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DFT-Calculated IR Absorption Spectra for PFAS Molecules (II)

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14. ABSTRACT

This study continues presentation of the concept of using Density function theory (DFT) to calculate template spectra for practical detection of target substances, by comparison with spectra within databases. DFT is used for calculation of vibration absorption spectra for PFAS molecules within the IR range of frequencies. The DFT software GAUSSIAN was used for the calculations of IR absorption spectra presented here.

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Introduction

Identification of target molecules using infrared (IR) spectroscopy can be achieved by comparison of measured (i.e., detected) spectra with template spectra of known molecules within a database [1] using signal processing algorithms [2]. Specifically, for comparison of measured spectra with template spectra within a database, algorithms are described in references [3-7]. Measured spectra can be compared with template spectra that are within different databases, providing complementary information, including 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, e.g., [10], providing complementary information to that obtained from laboratory measurement.

This report presents DFT calculated IR spectra for PFAS molecules as isolated structures and within a water background. The group of chemicals called PFASs, which are highly fluorinated aliphatic molecules, are among 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. This study continues presentation of the concept of using DFT to calculate template spectra for practical detection of target substances, by comparison with spectra within databases. Specifically, PFAS molecules [20-24], which include toxic and carcinogenic environmental contaminants, and whose detection based on IR spectroscopy is thus of great importance.

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 [25-27]. 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 [28-34]. The electronic density, the potential energy V, and the equilibrium geometry are calculated. The details followed by GAUSSIAN for IR analysis are given in references [27] and [33].

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DFT Calculation of IR Spectra

DFT-calculated IR spectra for a collection of PFAS molecules are presented, i.e., ground-state energies for energy-minimized configuration of these molecules within a water solvent background, 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 [34,35] and basis functions 6-311++g(3df,3pd) [36,37]. 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 [38]. DFT-calculated IR spectra of these molecules as isolated and within a water background are shown in Figs. (1) through (10). Values of the IR intensities ($M^{-1}cm^{-1}$) as a function of frequency (cm^{-1}) for these molecules are given in Tables 1 through 5.

Conclusion

The DFT calculated IR spectra given here are to be adopted as database information concerning spectral features of PFAS molecules, which is complementary to that obtained from laboratory measurement. These DFT calculated spectra continue previous calculations [20-25] for construction of a spectrum-template database for PFAS molecules. As demonstrated [20,21], the DFT calculated IR spectra given here should provide reasonable templates for filtering of IR spectral measurements associated with different types of detector schemes.

