Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information for

Rotational spectra and theoretical study of tetramers and trimers of 2-fluoroethanol: dramatic intermolecular compensation for intramolecular instability

Nathan A. Seifert,[a] Javix Thomas,[a] Wolfgang Jäger,[a] Yunjie Xu[a]*

[a] Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada, T6G 2G2

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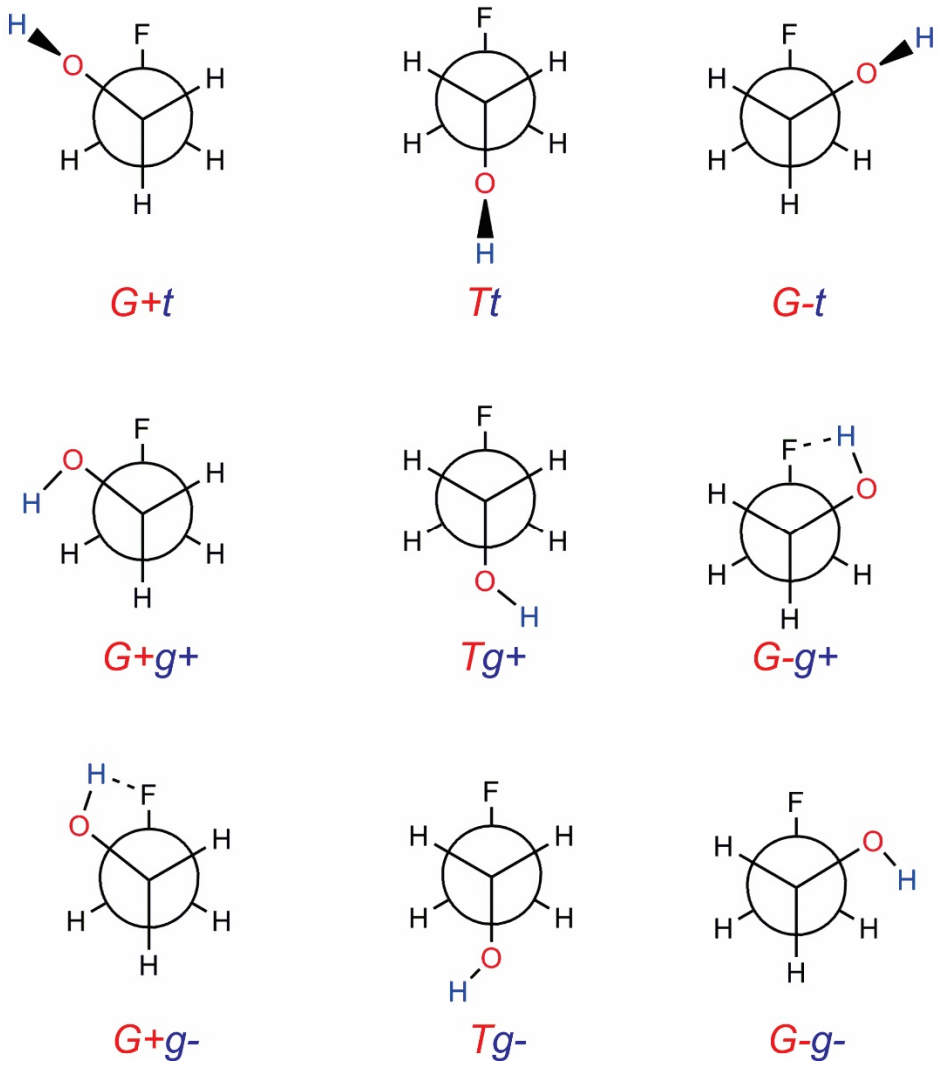


Figure S1. Newman projections of the 9 FE monomer conformations. The capital letters are for τ(FCCO) and the lower case for τ(CCOH).

Table S1. Measured transition frequencies of the (G+*g*-)$_4$, **I** FE tetramer.

