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IR Absorption Spectra for PFAS Molecules Calculated Using Density Functional Theory

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14. ABSTRACT

Vibration absorption spectra for PFAS molecules are calculated using density function theory (DFT). Absorption spectra within the IR range of frequencies for electromagnetic-wave excitation, calculated using DFT, can be interpreted with respect to molecular structure. DFT calculated absorption spectra corresponding to vibration excitation states of these molecules in continuous solvent backgrounds can be correlated with additional information obtained from laboratory measurements. The DFT software GAUSSIAN was used for the calculations of excitation states presented here. This study provides proof of concept for using DFT calculated spectra to construct templets, which are for spectral-feature comparison, and thus detection of spectral-signature features associated with target materials.

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Introduction

Identification of unknown materials using infrared (IR) spectroscopy is by comparison of measured spectra with reference spectra of known materials. Such comparison entails correlation of measured spectra with spectra within a database of known molecular structures [1] using signal processing algorithms [2]. Specifically, signature structure within a measured spectrum is filtered using spectral templets having patterns associated with known materials. References [3-7] describes algorithms for signal processing of measured spectra for correlation with reference spectra within a database. For detection in practice, measured spectra can be correlated with different databases, providing complementary information, which includes different types of information concerning interpretation of spectral features. Typically, databases of spectra consist of spectroscopic measurements, which are obtained using different types of spectroscopies, based on transmission and reflection [8,9]. Presented in this report are calculations of IR absorption spectra of molecular structures using density functional theory (DFT) and associated software technology (see reference [10] for the case of pure water), which provides complementary information to that obtained from laboratory measurement.

This report presents DFT calculated IR spectra for octafluorotetrahydrotiophene-oneone-dioxide (C_4F_8-SO_2), perfluoro-tert-butanol (C_4F_9-OH), ethyl-perfluorobutyl-ether (C_4F_9-O-C_2H_5), twotwotwo-trifluoroethyl-trifluoromethanesulfonate ($C_2F_6CH_2$-SO_3), perfluorooctanesulfonate (C_8F_{17}-SO_3), of isolated molecules and molecules within different solvent backgrounds. The properties of these molecules are of major importance for monitoring and detection of perfluoroalkyl and polyfluoroalkyl substances (PFASs) in water. This follows in that the group of chemicals called PFASs, which are highly fluorinated aliphatic molecules, are among toxic and carcinogenic contaminants commonly found in the environment [11-16].

IR spectral signatures can be correlated with the presence of target molecules (see references [17-19]). A previous study [17] introduced and demonstrated the concept of using DFT calculated IR spectra. The concept of database enhancement using DFT calculated spectra is independent of specific types of detection technology. Methodologies for comparison of detected spectral features with database spectra represent a separate problem.

Given in reference [17] is a description of the formalism underlying DFT calculation of IR spectra, and implementation of this formalism in terms of the DFT software GAUSSIAN16. The commercial computer program GAUSSIAN16 (G16) is designed to compute the IR spectrum of a molecule, including the effect of a continuous solvent background [20-22]. Second derivatives of the energy with respect to the Cartesian nuclear coordinates are calculated and subsequently changed to mass-weighted coordinates at the equilibrium geometry of the molecule. The IR spectrum is obtained from the ground state energy surface calculated in the Born-Oppenheimer approximation by solving the DFT Kohn-Sham equations [23-29]. The electronic density, the

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potential energy *V,* and the equilibrium geometry are calculated. The details followed by GAUSSIAN for IR analysis are given in references [22] and [28].

DFT Calculation of IR Spectra

Results of a computational investigation using DFT concerning the PFAS molecules C_4F_8-SO_2, C_4F_9-O-C_2H_5, C_4F_9-OH, $C_2F_6CH_2$-SO_3 and C_8F_{17}-SO_3 are presented. These results include the ground-state energies for energy-minimized configuration of these molecules as isolated and within different solvent backgrounds, and their ground-state oscillation frequencies and IR intensities For these calculations, geometry-energy optimization and vibration analysis was effected using the computer program Gaussian 16 with the DFT chemical model B3LYP [29,30] and basis functions 6-311++g(3df,3pd) [31,32]. These basis functions designate the 6-311G basis set supplemented by diffuse functions, indicated by the sign ++, and polarization functions (df), having a set of d and f functions on heavy atoms [33]. Shown in Figs. (1) through (5) are IR spectra of the PFAS molecules C_4F_8-SO_2, C_4F_9-O-C_2H_5, C_4F_9-OH, $C_2F_6CH_2$-SO_3 and C_8F_{17}-SO_3 within different backgrounds, i.e., individually and within solvents DMSO and toluene. Values of the IR intensities ($esu^2cm^2 10^{-40}$) as a function of frequency (cm^{-1}) for these molecules within different backgrounds are given in Tables 1 through 5.

Table 1. DFT Calculated IR Spectra of C_4F_8-SO_2 within Different Backgrounds

	C_4F_8-SO_2 (DMSO)			C_4F_8-SO_2			C_4F_8-SO_2 (TOLUENE)	
	Frequency (1/cm)	Intensity		Frequency (1/cm)	Intensity		Frequency (1/cm)	Intensity
1	74.4668	3.884	1	35.511	35.623	1	23.022	102.672
2	159.7533	181.443	2	81.2417	2.0918	2	78.842	2.2921
3	184.0918	3.4586	3	170.636	50.796	3	165.69	89.199
4	185.5773	53.25	4	187.688	1.4453	4	185.967	2.4155
5	213.0265	0.1198	5	189.270	31.974	5	187.08	40.241
6	235.3503	2.1883	6	215.682	0.06288	6	214.525	0.14505
7	235.3631	61.055	7	236.384	20.8005	7	235.676	1.6047
8	258.7448	23.699	8	236.860	0.92467	8	236.176	33.492
9	259.7975	103.84	9	262.812	44.869	9	261.327	66.925
10	283.7574	2.3099	10	263.701	17.178	10	261.591	19.386
11	289.4873	115.259	11	285.261	0.91042	11	284.614	1.5558
12	305.6479	52.8695	12	291.911	54.167	12	290.555	74.983
13	326.8909	21.0812	13	308.194	22.668	13	306.655	33.225
14	338.1937	56.0012	14	330.298	9.125	14	328.591	13.767
15	368.058	4.5458	15	341.186	27.338	15	339.923	37.294
16	371.1894	25.108	16	369.548	2.6793	16	368.861	3.2251
17	486.733	292.402	17	371.381	13.469	17	371.424	17.729
18	505.4425	875.052	18	490.158	114.380	18	488.724	172.112
19	544.8456	942.884	19	512.461	437.693	19	509.431	612.051
20	552.476	151.7914	20	554.287	538.249	20	549.849	707.482
21	601.361	94.07397	21	555.693	127.723	21	554.245	140.152
22	607.4144	21.09325	22	603.683	56.946	22	602.988	71.094

23	662.9561	165.8814	23	609.710	11.826	23	608.819	15.679
24	664.9285	21.99384	24	664.326	106.664	24	663.616	131.354
25	870.3743	13.03605	25	667.037	9.9274	25	666.317	14.093
26	923.9716	948.3175	26	874.498	11.945	26	872.776	12.738
27	968.8327	1276.885	27	935.362	514.168	27	930.495	686.820
28	1034.708	402.3695	28	980.612	748.820	28	975.844	960.622
29	1163.752	1663.043	29	1044.959	259.198	29	1040.441	320.081
30	1166.730	436.6481	30	1181.302	267.578	30	1174.87	350.499
31	1181.759	209.139	31	1183.035	515.107	31	1175.738	864.150
32	1191.078	330.4346	32	1193.559	125.518	32	1188.017	152.822
33	1217.390	74.66825	33	1201.980	307.441	33	1196.85	327.785
34	1220.031	1268.340	34	1229.015	51.1470	34	1223.836	61.829
35	1264.174	124.0991	35	1238.957	919.507	35	1230.567	1088.023
36	1277.051	829.7951	36	1270.012	73.7754	36	1267.445	92.619
37	1319.418	307.8870	37	1285.731	564.572	37	1281.682	680.798
38	1392.748	1071.850	38	1323.710	226.429	38	1322.057	263.587
			39	1421.622	623.941	39	1408.791	807.586

Table 2. DFT Calculated IR Spectra of C_4F_9-OH within Different Backgrounds

C_4F_9-OH (DMSO)			C_4F_9-OH			C_4F_9-OH (TOLUENE)		
	Frequency (1/cm)	Intensity		Frequency (1/cm)	Intensity		Frequency (1/cm)	Intensity
1	70.055	39.679	1	70.055	39.679	1	68.182	21.736
2	79.775	9.2564	2	79.775	9.2565	2	77.946	6.7764
3	169.828	16.314	3	169.828	16.314	3	169.491	10.806
4	172.169	0.002317	4	172.169	0.002317	4	171.755	0.7200
5	196.940	65.634	5	196.940	65.636	5	195.434	39.727
6	263.691	81.212	6	263.691	81.211	6	263.849	12.161
7	265.623	62.468	7	265.622	62.468	7	269.386	43.060
8	278.684	531.410	8	278.684	531.410	8	282.240	89.972
9	297.573	1317.155	9	297.573	1317.153	9	305.391	601.504
10	316.723	23.513	10	316.723	23.513	10	317.643	15.990
11	319.574	3.2606	11	319.574	3.2606	11	319.699	2.5905
12	324.924	958.117	12	324.924	958.121	12	335.959	1181.200
13	349.857	53.418	13	349.857	53.418	13	351.372	46.477
14	351.815	8.5102	14	351.815	8.5102	14	353.471	143.803
15	488.053	114.555	15	488.053	114.555	15	488.681	77.336
16	529.450	71.684	16	529.450	71.684	16	530.243	50.493
17	532.565	72.344	17	532.565	72.344	17	533.470	47.836
18	533.707	13.143	18	533.707	13.143	18	534.051	18.233
19	567.900	6.1994	19	567.900	6.1994	19	568.495	4.3213
20	568.532	0.9304	20	568.532	0.9304	20	569.655	0.5763
21	645.792	20.949	21	645.792	20.949	21	645.584	14.946
22	721.072	406.358	22	721.072	406.358	22	723.132	312.628
23	721.964	386.651	23	721.964	386.651	23	724.314	293.035
24	766.802	7.70927	24	766.802	7.7092	24	767.276	7.3629
25	937.290	838.582	25	937.290	838.582	25	939.013	650.592
26	964.252	1017.115	26	964.252	1017.115	26	969.316	759.614
27	1103.424	0.1236	27	1103.424	0.12364	27	1108.508	0.10724
28	1133.998	2000.925	28	1133.998	2000.923	28	1144.397	1220.720
29	1150.403	387.381	29	1150.403	387.383	29	1159.736	214.446