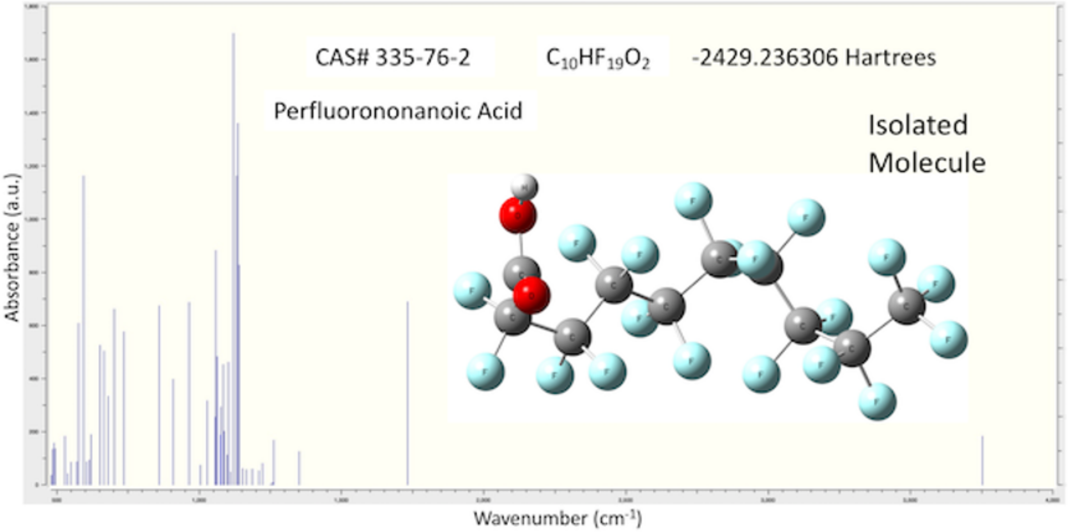

Figure 1. DFT-calculated IR spectra and molecular geometry for CAS# 335-76-2

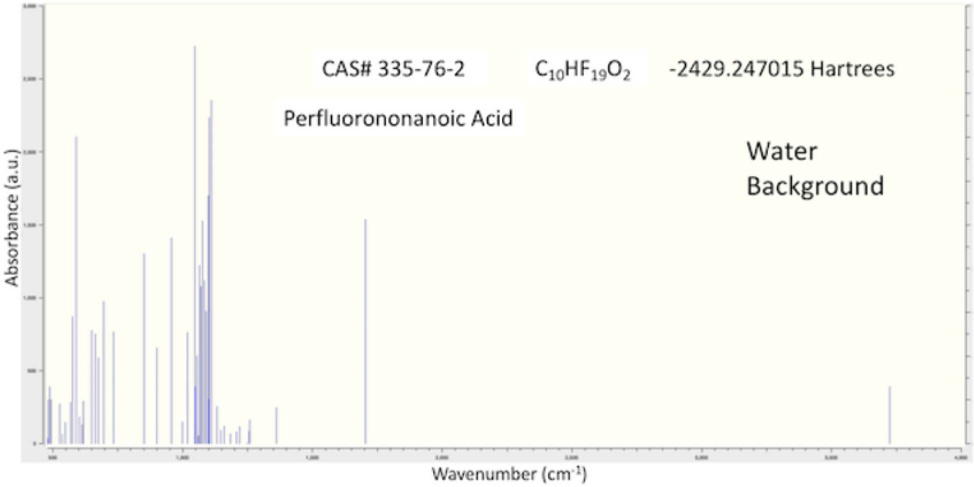

Figure 2. DFT-calculated IR spectra and molecular geometry for CAS# 335-76-2

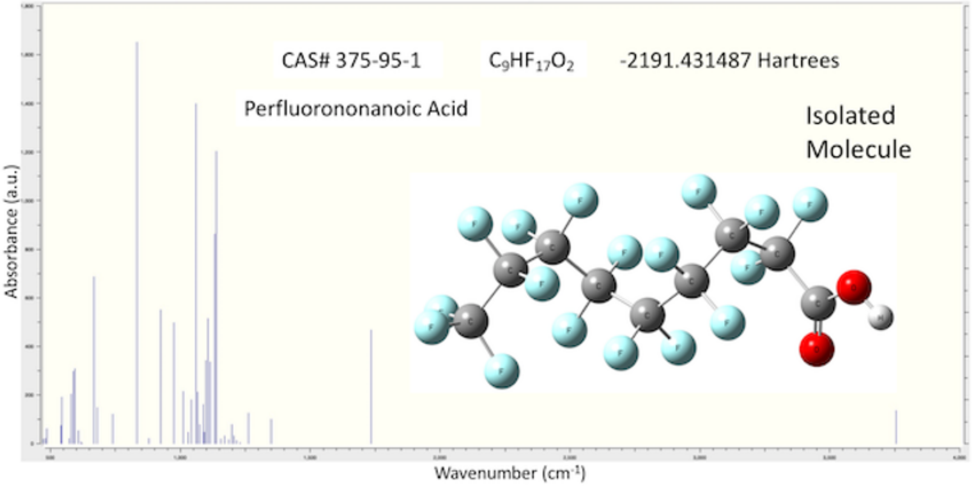

Figure 3. DFT-calculated IR spectra and molecular geometry for CAS# 375-95-1

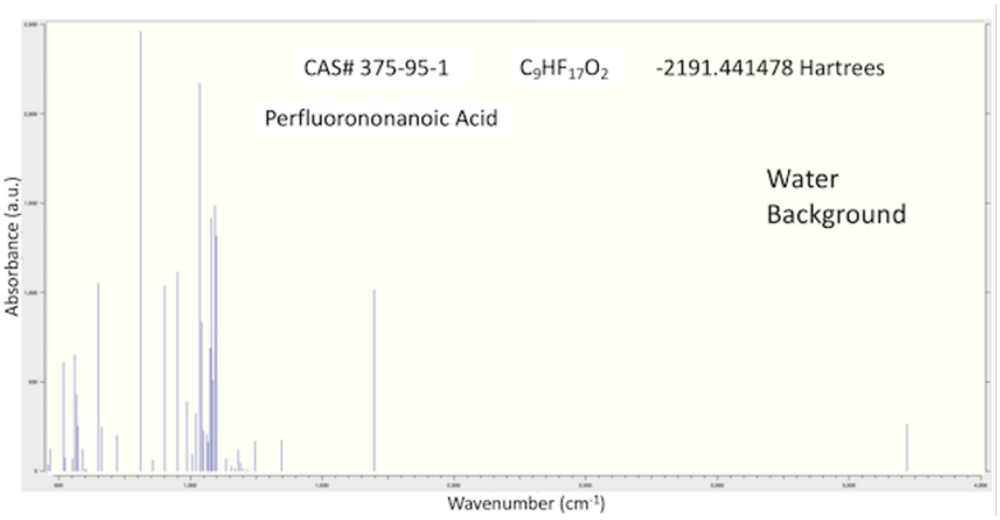

Figure 4. DFT-calculated IR spectra and molecular geometry for CAS# 375-95-1

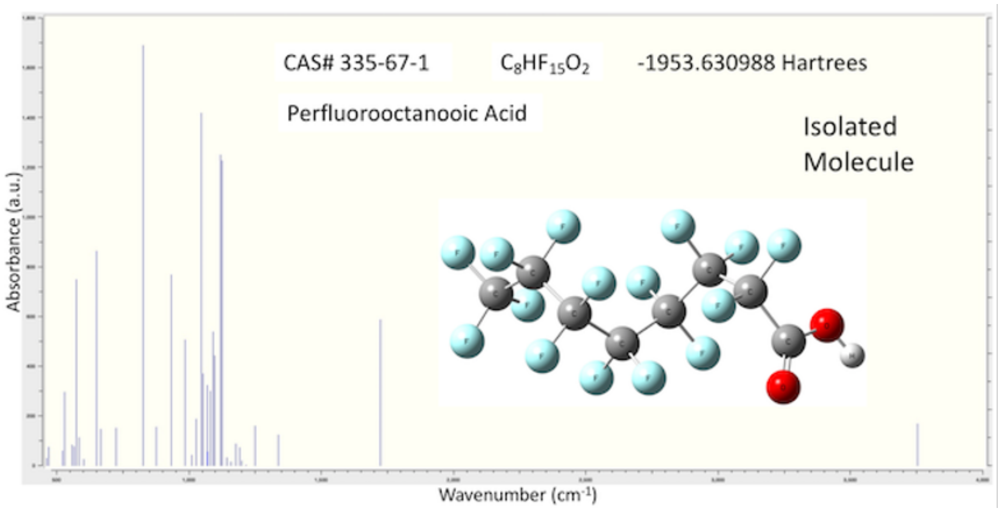

Figure 5. DFT-calculated IR spectra and molecular geometry for CAS# 335-67-1

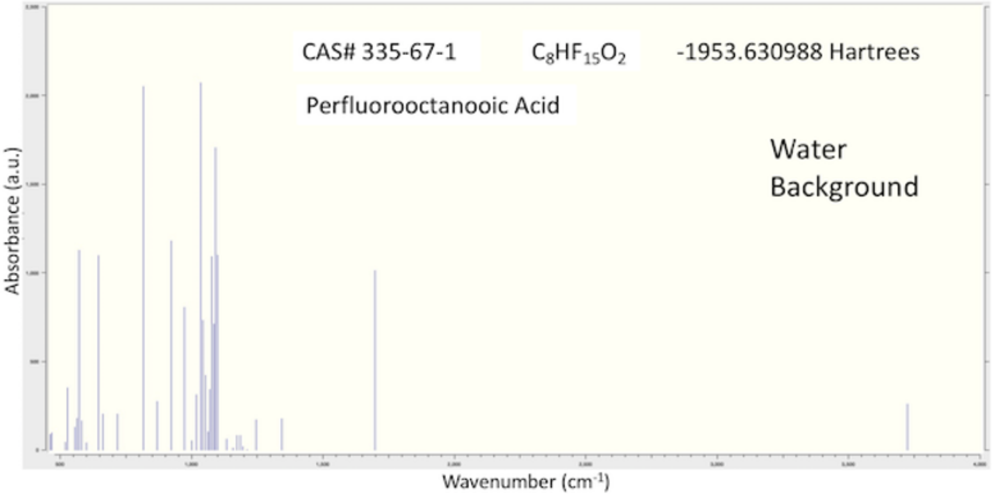

Figure 6. DFT-calculated IR spectra and molecular geometry for CAS# 335-67-1

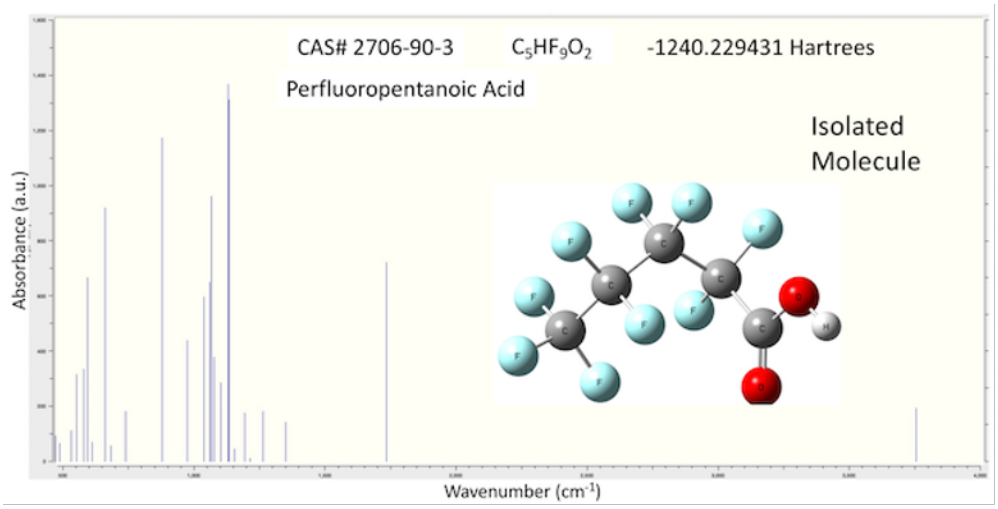

Figure 7. DFT-calculated IR spectra and molecular geometry for CAS# 2706-90-3

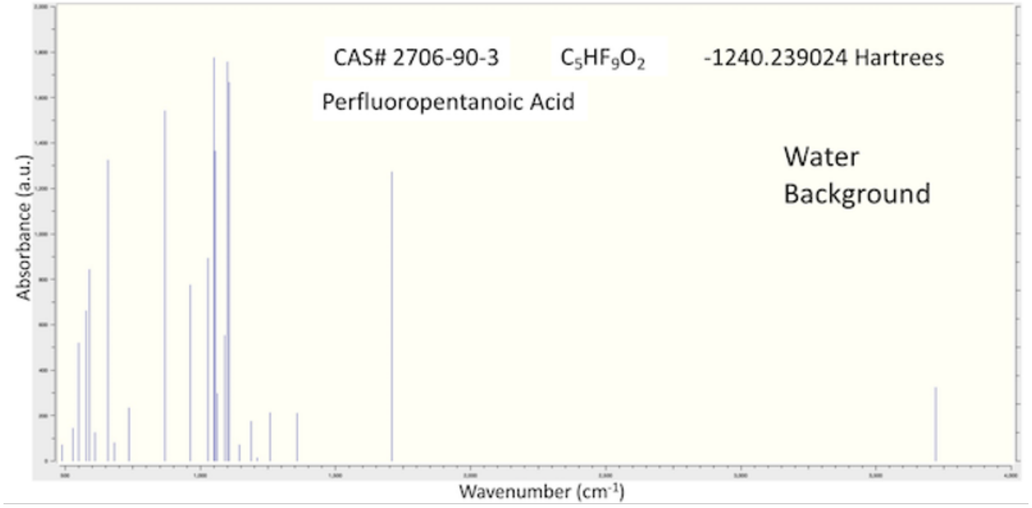

Figure 8. DFT-calculated IR spectra and molecular geometry for CAS# 2706-90-3