J'	K_a'	K_c'	J''	K_a''	K_c''	ν_{EXP} / MHz	$\Delta\nu$[a]/ MHz
4	2	2	3	1	2	2970.6434	-0.006
3	3	0	2	2	0	3074.3290	0.0019
3	3	1	2	2	1	3078.0498	0.004
4	2	3	3	1	3	3149.4297	-0.0039
5	1	4	4	0	4	3309.2560	-0.0032
5	2	3	4	1	3	3500.7274	-0.0048
4	3	1	3	2	1	3606.8600	0.0026
4	3	2	3	2	2	3624.6906	-0.0051
5	2	4	4	1	4	3765.9605	-0.0037
6	1	5	5	0	5	3997.3550	0.0034
6	2	4	5	1	4	4052.6283	0.0028
5	3	2	4	2	2	4128.2707	0.0044
5	3	3	4	2	3	4178.3964	-0.0033
4	4	0	3	3	0	4198.5442	-0.0036
4	4	1	3	3	1	4198.7752	-0.0114
6	2	5	5	1	5	4400.9335	-0.0076
7	2	5	6	1	5	4632.7532	0.0197
6	3	3	5	2	3	4635.9733	0.0017
7	1	6	6	0	6	4715.9862	0.0023
5	4	1	4	3	1	4738.1464	0.0106
5	4	2	4	3	2	4739.7763	0.0058
6	3	4	5	2	4	4742.1064	-0.004
7	3	4	6	2	4	5132.8425	-0.0025
8	2	6	7	1	6	5245.7279	-0.0088
6	4	3	5	3	3	5281.3340	0.0066
6	4	2	5	3	2	5274.9923	0.0091
5	5	1	4	4	1	5321.0716	-0.0019
5	5	0	4	4	0	5321.0716	0.0107
8	3	5	7	2	5	5627.8281	-0.0021
7	4	3	6	3	3	5806.1710	-0.0056
7	4	4	6	3	4	5824.4187	0.0006
6	5	2	5	4	2	5861.6390	0.0029
6	5	1	5	4	1	5861.5164	-0.0078
8	7	2	7	6	2	8106.4378	-0.0005
8	7	1	7	6	1	8106.4378	-0.0002

[a] $\Delta\nu = \nu_{CALC.} - \nu_{EXP.}$

Table S2. Measured transition frequencies of the $(G\text{-}g+)_3$, **II** TFE trimer.

J'	K'	J''	K''	ν_{EXP} / MHz	$\Delta\nu^{[a]}$/ MHz
2	0	1	0	2670.9503	0.0131
2	1	1	1	2670.9503	0.0092
3	0	2	0	4006.4063	0.0146
3	1	2	1	4006.4063	0.0086
3	2	2	2	4006.4063	-0.0093
4	0	3	0	5341.8379	0.0093
4	1	3	1	5341.8379	0.0014
4	2	3	2	5341.8379	-0.0225
5	0	4	0	6677.2380	-0.0025
5	1	4	1	6677.2380	-0.0124
6	0	5	0	8012.6150	-0.0040
6	1	5	1	8012.6150	-0.0159
6	2	5	2	8012.6700	0.0033
8	0	7	0	10683.2377	0.0033
8	1	7	1	10683.2529	0.0025
8	2	7	2	10683.2971	-0.0010
9	0	8	0	12018.4452	-0.0007
9	1	8	1	12018.4649	0.0011
9	2	8	2	12018.5139	-0.0036
9	4	8	4	12018.7333	0.0010

[a] $\Delta\nu = \nu_{CALC.} - \nu_{EXP.}$

Table S3. Measured transition frequencies of (*G*-*g*+)$_2$(+-*g*-), **III** TFE trimer.