30	1152.281	91.112	30	1152.281	91.112	30	1166.586	48.185
31	1174.314	152.411	31	1174.314	152.412	31	1182.279	130.843
32	1175.435	110.863	32	1175.435	110.863	32	1185.670	19.505
33	1203.189	2234.114	33	1203.189	2234.114	33	1217.538	1785.804
34	1216.229	1991.248	34	1216.229	1991.247	34	1235.618	1751.786
35	1238.010	2237.507	35	1238.010	2237.507	35	1253.527	1951.928
36	1283.910	161.433	36	1283.910	161.433	36	1286.985	260.364
37	1374.000	230.013	37	1374.000	230.013	37	1375.416	202.491
38	3771.400	160.518	38	3771.400	160.518	38	3783.339	118.779

Table 3. DFT Calculated IR Spectra of C_4F_9-O-C_2H_5 within Different Backgrounds

C_4F_9-O-C_2H_5 (DMSO)			C_4F_9-O-C_2H_5			C_4F_9-O-C_2H_5 (TOLUENE)		
	Frequency (1/cm)	Intensity		Frequency (1/cm)	Intensity		Frequency (1/cm)	Intensity
1	25.640	4.5587	1	37.480	9.696	1	27.096	3.3862
2	35.505	22.247	2	54.820	100.149	2	38.040	30.234
3	53.499	216.993	3	62.068	54.620	3	55.888	143.333
4	56.805	48.507	4	78.792	17.741	4	58.335	26.629
5	85.569	22.616	5	99.459	45.140	5	85.440	18.429
6	97.362	122.953	6	155.432	17.530	6	98.227	85.853
7	152.654	35.891	7	188.839	3.8575	7	153.466	23.294
8	183.377	4.6621	8	207.528	71.503	8	183.536	3.7777
9	207.547	170.109	9	232.981	0.07362	9	210.763	97.282
10	239.866	1.3188	10	243.318	0.13608	10	240.252	0.52139
11	240.526	4.7320	11	250.316	8.7400	11	241.511	2.7404
12	251.916	17.369	12	285.982	5.0763	12	250.365	13.274
13	285.716	4.0170	13	293.607	240.147	13	286.804	2.4369
14	289.628	389.391	14	320.528	10.579	14	291.537	314.184
15	322.374	9.9915	15	330.659	0.86988	15	322.843	7.7145
16	330.821	5.8462	16	355.109	3.0467	16	331.258	4.08142
17	354.546	8.2106	17	358.780	30.751	17	355.036	10.727
18	358.512	34.413	18	379.961	2.1954	18	358.793	28.965
19	380.248	3.7234	19	422.197	23.583	19	381.371	2.4519
20	418.422	49.770	20	510.215	0.03909	20	419.336	30.777
21	504.841	8.8560	21	531.018	51.505	21	505.830	7.1596
22	528.701	101.653	22	554.505	12.976	22	530.218	68.955
23	552.720	21.643	23	581.415	3.4019	23	553.9209	13.987
24	579.304	7.3665	24	601.170	91.874	24	580.232	4.29513
25	596.926	95.599	25	611.271	0.96198	25	598.135	74.504
26	613.875	47.828	26	692.715	36.685	26	614.760	37.329
27	690.382	60.066	27	734.992	439.316	27	691.448	46.332
28	729.871	595.032	28	793.106	180.153	28	732.961	512.695
29	788.558	239.604	29	826.596	4.4421	29	791.126	214.498
30	819.114	3.0561	30	830.298	12.251	30	825.196	2.4008
31	825.484	10.649	31	940.624	568.545	31	826.065	7.5589
32	934.163	880.783	32	1031.556	544.493	32	937.721	708.742
33	1013.210	774.010	33	1082.934	437.041	33	1022.301	662.603
34	1042.371	1273.352	34	1087.963	98.018	34	1063.542	685.486
35	1075.315	428.541	35	1133.380	131.007	35	1083.024	234.807
36	1119.888	957.121	36	1143.787	491.068	36	1127.770	381.911
37	1131.467	444.504	37	1163.928	86.979	37	1137.525	515.999

38	1145.588	662.760	38	1180.177	10.083	38	1157.018	260.865
39	1160.657	1265.367	39	1187.777	487.600	39	1173.108	598.759
40	1168.640	1215.83	40	1197.189	1095.056	40	1177.926	41.898
41	1175.368	39.320	41	1201.387	347.451	41	1184.445	1134.101
42	1185.606	1579.742	42	1224.974	1555.324	42	1201.042	954.722
43	1195.962	368.608	43	1272.209	244.871	43	1206.874	1236.015
44	1265.746	207.640	44	1292.695	1220.781	44	1268.837	166.855
45	1288.445	1583.355	45	1307.787	0.56647	45	1292.211	1449.255
46	1306.960	2.2267	46	1350.865	19.653	46	1307.565	2.0408
47	1349.524	30.723	47	1413.238	38.696	47	1350.795	26.261
48	1410.417	60.086	48	1435.674	1.8328	48	1411.871	49.448
49	1430.300	8.6984	49	1486.048	18.769	49	1433.418	5.0305
50	1476.317	28.915	50	1503.437	8.1123	50	1481.502	23.234
51	1490.351	11.427	51	1525.541	5.0285	51	1497.792	9.5250
52	1517.971	9.3329	52	3043.862	14.765	52	1522.058	6.2509
53	3044.388	19.860	53	3057.589	23.969	53	3044.195	16.423
54	3071.086	31.411	54	3100.014	0.92746	54	3063.873	26.401
55	3108.764	4.4683	55	3111.988	22.400	55	3105.440	0.04380
56	3114.186	33.591	56	3126.139	31.344	56	3112.780	26.512
57	3133.748	50.910				57	3129.165	39.264

Table 4. DFT Calculated IR Spectra of $C_2F_6CH_2$-SO_3 within Different Backgrounds

$C_2F_6CH_2$-SO_3 (DMSO)			$C_2F_6CH_2$-SO_3			$C_2F_6CH_2$-SO_3 (TOLUENE)		
	Frequency (1/cm)	Intensity		Frequency (1/cm)	Intensity		Frequency (1/cm)	Intensity
1	34.010	131.223	1	18.942	162.193	1	23.957	168.502
2	41.434	5.1510	2	36.364	9.3689	2	39.170	8.01535
3	44.271	13.345	3	43.089	5.2217	3	46.590	6.2850
4	78.026	257.948	4	76.673	120.916	4	75.801	165.204
5	121.832	46.236	5	120.719	23.384	5	121.051	31.743
6	187.475	88.295	6	194.184	36.144	6	191.601	54.150
7	213.268	239.006	7	220.194	86.568	7	218.511	130.035
8	221.580	59.853	8	225.276	53.185	8	223.571	63.187
9	283.159	29.151	9	286.123	11.305	9	284.999	16.808
10	301.669	15.173	10	303.675	2.7167	10	302.364	5.9927
11	328.206	5.9693	11	328.907	2.0328	11	328.763	3.27026
12	364.621	28.226	12	361.328	19.731	12	361.605	25.043
13	367.976	43.146	13	366.898	20.956	13	366.693	27.791
14	477.958	418.491	14	480.618	171.873	14	479.684	260.269
15	503.016	178.855	15	506.681	120.971	15	505.304	147.438
16	529.873	5.5021	16	528.824	4.05032	16	528.615	5.07151
17	543.887	60.791	17	544.408	26.676	17	544.518	40.312
18	562.138	125.847	18	564.571	81.955	18	563.683	98.384
19	572.472	297.378	19	575.039	118.668	19	574.088	176.631
20	589.526	1462.511	20	602.669	855.034	20	597.082	1108.724
21	650.080	43.365	21	654.670	25.289	21	652.634	32.480
22	755.961	295.717	22	756.986	179.630	22	756.578	234.743
23	802.967	1156.308	23	803.686	834.166	23	803.007	981.368
24	842.501	113.071	24	846.775	89.787	24	844.484	94.127
25	962.864	534.360	25	972.467	230.388	25	968.072	333.099
26	1014.109	1787.224	26	1036.401	1116.792	26	1026.282	1400.767

27	1111.847	1400.512	27	1133.005	797.172	27	1123.937	1016.506
28	1136.015	1429.972	28	1161.981	905.414	28	1149.714	1140.555
29	1163.977	616.174	29	1187.356	522.716	29	1178.480	450.041
30	1174.218	1264.736	30	1190.920	588.308	30	1181.841	940.233
31	1182.936	1239.682	31	1216.114	684.156	31	1202.275	937.019
32	1233.433	428.199	32	1242.855	494.168	32	1238.639	468.482
33	1273.388	528.346	33	1285.574	389.972	33	1280.154	447.950
34	1311.964	333.589	34	1318.804	301.059	34	1317.144	305.495
35	1409.104	1125.380	35	1425.109	155.027	35	1425.366	573.859
36	1436.273	69.818	36	1448.324	553.816	36	1437.709	331.919
37	1483.37	29.233	37	1486.993	16.839	37	1483.708	19.781
38	3112.599	19.549	38	3094.563	18.642	38	3102.437	19.272
39	3180.959	1.62375	39	3160.917	1.52209	39	3169.584	1.45059

Table 5. DFT Calculated IR Spectra of C_8F_{17}-SO_3 within Different Backgrounds

C_8F_{17}-SO_3 (DMSO)			C_8F_{17}-SO_3			C_8F_{17}-SO_3 (TOLUENE)		
	Frequency (1/cm)	Intensity		Frequency (1/cm)	Intensity		Frequency (1/cm)	Intensity
1	23.172	13.274	1	19.342	67.052	1	24.189	10.983
2	26.700	0.71718	2	22.991	4.37260	2	26.458	1.67363
3	31.822	21.149	3	28.938	34.727	3	32.192	13.061
4	38.391	0.90405	4	34.076	3.12589	4	40.61	0.35364
5	45.891	3.96410	5	42.998	15.541	5	46.190	2.7551
6	49.815	1.84993	6	44.441	5.90672	6	52.447	0.97363
7	60.188	5.46827	7	61.733	5.3507	7	61.636	3.4433
8	69.687	2.19828	8	65.415	6.46445	8	69.638	2.0222
9	82.655	24.919	9	77.590	20.206	9	83.536	16.686
10	99.341	4.94752	10	97.613	3.00390	10	99.877	2.888
11	113.356	23.002	11	107.765	41.476	11	113.605	14.457
12	149.897	9.98299	12	121.825	43.308	12	151.079	4.2698
13	157.699	54.979	13	135.074	12.121	13	162.672	43.336
14	171.393	16.929	14	150.267	260.352	14	172.379	4.897
15	173.812	10.776	15	158.735	15.145	15	174.838	11.064
16	183.633	107.690	16	168.069	9.14097	16	187.990	58.891
17	197.893	95.005	17	173.784	16.305	17	200.322	44.956
18	211.792	28.375	18	197.695	82.657	18	214.560	20.380
19	220.801	91.571	19	207.462	16.137	19	223.027	45.794
20	234.038	129.021	20	212.178	70.660	20	236.891	90.951
21	241.053	10.340	21	220.659	60.436	21	242.519	6.756
22	243.896	11.039	22	232.420	11.157	22	245.062	10.358
23	245.982	17.233	23	234.431	2.74319	23	247.352	17.680
24	248.870	60.913	24	235.606	28.184	24	250.720	40.796
25	251.665	3.16564	25	240.799	35.240	25	252.959	10.041
26	273.640	60.059	26	262.282	176.409	26	274.655	52.101
27	287.475	73.068	27	265.549	57.585	27	288.599	60.029
28	295.215	8.78245	28	278.297	149.209	28	296.257	4.08423
29	299.231	73.532	29	282.189	147.926	29	300.376	57.438
30	310.465	33.184	30	290.105	66.384	30	311.706	26.503
31	323.295	5.91446	31	299.949	4.83464	31	323.866	3.69664
32	336.509	16.396	32	315.610	2.56597	32	337.140	12.841
33	341.056	13.199	33	323.809	21.424	33	341.979	8.62204