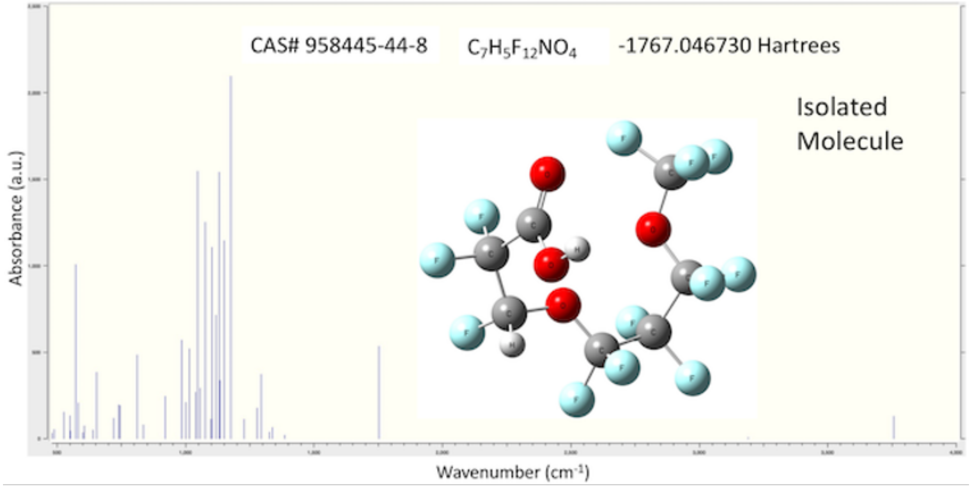

Figure 9. DFT-calculated IR spectra and molecular geometry for CAS# 958445-44-8

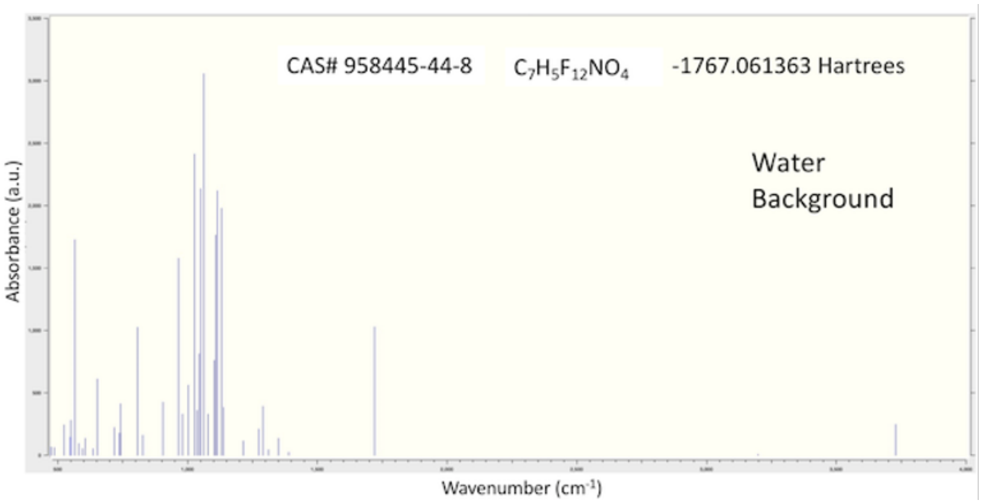

Figure 10. DFT-calculated IR spectra and molecular geometry for CAS# 958445-44-8

Acknowledgments

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Table 1

CAS# 335-76-2 (Water Background)					
Frequency (cm^{-1})	Intensity (M^{-1}cm^{-1})	Frequency (cm^{-1})	Intensity (M^{-1}cm^{-1})	Frequency (cm^{-1})	Intensity (M^{-1}cm^{-1})
16.6000	80.5330	306.9486	23.7129	850.1191	869.6109
23.1998	104.1895	308.2737	12.4429	900.4930	437.6445
29.9834	68.7754	318.1906	24.6217	956.3631	939.9294
38.4451	21.3763	334.9384	10.6709	998.8942	99.6676
46.4617	24.8491	342.2096	23.2945	1017.6542	508.6434
52.1555	71.6104	346.9776	14.7594	1046.6330	1816.1775
57.7938	80.5972	350.9119	2.5739	1047.5463	259.7057
64.5665	92.2486	360.8069	79.2148	1053.3815	401.5978