J'	K_a'	K_c'	J''	K_a''	K_c''	ν_{EXP} / MHz	$\Delta\nu$[a]/ MHz
2	2	0	1	1	0	2806.4780	0.0014
3	1	2	2	0	2	3733.9177	0.0095
3	2	1	2	1	1	3849.4306	-0.0009
3	2	2	2	1	2	4046.9898	-0.0045
3	3	0	2	2	0	4360.0794	-0.0010
3	3	1	2	2	1	4401.6667	-0.0002
4	2	2	3	1	2	4975.1995	-0.0107
4	1	3	3	0	3	5056.6772	-0.0020
4	2	3	3	1	3	5255.5372	0.0136
4	3	1	3	2	1	5337.7093	0.0021
4	3	2	3	2	2	5486.8098	-0.0075
4	4	0	3	3	0	5922.3186	0.0064
4	4	1	3	3	1	5933.9228	-0.0017
6	5	1	5	4	1	8485.7231	-0.0083
7	3	4	6	2	4	8651.5528	-0.0004
7	4	3	6	3	3	8845.3210	0.0016
6	6	0	5	5	0	9023.7635	-0.0020
6	6	1	5	5	1	9024.2747	0.0036
7	4	4	6	3	4	9185.3192	-0.0016
7	5	2	6	4	2	9465.7708	0.0043

[a] $\Delta\nu = \nu_{CALC.} - \nu_{EXP.}$

Table S4. Interaction energies (in kJ mol^{-1}) and Laplacian curvature values for the bond critical points of the five lowest energy $(FE)_4$ isomers based on the QTAIM analysis.

	$(FE)_4$ **I**		$(FE)_4$ **II**		$(FE)_4$ **III**	
Bond	E_{BCP}	$\nabla^2\rho$	E_{BCP}	$\nabla^2\rho$	E_{BCP}	$\nabla^2\rho$
C-H ··· F-C	6.47	0.0349	6.47	0.0349	4.80	0.0256
C-H ··· F-C	6.47	0.0349	6.47	0.0349	4.80	0.0256
C-H ··· F-C	5.17	0.0275	5.17	0.0275	7.72	0.0414
C-H ··· F-C	5.17	0.0275	5.17	0.0275	7.72	0.0414
C-H ··· F-C	4.42	0.0246	4.42	0.0246	4.07	0.0225
C-H ··· F-C	4.42	0.0246	4.42	0.0246	4.07	0.0225
C-H ··· F-C	5.48	0.0286	5.48	0.0286	5.39	0.0028
C-H ··· F-C	5.48	0.0286	5.48	0.0286	5.39	0.0028
O-H ··· H-O	52.9	0.1148	52.9	0.1148	51.5	0.1174
O-H ··· H-O	52.9	0.1148	52.9	0.1148	51.5	0.1174
O-H ··· H-O	46.8	0.1157	46.8	0.1157	50.1	0.1141
O-H ··· H-O	46.8	0.1157	46.8	0.1157	50.1	0.1141
Sum	242.5		242.5		247.1	

	$(FE)_4$ **IV**		$(FE)_4$ **V**	
Bond	E_{BCP}	$\nabla^2\rho$	E_{BCP}	$\nabla^2\rho$
C-H ··· F-C	8.46	0.0337	4.30	0.0214
C-H ··· F-C	8.46	0.0337	7.48	0.0306
C-H ··· F-C	8.46	0.0337	9.21	0.0366
C-H ··· F-C	8.46	0.0337	3.82	0.0200
C-H ··· F-C			7.04	0.0287
C-H ··· F-C			7.74	0.0312
C-H ···H-C			0.22	0.00204
O-H ··· H-O	43.5	0.1247	47.3	0.127
O-H ··· H-O	43.5	0.1247	40.4	0.122
O-H ··· H-O	43.5	0.1247	48.1	0.13
O-H ··· H-O	43.5	0.1247	43.3	0.119
Sum	207.8		218.9	

Figure S2. The 2-6 GHz experimental chirped-pulse spectrum of 2-fluoroethanol (top) and predicted spectra of the dimers, trimers, and tetramer (colored spectra, bottom), with an inset showing a sequence of transitions assigned to the tetramer. For visual clarity, predicted spectra for all 3 trimers have been plotted together as a single entry. Transitions associated with the 2-fluoroethanol monomer are shown without predictions.