34	357.326	11.863	34	335.843	2.60382	34	358.436	9.76769
35	361.223	7.45479	35	342.721	6.46855	35	362.234	5.72362
36	371.634	20.603	36	347.896	18.127	36	372.396	16.842
37	378.713	2.24060	37	353.906	7.56383	37	380.089	1.68879
39	382.184	14.662	38	356.259	25.865	38	383.312	10.987
40	420.379	22.683	39	388.728	27.355	39	420.964	17.815
41	462.404	49.144	40	398.785	915.521	40	463.112	36.013
42	508.384	64.581	41	434.058	53.470	41	508.932	54.127
43	526.337	687.812	42	475.423	149.111	42	527.785	493.339
44	538.028	441.885	43	479.220	819.089	43	539.599	298.455
45	551.533	648.594	44	488.037	376.319	44	553.757	537.465
46	570.723	92.558	45	506.621	49.581	45	571.740	75.506
47	579.410	86.538	46	511.399	54.210	46	580.569	73.019
48	585.058	559.969	47	530.077	128.462	47	588.352	485.288
49	598.324	152.071	48	538.145	190.375	48	598.955	134.916
50	610.327	502.237	49	558.981	63.483	49	611.597	524.488
51	639.471	6.28288	50	563.695	15.382	50	640.533	7.58600
52	668.914	36.146	51	589.204	140.754	51	669.361	30.913
53	693.327	158.855	52	618.876	20.448	52	694.541	119.823
54	709.223	530.833	53	635.767	335.927	53	709.846	428.274
55	730.324	709.531	54	653.562	482.748	54	731.885	686.610
56	736.714	202.516	55	669.814	282.744	56	738.809	165.535
57	808.633	553.702	56	676.959	128.164	57	811.059	506.157
58	905.236	203.151	57	762.172	408.396	58	914.039	109.287
59	927.656	159.106	58	771.991	528.093	59	932.179	112.949
60	1026.955	94.887	59	865.817	136.353	60	1031.120	68.290
61	1050.339	487.897	60	901.902	213.530	61	1053.654	411.681
62	1107.341	33.973	61	986.831	13.838	62	1109.931	15.491
63	1123.536	76.559	62	1020.866	93.568	63	1126.589	42.574
64	1130.292	398.161	63	1056.972	94.937	64	1137.089	185.199
65	1138.325	1827.562	64	1060.893	64.519	65	1145.903	578.770
66	1146.349	640.689	65	1068.053	222.192	66	1153.424	548.053
67	1151.606	86.798	66	1076.158	5.28258	67	1157.256	351.068
68	1158.492	256.573	67	1078.181	648.831	68	1161.663	252.317
69	1161.633	419.792	68	1093.516	222.896	69	1169.685	162.505
70	1167.224	301.678	69	1099.376	38.324	70	1175.090	48.195
71	1170.599	418.061	70	1108.516	518.259	71	1181.145	288.485
72	1174.934	1201.534	71	1115.880	374.204	72	1183.888	479.975
73	1177.445	3678.917	72	1118.363	413.925	73	1191.193	24.879
74	1184.958	62.484	73	1135.839	1491.531	74	1196.424	1180.989
75	1191.153	1253.607	74	1145.257	265.971	75	1204.427	1238.499
76	1200.323	1043.247	75	1150.849	1074.515	76	1214.919	2639.577
77	1224.437	127.431	76	1190.540	49.072	77	1227.161	155.087
78	1239.349	240.317	77	1200.969	105.673	78	1242.086	313.395
79	1247.754	142.280	78	1217.986	107.307	79	1250.669	181.327
80	1271.557	139.490	79	1251.409	172.101	80	1273.761	149.449
81	1312.746	11.342	80	1261.781	14.374	81	1314.429	8.47971
82	1340.719	137.422	81	1279.697	81.289	82	1341.640	123.725

Discussion

The DFT calculated IR spectra calculated here should provide reasonable templets for filtering of IR spectral measurements associated with different types of detector schemes and complex spectral-signature backgrounds. In principle, these templets can be linear combinations of spectra given in the tables below, having adjustable weight coefficients of the component spectra, as well as correlation-lag parameters for adjustment of absorption-maxima frequencies. The DFT calculated IR spectra given here are to be adopted as complementary database information concerning spectral features to that obtained from laboratory measurement.

Conclusion

The DFT calculated absorption spectra given here provide information concerning molecular level dielectric response structure. The calculations of IR spectra associated with PFAS molecules C_4F_8-SO_2, C_4F_9-O-C_2H_5, C_4F_9-OH, $C_2F_6CH_2$-SO_3 and C_8F_{17}-SO_3 within different backgrounds using DFT are meant to serve as reasonable estimates of molecular level response characteristics, providing interpretation of dielectric response features for comparison with experimental measurements. Specifically, the DFT calculated IR spectra calculated here should provide reasonable templets for filtering of IR spectral measurements associated with different types of detector schemes.

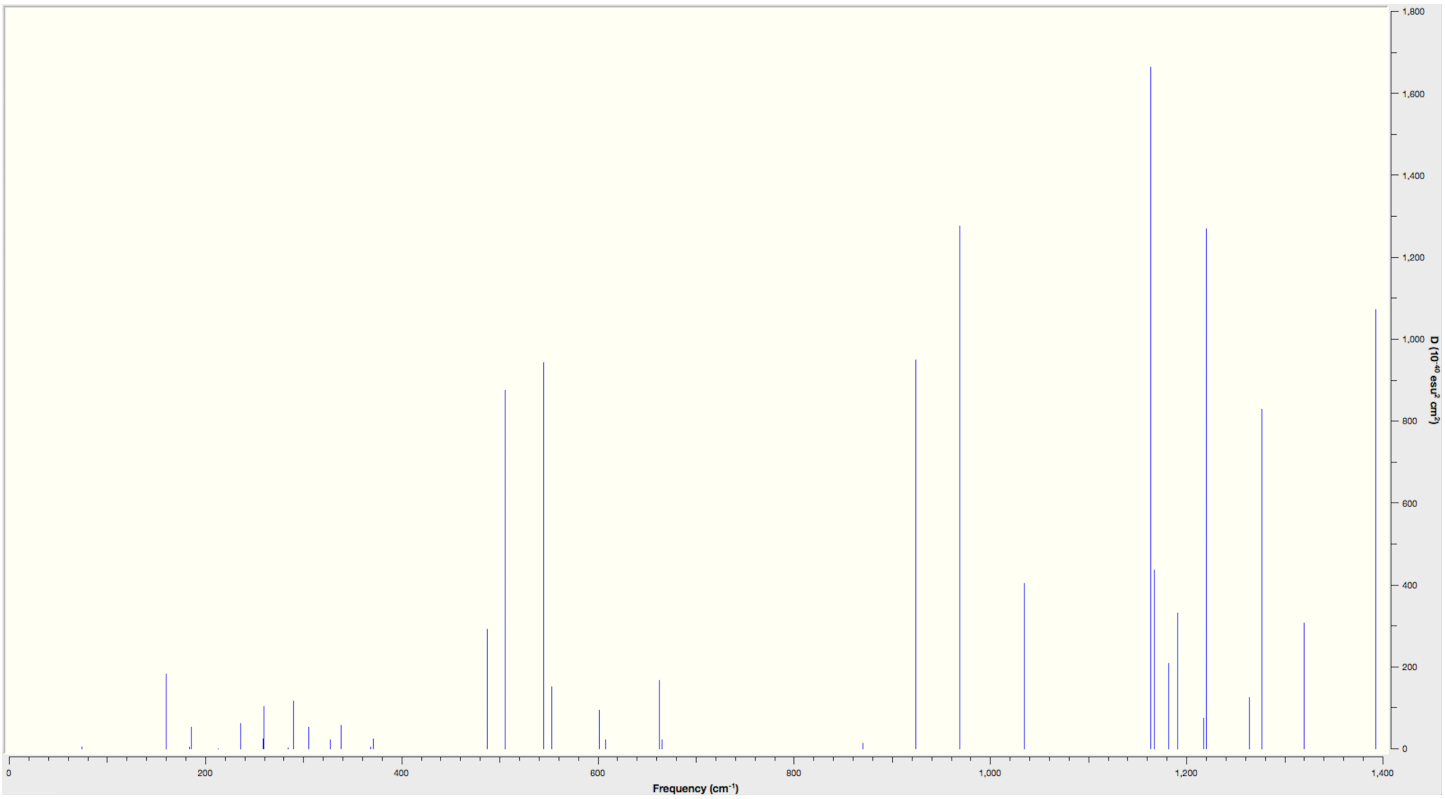

Figure 1A. DFT calculated IR spectra of C_4F_8-SO_2. DMSO background (Energy: -1500.153387 Hartrees).