84.9762	22.5347	364.0129	15.6447	1061.0924	34.9694
92.3354	14.8152	406.7751	85.3840	1064.9077	814.4441
114.0177	7.6452	427.2848	171.0012	1070.2294	718.3085
125.0013	14.1032	451.9041	49.9734	1075.3501	1017.8470
140.0009	63.1689	480.1599	24.7177	1085.1382	745.6889
155.4289	99.4392	481.8685	201.1991	1089.9441	604.6443
160.9575	5.4379	487.6558	259.4456	1098.1308	1133.2768
171.2843	60.1655	493.5731	200.9486	1099.8822	202.7524
196.9503	192.0357	526.7810	182.3133	1103.2167	1489.6460
202.4845	304.9256	536.4295	43.1596	1109.2455	1568.9151
208.6135	128.7081	548.5532	97.8868	1132.4941	170.1405
225.6628	117.4105	567.5334	188.7180	1145.2214	61.7209
239.0428	7.7070	574.7411	581.2061	1160.4589	79.6216
244.6499	40.4778	590.0562	1403.4452	1183.9112	45.3747
253.4418	35.4595	602.0752	122.3876	1207.1824	55.2463
256.1548	1.8082	612.2417	87.1496	1218.9436	76.8661
263.8090	39.8367	618.4843	194.1689	1248.1919	5.6690
266.4380	48.0501	649.9629	516.2876	1255.1772	55.4912