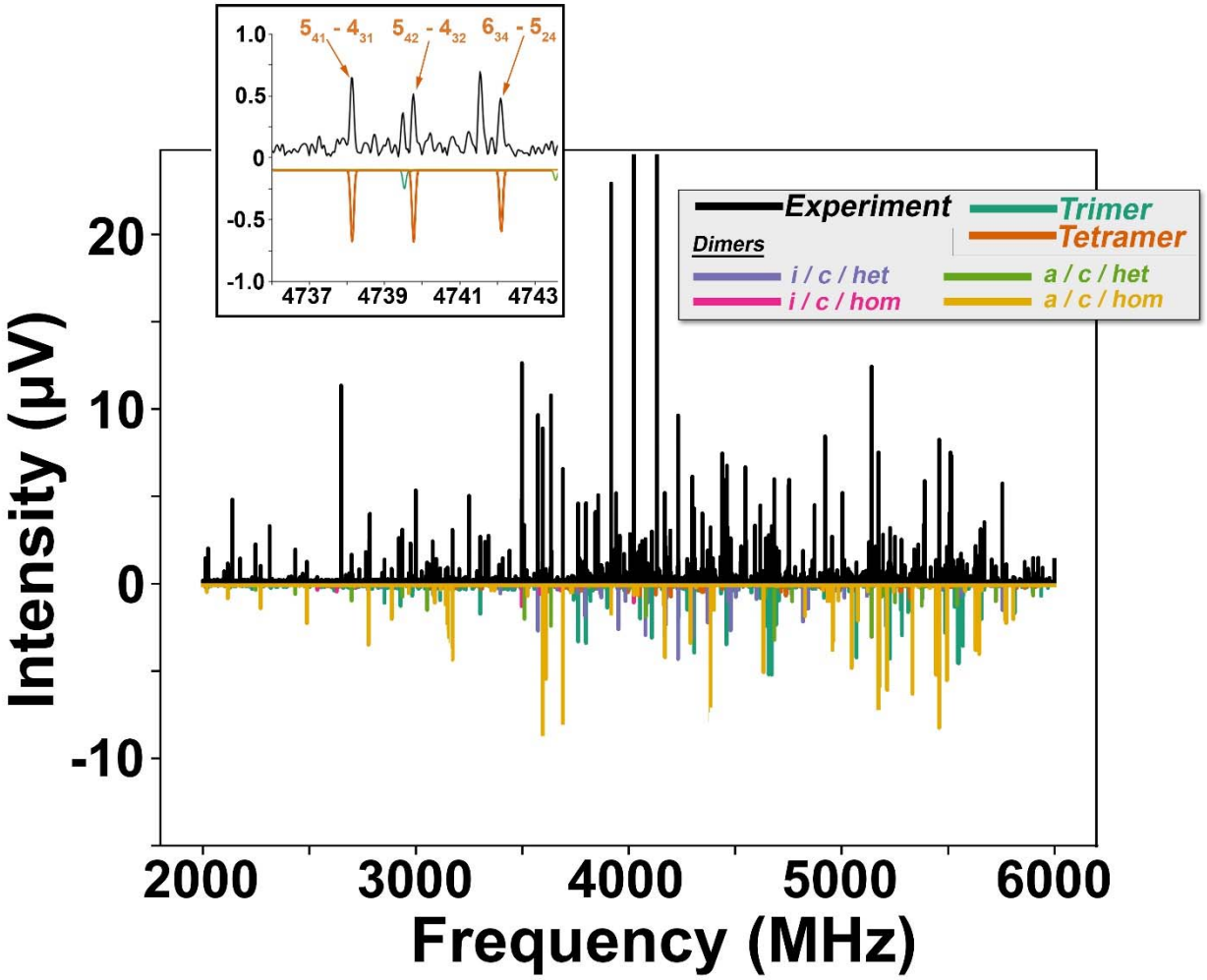


Figure S3. QTAIM diagrams for isomers **I**, **II** and **III** of the 2-fluoroethanol tetramer with emphasis on their structural interconnection. For isomer **I**, the enantiomeric form $(G+g-)_4$ is used instead of $(G-g+)_4$, as in Figure 1 and 2, in order to show its structural similarity to the $(G+g+)$-containing isomers **II** and **III**. C-H···F H-bond paths are shown in green, with the bond critical points (BCPs) shown as golden spheres. Red paths and translucent blue spheres indicating the O···HO bond paths and BCPs, respectively. Higher order cage and ring critical points are omitted for visual clarity. Note that *g*+ or *g*- dictates the cooperative O-H···O H-bond direction in clockwise (looking down) or counter clockwise fashion, respectively. The energy differences given below are based on the ΔE_0 energy values listed in Table I.