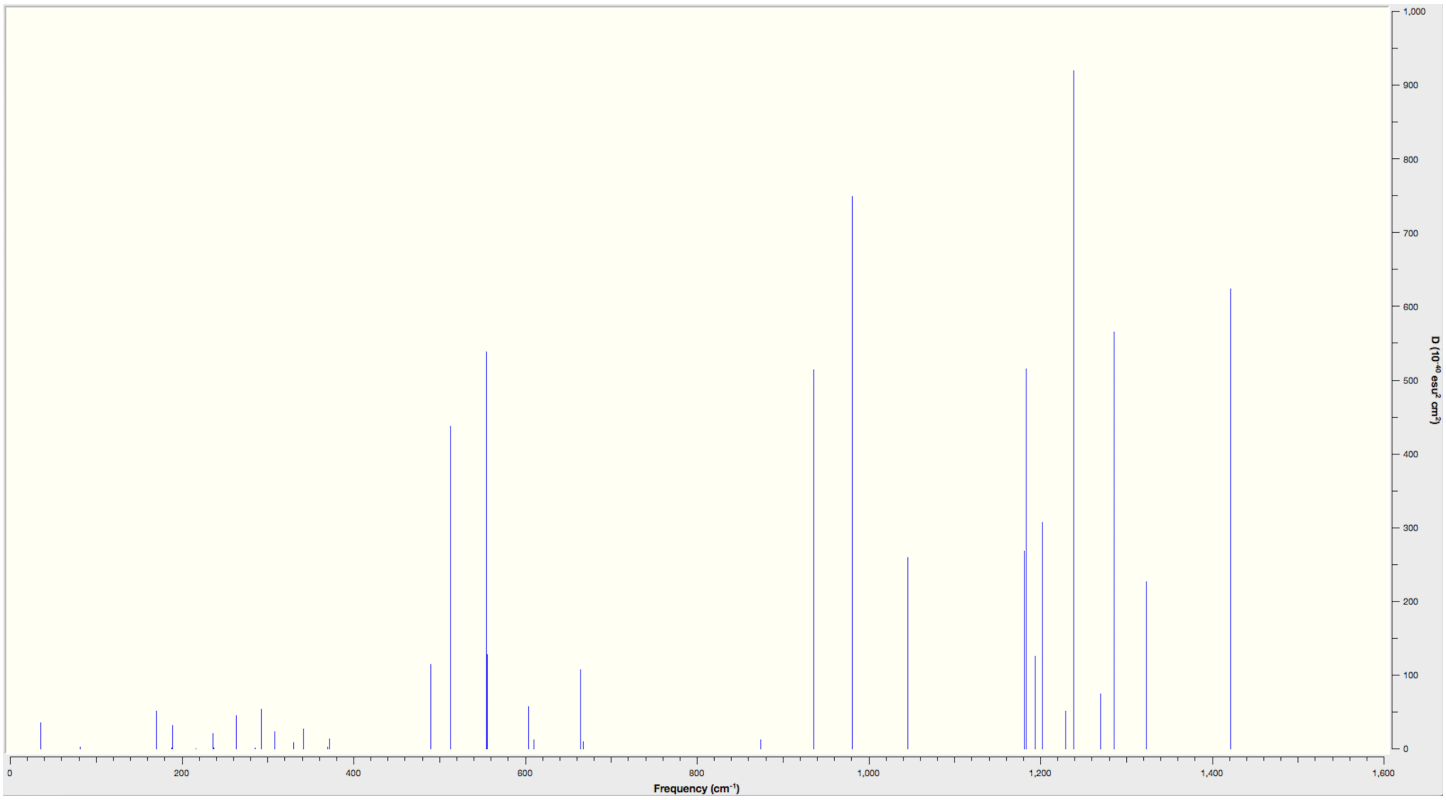

Figure 1B. DFT calculated IR spectra of C_4F_8-SO_2. Isolated molecule (Energy: -1500.153706 Hartrees).

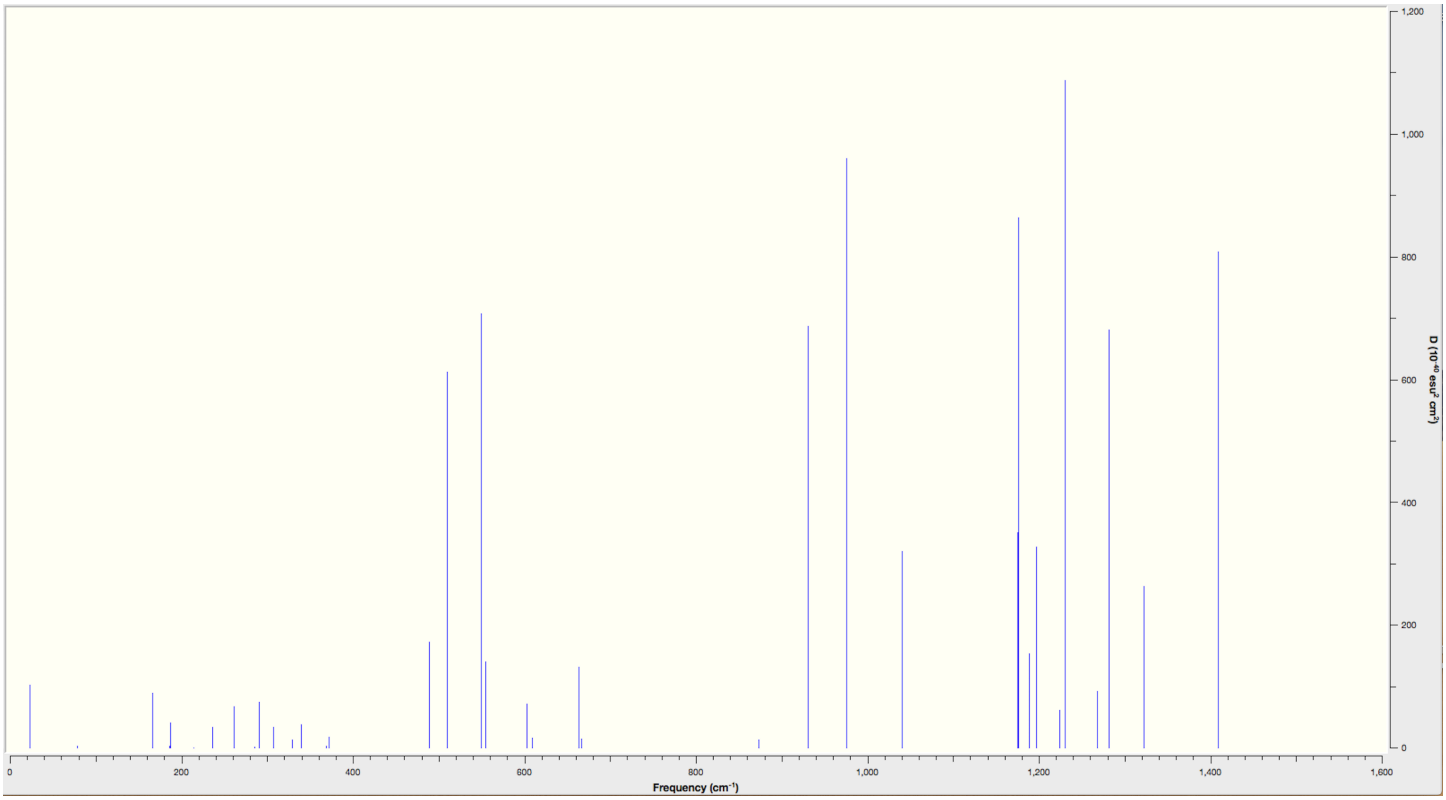

Figure 1C. DFT calculated IR spectra of C_4F_8-SO_2. Toluene background (Energy: -1500.155725 Hartrees).

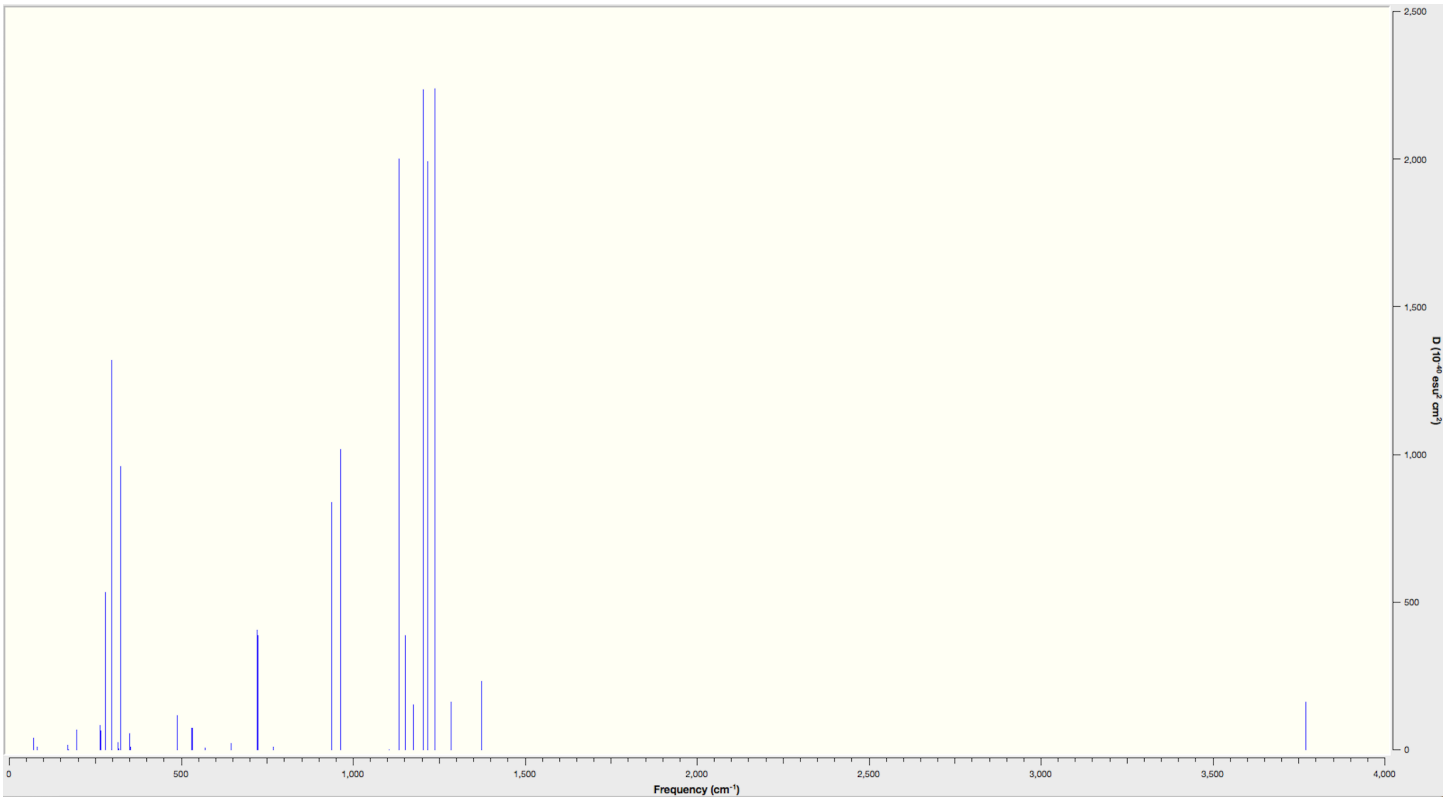

Figure 2A. DFT calculated IR spectra of C_4F_9-O-C_2H_5. DMSO background (Energy: -1127.26216 Hartrees).