279.2874	28.9012	664.0013	500.8246	1257.6284	108.3917
283.8106	37.7292	676.2688	391.8037	1361.3331	164.7663
293.0312	33.9771	696.1847	649.3686	1704.6489	1025.7568
302.3452	6.2768	732.9767	510.6673	3723.9654	260.5129

Table 1 (continued)

CAS# 335-76-2 (Isolated Molecule)					
Frequency (cm^{-1})	Intensity (M^{-1}cm^{-1})	Frequency (cm^{-1})	Intensity (M^{-1}cm^{-1})	Frequency (cm^{-1})	Intensity (M^{-1}cm^{-1})
18.5609	60.3539	310.7595	12.7272	859.3103	523.9683
24.0202	39.6113	311.8601	3.5997	907.9125	308.9392
30.6205	23.8552	320.1758	15.8404	965.4434	533.5197
38.2692	16.3770	337.6626	7.3972	1005.2484	57.4831
47.6733	35.2385	345.8434	15.6338	1028.0120	246.5454
53.2735	26.8988	349.5718	7.2388	1055.5571	197.7058
58.4165	40.9071	354.6154	5.6508	1057.7063	685.2093
65.2909	53.9469	361.3721	35.4050	1061.9172	375.6115
86.8906	8.4434	365.7070	13.2879	1073.4830	145.8671
92.7264	7.9808	409.0291	46.5097	1076.8756	228.9012