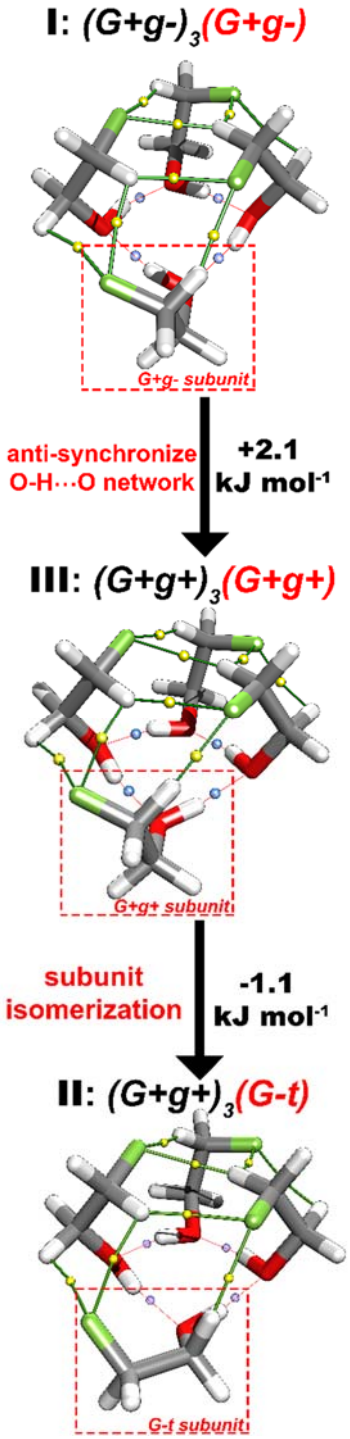
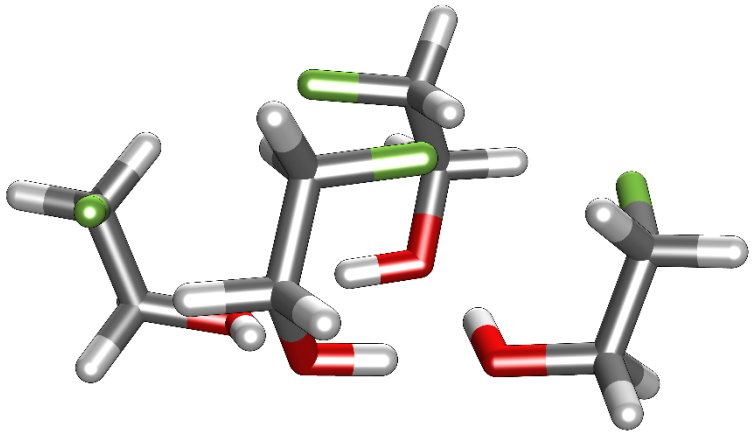
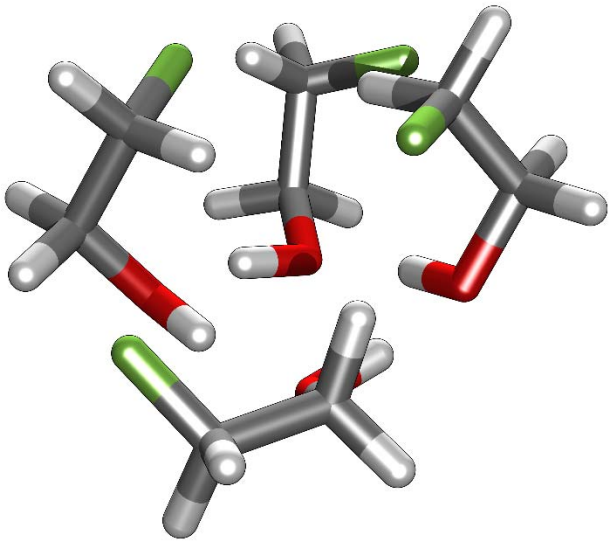