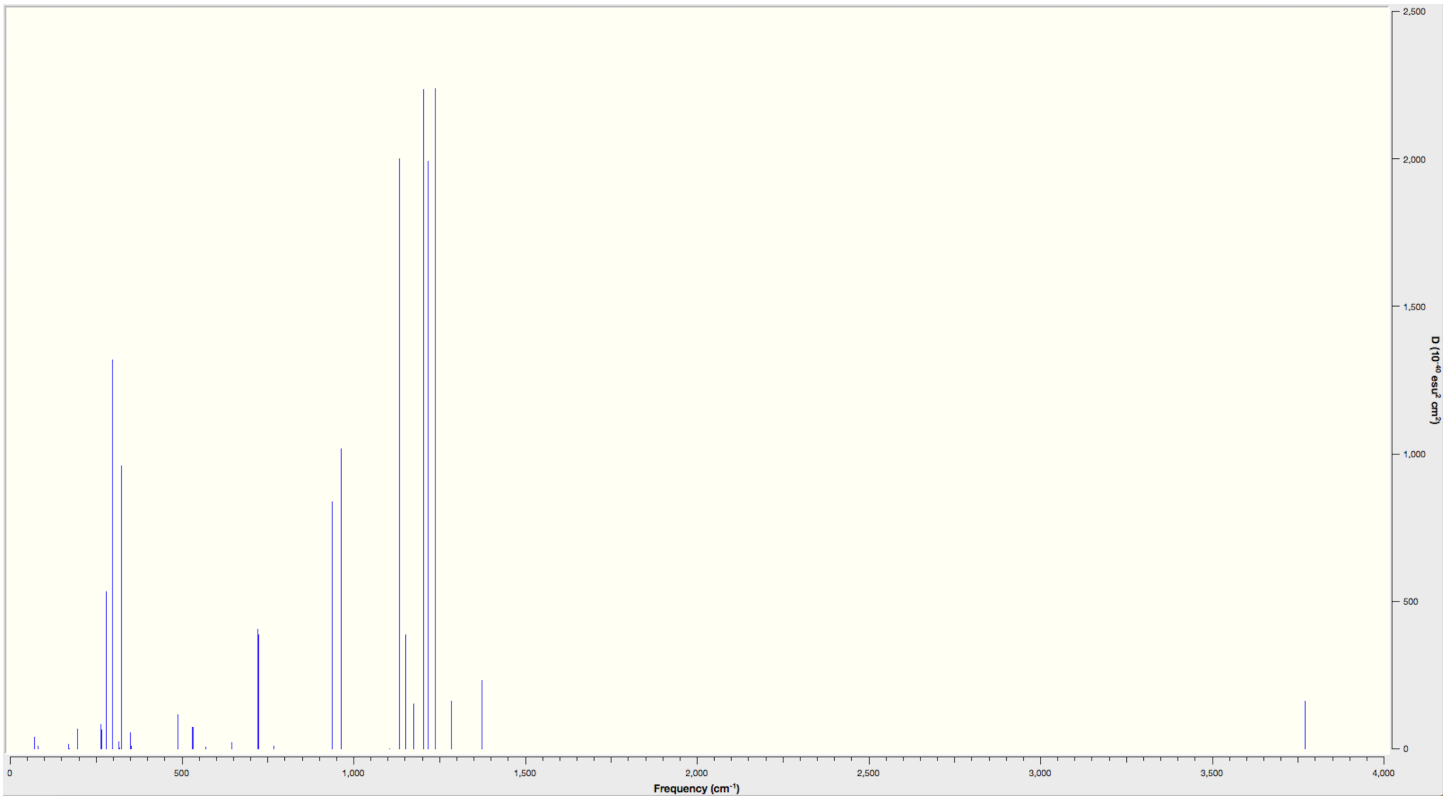

Figure 2B. DFT calculated IR spectra of C_4F_9-O-C_2H_5. Isolated molecule (Energy: -1127.257853 Hartrees).

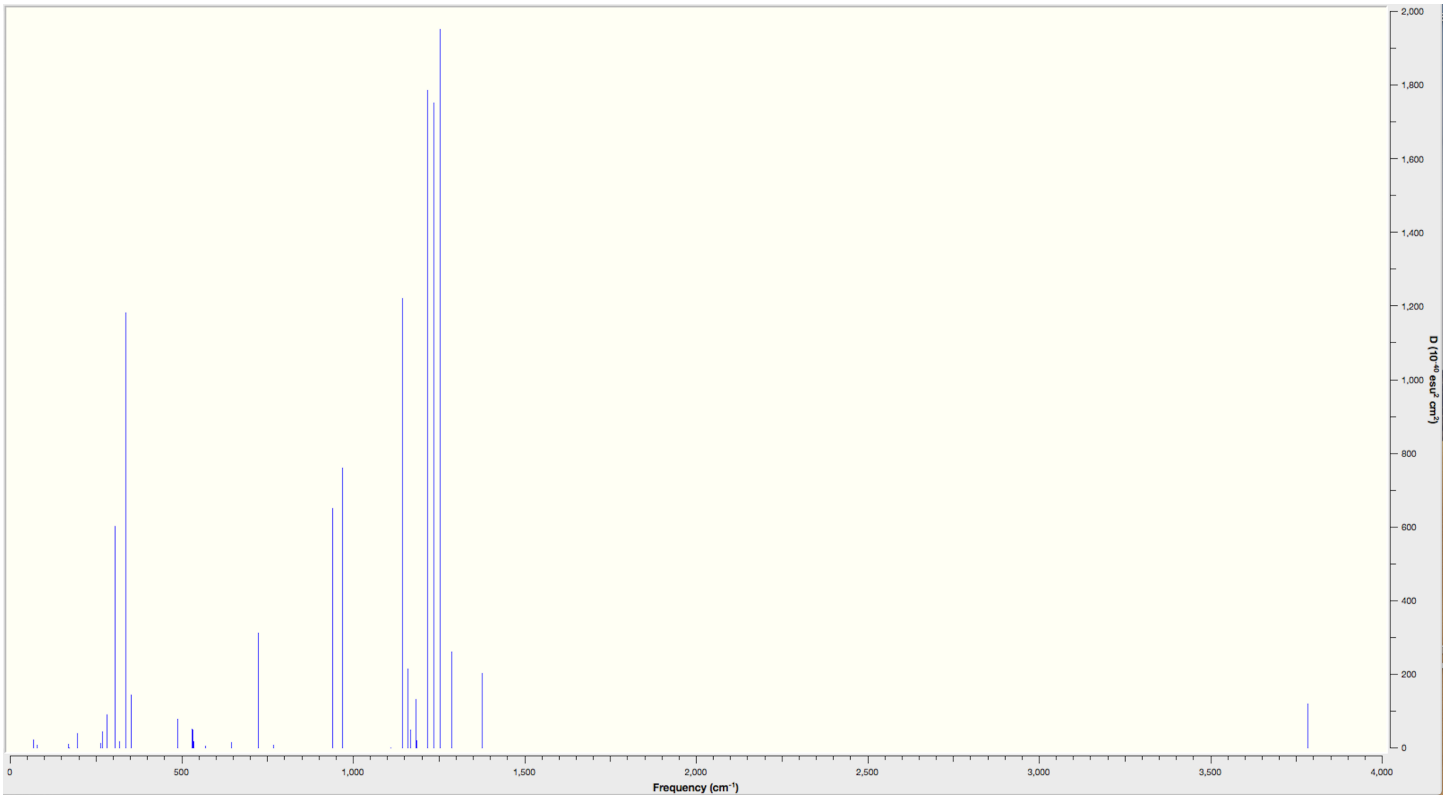

Figure 2C. DFT calculated IR spectra of C_4F_9-O-C_2H_5. Toluene background (Energy: -1127.259741 Hartrees).

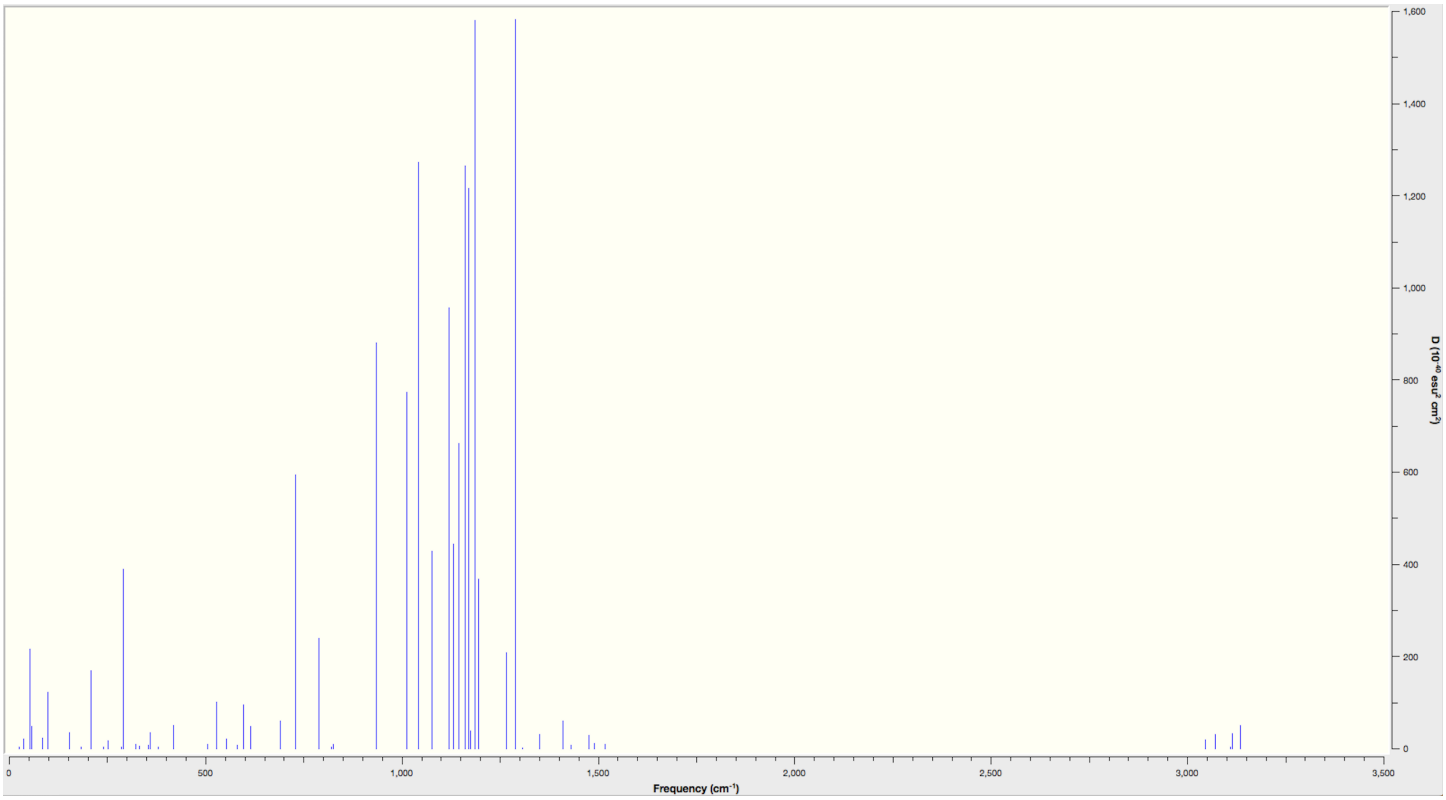

Figure 3A. DFT calculated IR spectra of C_4F_9-OH. DMSO background (Energy: -1205.902946 Hartrees).

