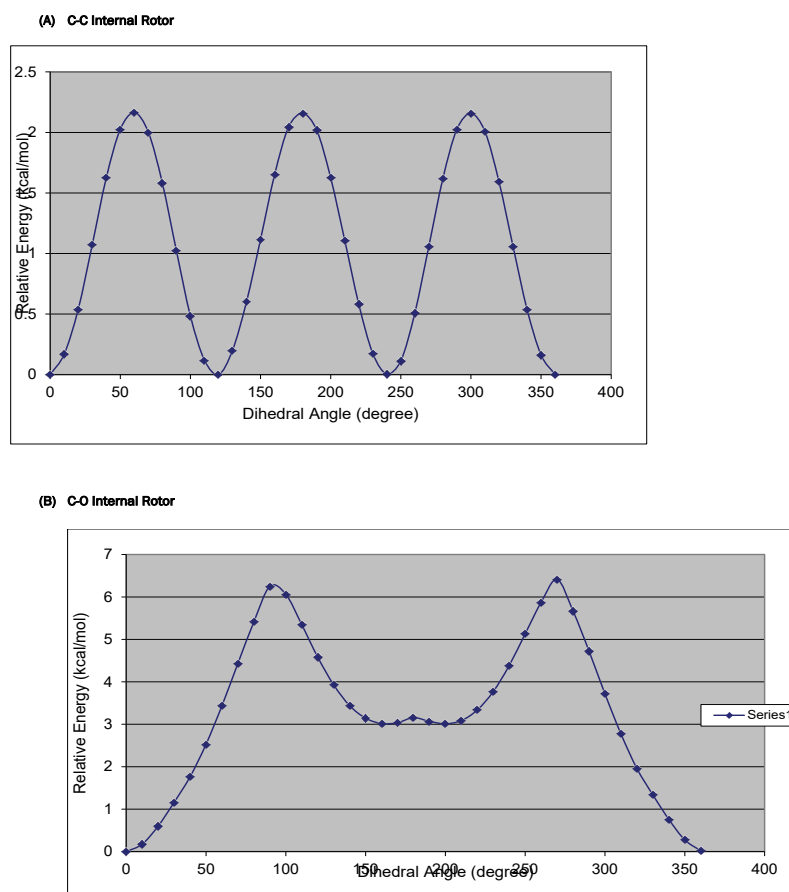


Figure 39. Potential energy profile of C-C and C-O internal rotors for $\text{CH}_3\text{CF}_2\text{O} \cdot$. The solid lines indicate Fourier series expansion.

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 (**Figures 21-40**)^[37-40].

CONCLUSION

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°- 1500°K, Standard Enthalpy of formation 298° K, and the C–F and C–H Bond Dissociation Energies (BDEs) for Mono and Difluorinated Ethanols and Radicals: CH₃-xCHF_xOH, CH₃CH₂-xF_xOH 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.

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