Table S5. Cartesian coordinates for the predicted B3LYP-D3/def2TZVP geometries of the FE tetramers **I-V**.

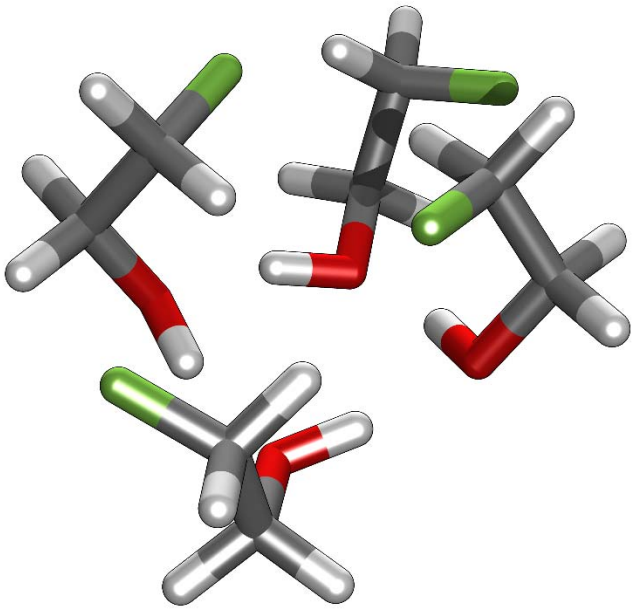
	I		
Atom	X	Y	Z
C	3.1479	-0.7879	-1.3511
C	3.6207	-0.6373	0.0735
O	1.7536	-0.6202	-1.4982
H	3.3908	-1.7995	-1.6869
H	3.6909	-0.0836	-1.9917
H	4.6804	-0.8900	0.1596
H	1.4902	0.3140	-1.3274
F	3.4774	0.7001	0.4828
H	3.0256	-1.2468	0.7530
C	-0.8645	-2.5711	0.1294
C	-0.5891	-1.8258	1.4099
O	-0.6399	-1.8032	-1.0404
H	-1.9188	-2.8520	0.1241
H	-0.2660	-3.4888	0.1056
H	-0.9201	-2.4086	2.2723
H	0.3075	-1.5567	-1.1258
F	0.7980	-1.6196	1.5582
H	-1.0632	-0.8464	1.4157
C	-3.1479	0.7879	-1.3511
C	-3.6207	0.6373	0.0735
O	-1.7536	0.6202	-1.4982
H	-3.3908	1.7995	-1.6869
H	-3.6909	0.0836	-1.9917
H	-4.6804	0.8900	0.1596
H	-1.4902	-0.3140	-1.3274
F	-3.4774	-0.7001	0.4828
H	-3.0256	1.2468	0.7530
C	0.8645	2.5711	0.1294
C	0.5891	1.8258	1.4099
O	0.6399	1.8032	-1.0404
H	1.9188	2.8520	0.1241
H	0.2660	3.4888	0.1056
H	0.9201	2.4086	2.2723
H	-0.3075	1.5567	-1.1258
F	-0.7980	1.6196	1.5582
H	1.0632	0.8464	1.4157