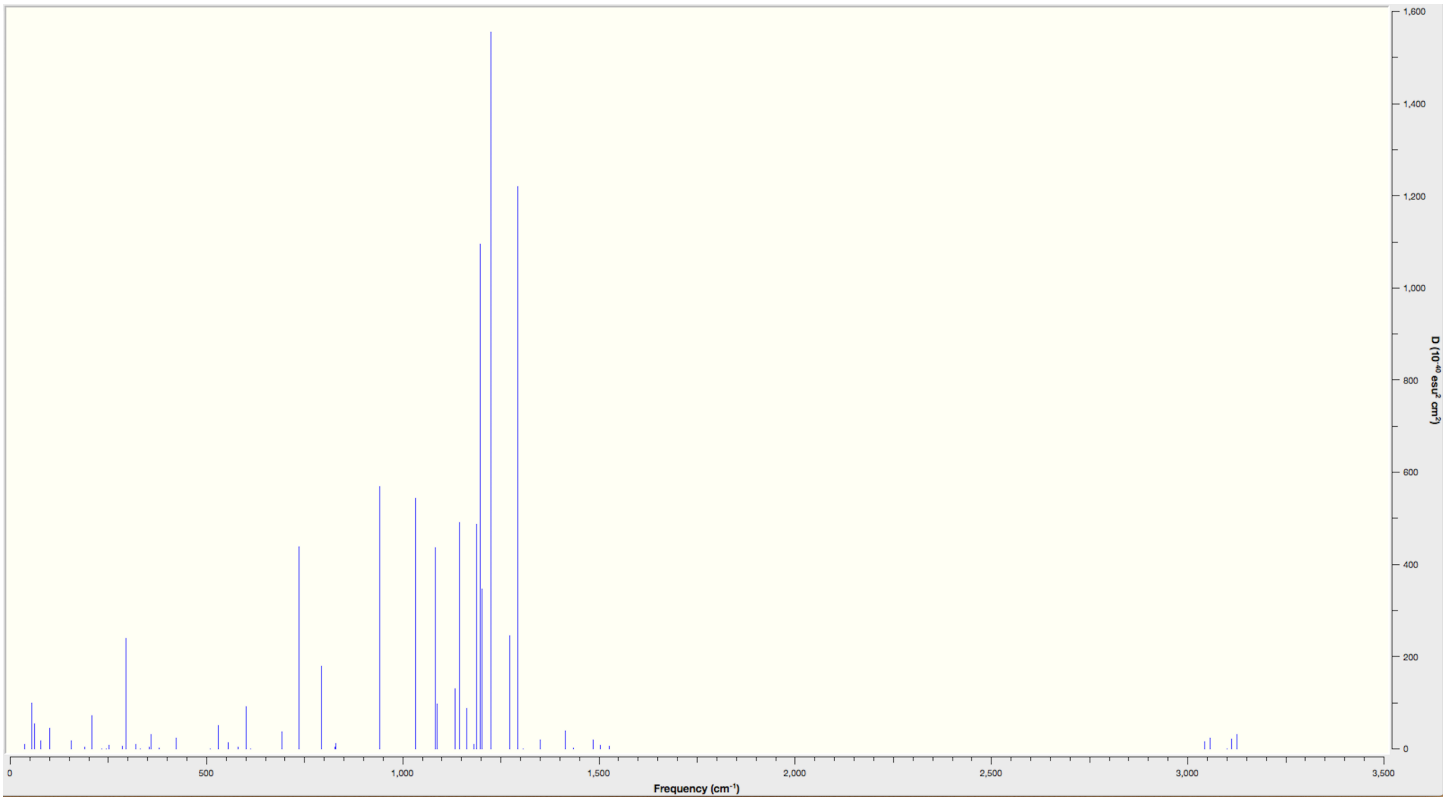

Figure 3B. DFT calculated IR spectra of C_4F_9-OH. Isolated molecule (Energy: -1205.899071 Hartrees).

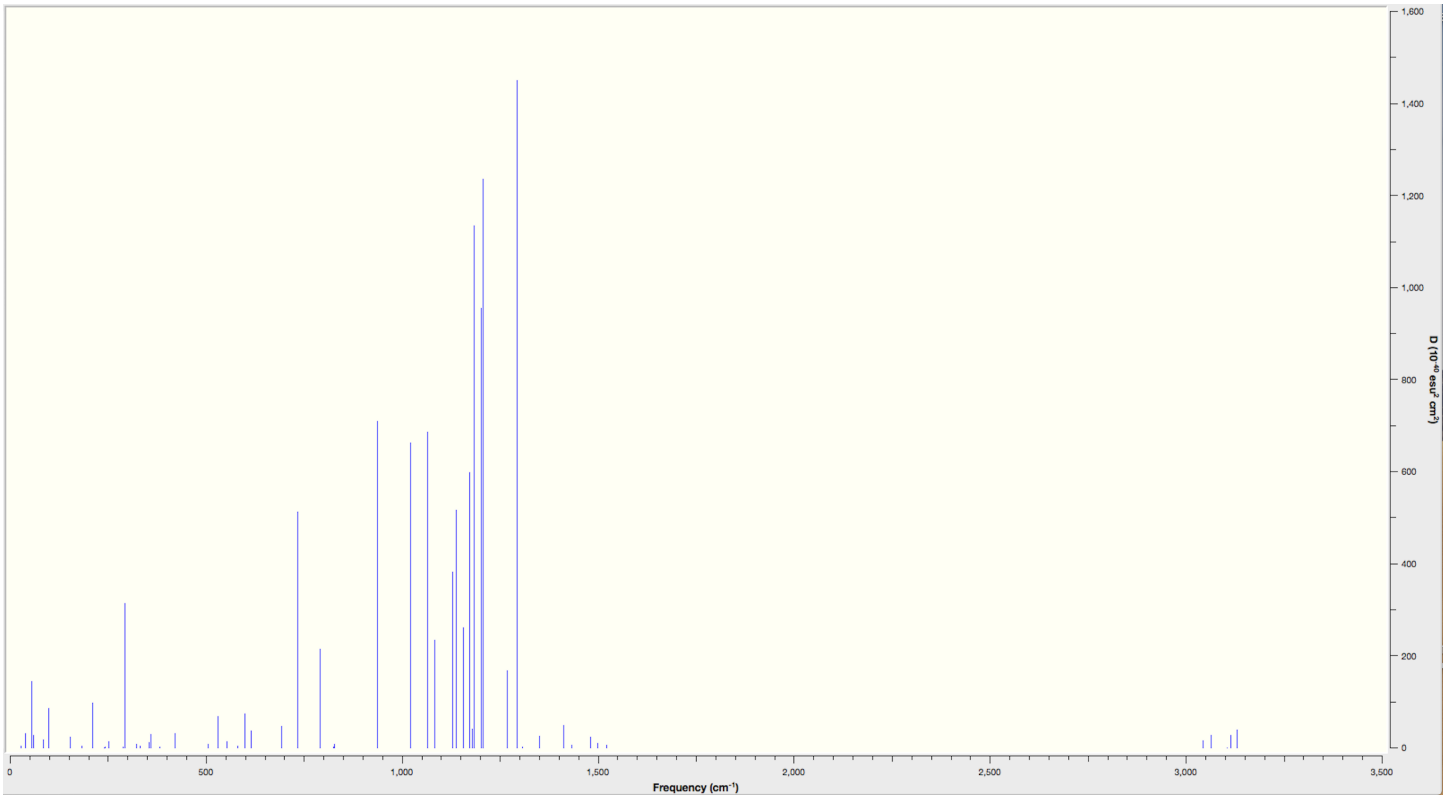

Figure 3C. DFT calculated IR spectra of C_4F_9-OH. Toluene background (Energy: -1205.901063 Hartrees).

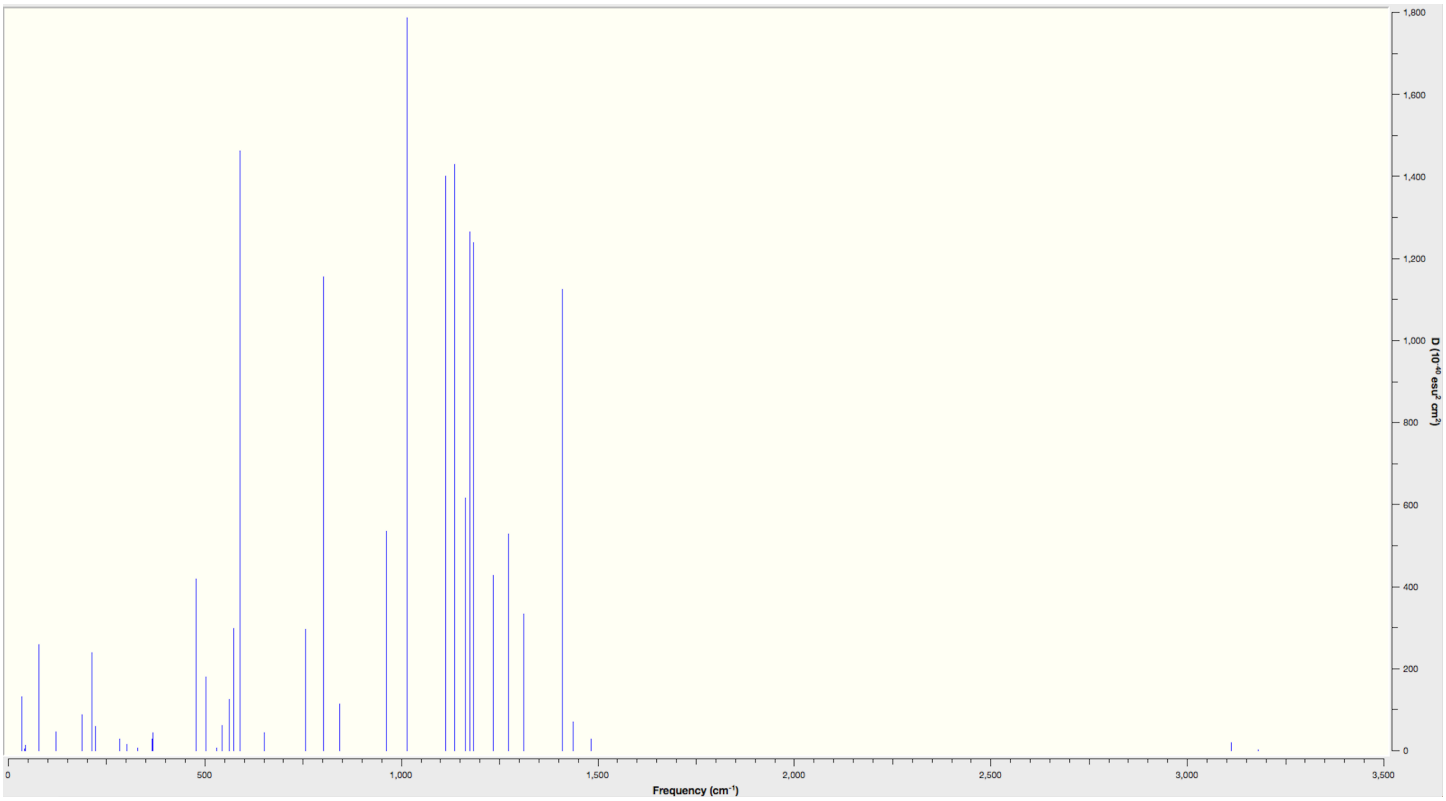

Figure 4A. DFT calculated IR spectra of $C_2F_6CH_2$-SO_3. DMSO background (Energy: -1338.803766 Hartrees).

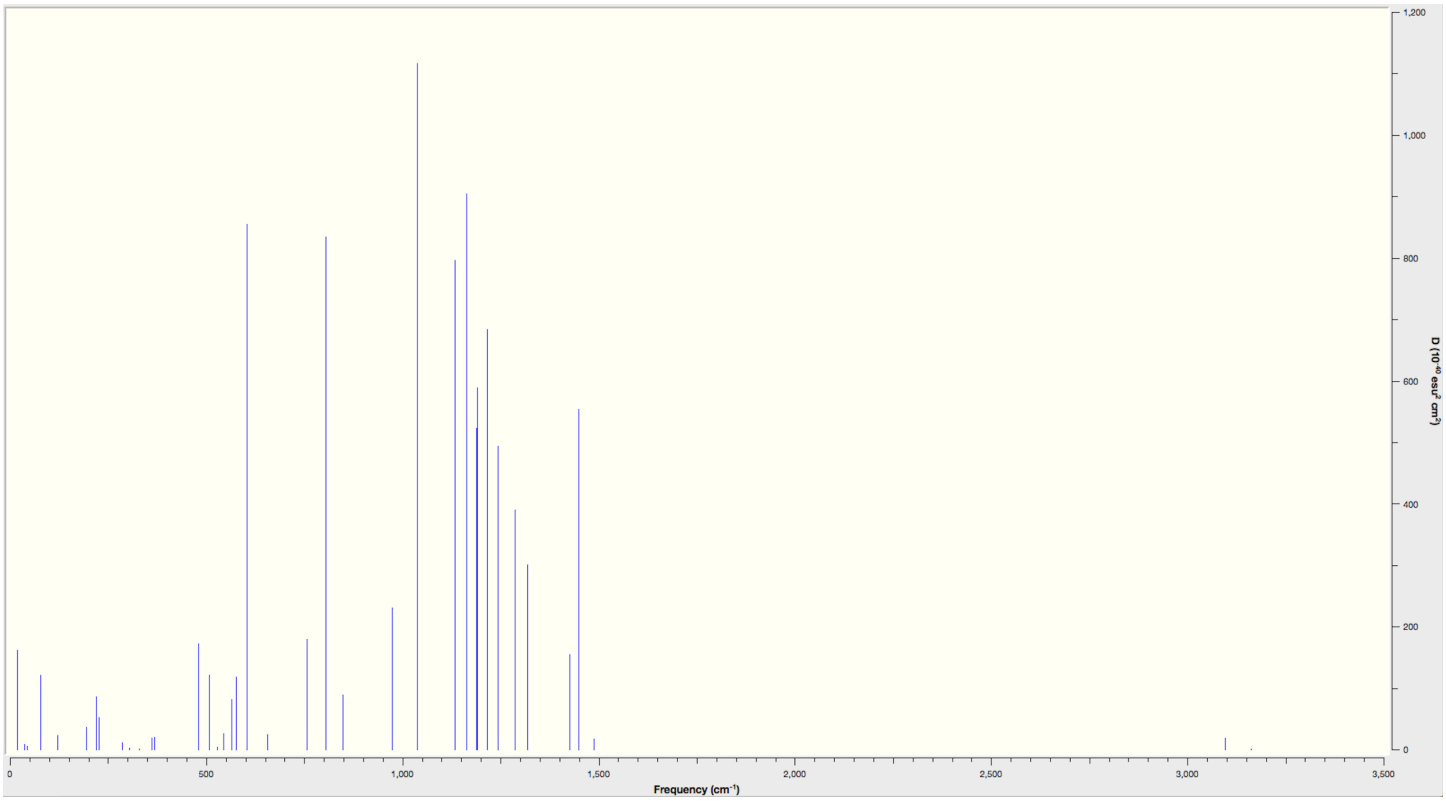

Figure 4B. DFT calculated IR spectra of $C_2F_6CH_2$-SO_3. Isolated molecule (Energy: -1338.796312 Hartrees).

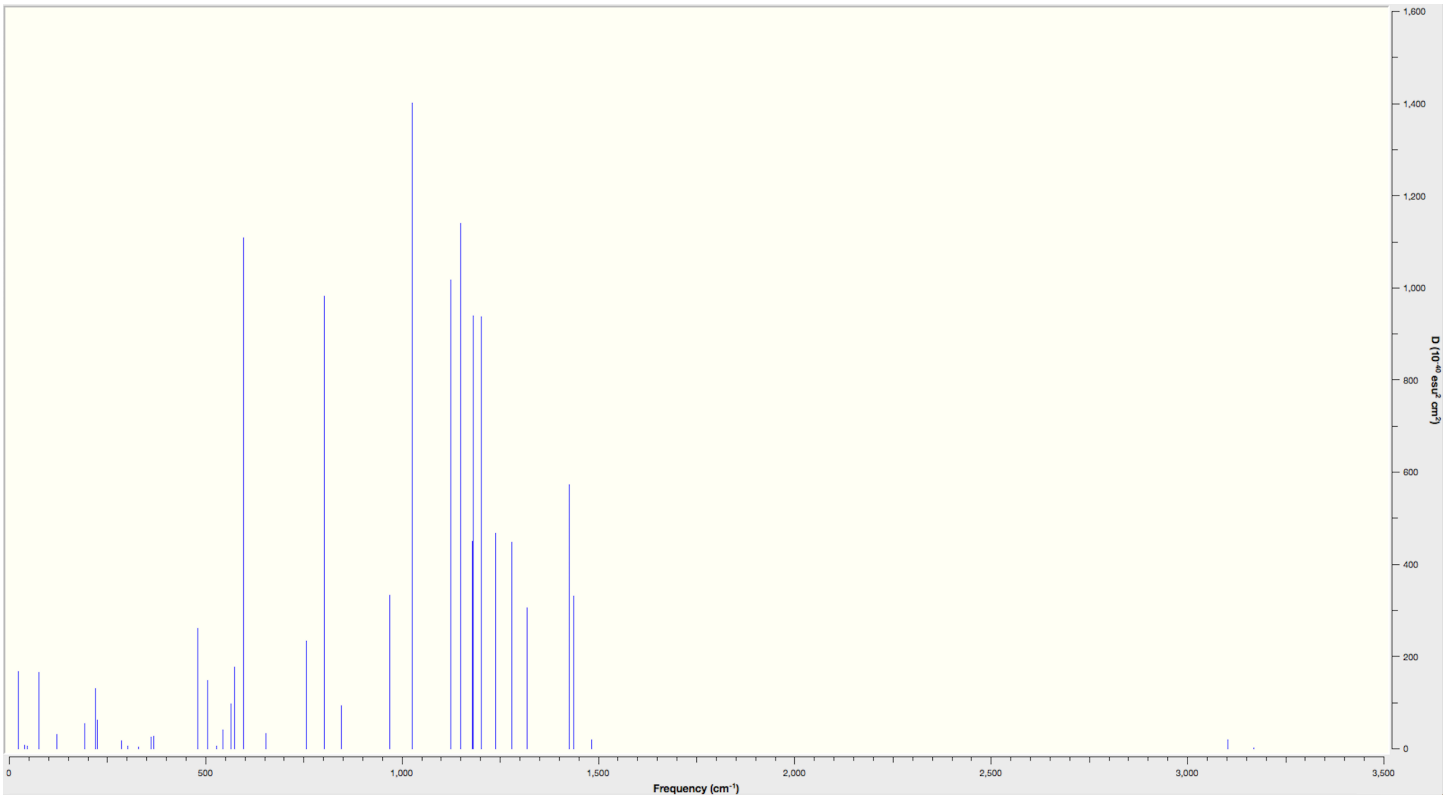

Figure 4C. DFT calculated IR spectra of $C_2F_6CH_2$-SO_3. Toluene background (Energy: -1338.799601 Hartrees).