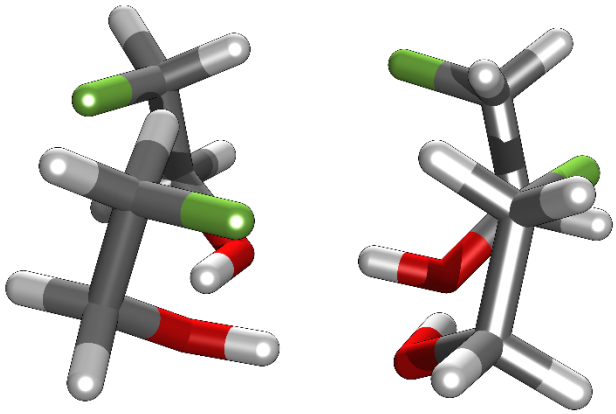
	II		
Atom	X	Y	Z
C	2.878	1.297	-0.595
C	4.002	0.299	-0.571
O	1.767	0.736	-1.269
H	3.238	2.192	-1.120
H	2.614	1.581	0.427
H	4.912	0.754	-0.175
H	0.972	1.306	-1.146
F	3.678	-0.783	0.263
H	4.188	-0.107	-1.566
C	0.968	-2.460	0.109
C	0.731	-1.766	1.427
O	0.560	-1.696	-1.013
H	0.401	-3.393	0.082
H	2.033	-2.704	0.042
H	1.151	-0.761	1.437
H	1.129	-0.897	-1.092
F	-0.651	-1.641	1.667
H	1.148	-2.351	2.250
C	-1.132	2.561	0.173
C	-0.846	1.742	1.407
O	-0.631	1.980	-1.021
H	-0.663	3.542	0.270
H	-2.215	2.704	0.107
H	-1.185	0.714	1.302
H	-1.171	1.191	-1.253
F	0.541	1.698	1.648
H	-1.312	2.195	2.285
C	-3.008	-0.995	-1.437
C	-3.469	-0.937	-0.001
O	-1.734	-0.415	-1.638
H	-3.712	-0.447	-2.066
H	-3.016	-2.043	-1.760
H	-2.740	-1.386	0.674
H	-1.012	-1.020	-1.352
F	-3.632	0.401	0.394
H	-4.438	-1.430	0.112



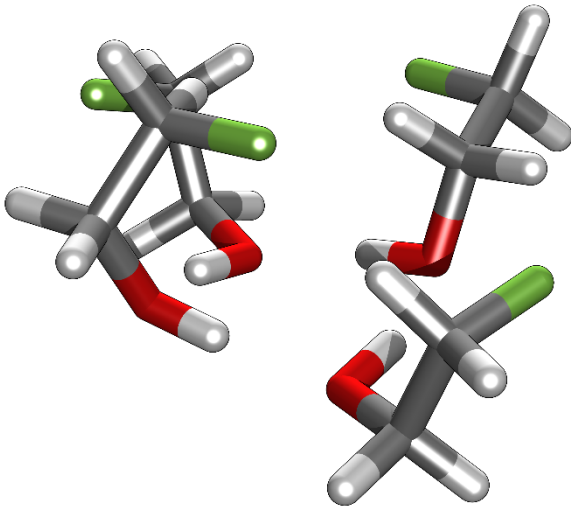
	III		
Atom	X	Y	Z
C	-3.0823	-0.8282	-1.3335
C	-3.5283	-0.6837	0.1015
O	-1.7564	-0.3883	-1.5514
H	-3.1997	-1.8778	-1.6281
H	-3.7293	-0.2268	-1.9756
H	-4.5435	-1.0681	0.2288
H	-1.0982	-1.0714	-1.2882
F	-3.5469	0.6740	0.4598
H	-2.8468	-1.1891	0.7853
C	0.8666	-2.5836	0.1177
C	0.6424	-1.7990	1.3855
O	0.4209	-1.9121	-1.0496
H	1.9351	-2.8111	0.0472
H	0.3194	-3.5268	0.1714
H	1.0704	-2.3225	2.2431
H	1.0298	-1.1642	-1.2474
F	-0.7390	-1.6612	1.6298
H	1.0588	-0.7955	1.3223
C	3.0823	0.8282	-1.3335
C	3.5283	0.6837	0.1015
O	1.7564	0.3883	-1.5514
H	3.1997	1.8778	-1.6280
H	3.7293	0.2268	-1.9756
H	4.5435	1.0681	0.2288
H	1.0982	1.0714	-1.2882
F	3.5469	-0.6740	0.4598
H	2.8468	1.1891	0.7853
C	-0.8666	2.5836	0.1177
C	-0.6424	1.7990	1.3855
O	-0.4209	1.9122	-1.0496
H	-1.9351	2.8111	0.0472
H	-0.3194	3.5268	0.1714
H	-1.0704	2.3225	2.2431
H	-1.0298	1.1642	-1.2474
F	0.7390	1.6612	1.6298
H	-1.0588	0.7955	1.3223