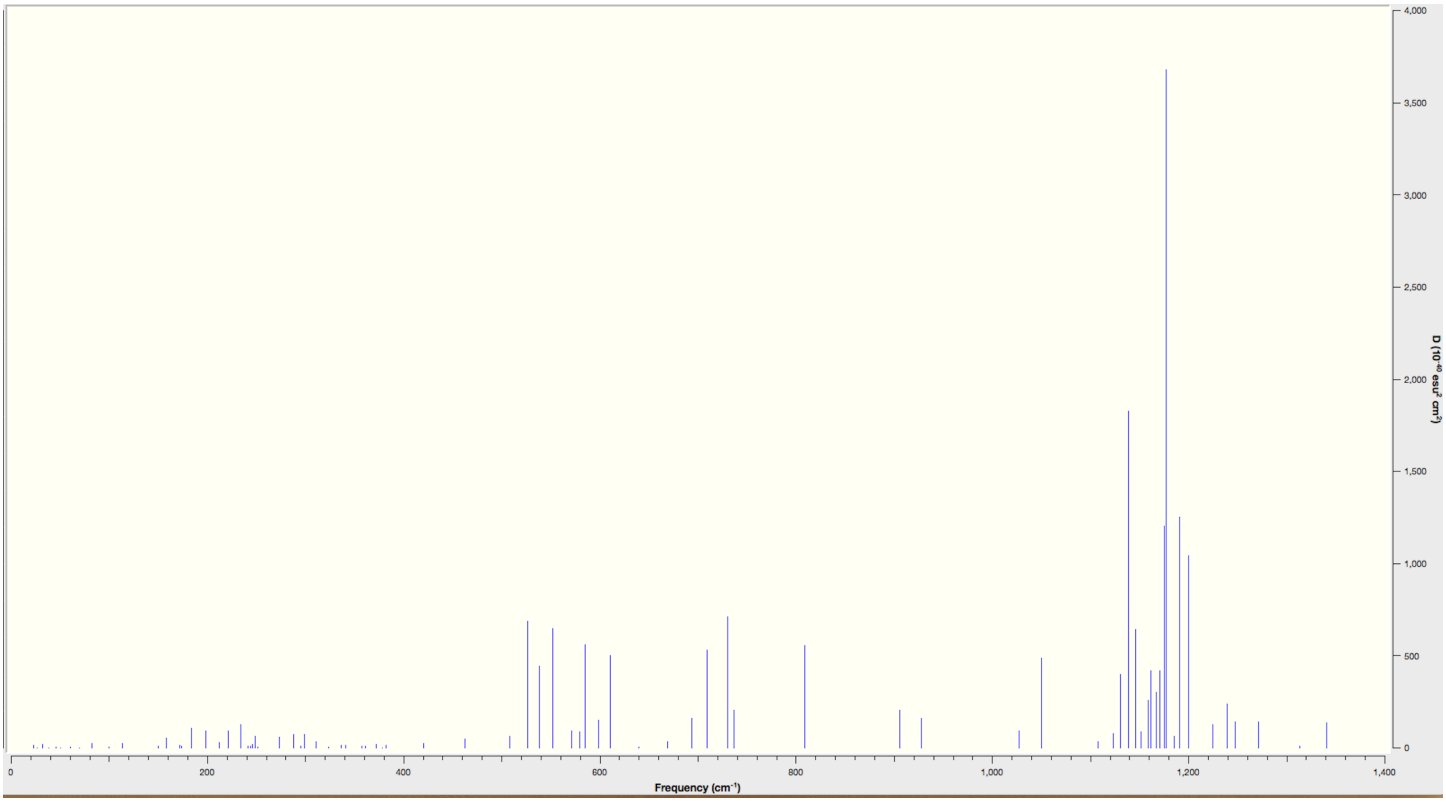

Figure 5A. DFT calculated IR spectra of C_8F_{17}-SO_3. DMSO background (Energy: -2626.736028 Hartrees).

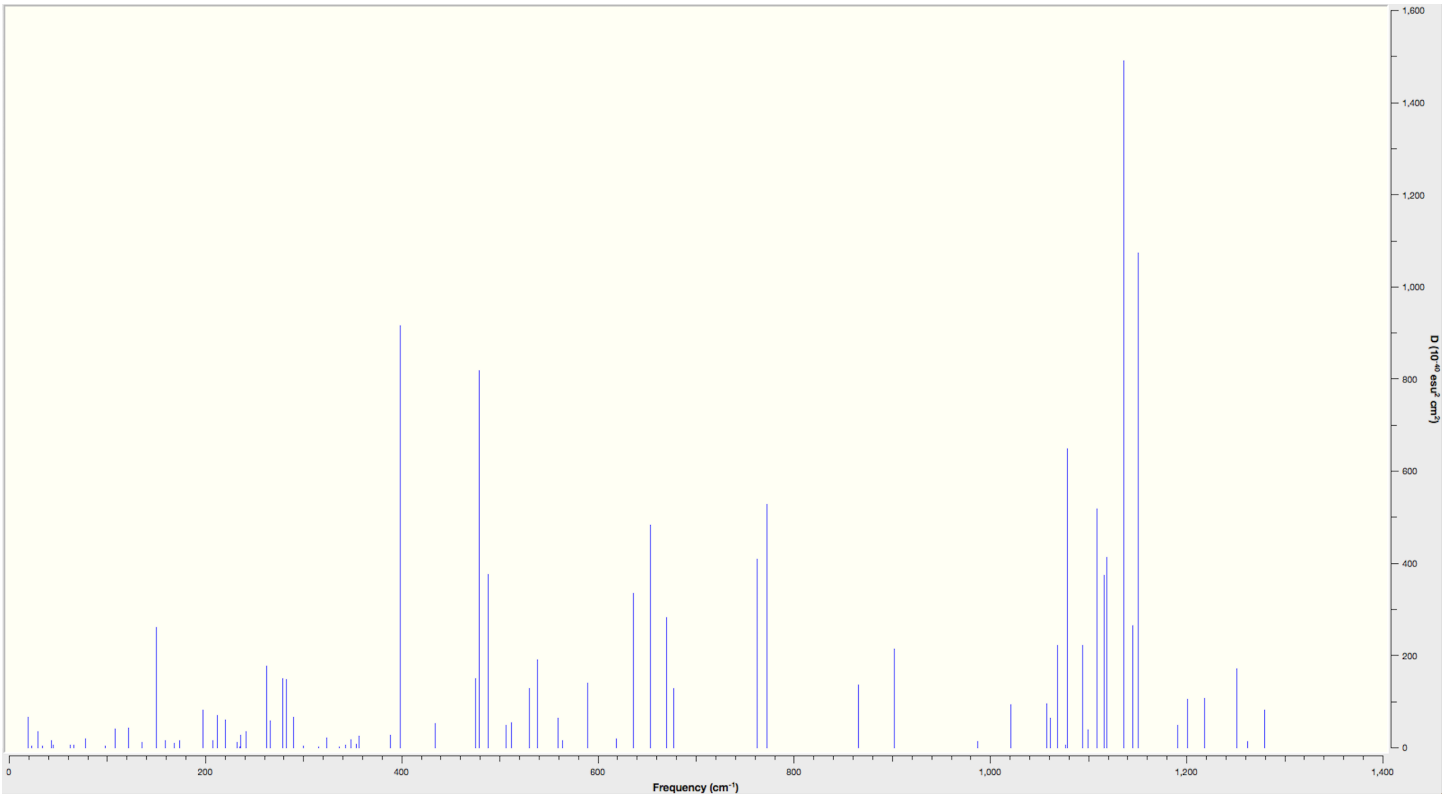

Figure 5B. DFT calculated IR spectra of C_8F_{17}-SO_3. Isolated molecule (Energy: -2626.834837 Hartrees).

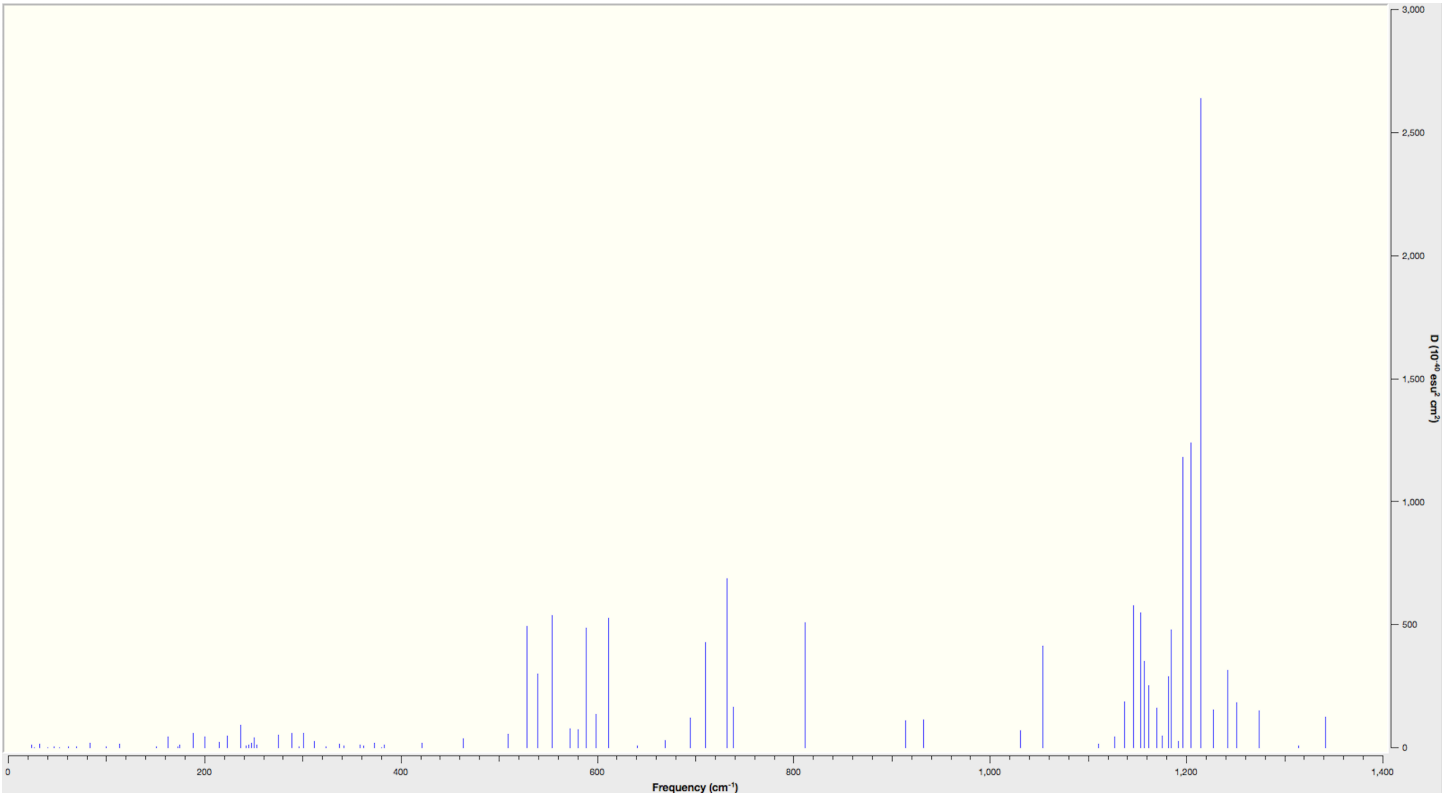

Figure 5C. DFT calculated IR spectra of C_8F_{17}-SO_3. Toluene background (Energy: -2626.734457 Hartrees).

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