	IV		
Atom	X	Y	Z
C	1.5526	-2.7297	0.5906
C	1.1188	-2.8076	-0.8507
O	1.0407	-1.6053	1.2768
H	2.6413	-2.6491	0.6120
H	1.2700	-3.6566	1.1040
H	1.6451	-3.6109	-1.3711
H	0.0572	-1.5840	1.2469
F	-0.2570	-3.0985	-0.9229
H	1.2815	-1.8595	-1.3616
C	-2.7297	-1.5526	0.5906
C	-2.8076	-1.1188	-0.8507
O	-1.6053	-1.0407	1.2768
H	-2.6491	-2.6413	0.6120
H	-3.6566	-1.2700	1.1040
H	-3.6109	-1.6451	-1.3711
H	-1.5840	-0.0572	1.2469
F	-3.0985	0.2570	-0.9229
H	-1.8595	-1.2815	-1.3616
C	2.7297	1.5526	0.5906
C	2.8076	1.1188	-0.8507
O	1.6053	1.0407	1.2768
H	2.6491	2.6413	0.6120
H	3.6566	1.2700	1.1040
H	3.6109	1.6451	-1.3711
H	1.5840	0.0572	1.2469
F	3.0985	-0.2570	-0.9229
H	1.8595	1.2815	-1.3616
C	-1.5526	2.7297	0.5906
C	-1.1188	2.8076	-0.8507
O	-1.0407	1.6053	1.2768
H	-2.6413	2.6491	0.6120
H	-1.2700	3.6566	1.1040
H	-1.6451	3.6109	-1.3711
H	-0.0572	1.5840	1.2469
F	0.2570	3.0985	-0.9229
H	-1.2815	1.8595	-1.3616



	V		
Atom	X	Y	Z
C	3.3575	-0.5517	-1.2229
C	3.8033	-0.2498	0.1865
O	1.9533	-0.5627	-1.3809
H	3.7185	-1.5478	-1.4920
H	3.8172	0.1679	-1.9101
H	4.8808	-0.4016	0.2901
H	1.5647	0.3271	-1.2102
F	3.5416	1.0950	0.4907
H	3.2606	-0.8569	0.9110
C	0.4347	2.0383	0.4865
C	-0.5156	3.1785	0.7394
O	0.4542	1.6423	-0.8760
H	0.1858	1.1942	1.1386
H	1.4451	2.3601	0.7419
H	-0.3522	3.9912	0.0300
H	-0.3986	1.2023	-1.0935
F	-1.8450	2.7500	0.5743
H	-0.4185	3.5462	1.7637
C	-0.2253	-2.8297	0.3913
C	-0.2360	-1.9103	1.5868
O	-0.1671	-2.1522	-0.8505
H	-1.1562	-3.4004	0.3997
H	0.6071	-3.5367	0.4828
H	-0.4120	-2.4755	2.5050
H	0.7029	-1.7062	-0.9664
F	1.0084	-1.2708	1.7211
H	-0.9924	-1.1345	1.4794
C	-3.0492	0.0591	-1.3518
C	-3.5503	-0.0805	0.0632
O	-1.6396	0.0355	-1.4459
H	-3.3825	1.0256	-1.7365
H	-3.4898	-0.7255	-1.9770
H	-4.6350	0.0412	0.1068
H	-1.2754	-0.8545	-1.2358
F	-3.2552	-1.3686	0.5478
H	-3.0632	0.6375	0.7226



Completed Abbreviated References

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