116.4852	4.1714	430.3505	78.2490	1084.4775	352.2978
127.3970	6.0719	454.7590	24.2175	1089.1916	157.3403
141.7313	29.1300	480.9286	27.6496	1099.1027	87.4580
157.2169	35.8500	484.7674	104.1716	1102.3731	358.2291
162.6380	4.2632	490.0673	121.6412	1109.8911	38.5205
175.1256	13.3241	494.7941	106.2266	1119.2235	1321.3543
201.0470	98.9754	527.1962	142.6969	1130.3586	904.2863
206.9153	204.8690	538.6764	32.7475	1136.7033	1057.4438
214.1459	58.6191	550.2148	66.4787	1140.5585	643.6609
230.0079	96.5349	569.8059	67.9290	1152.0652	47.6980
242.3820	4.2794	576.1596	472.2145	1165.5989	44.6008
246.8492	28.2968	593.3992	903.4633	1186.5242	46.0800
251.0677	19.6000	604.2405	67.4745	1210.2596	41.5975
258.4115	1.5315	613.7759	72.0967	1222.2226	62.1087
265.2170	31.4619	620.0403	147.3543	1251.4857	3.8087
268.8705	27.5920	652.3663	408.2501	1257.8225	6.7918
282.4596	22.5938	665.2234	392.3673	1262.2484	130.7007
285.0346	18.9424	679.6868	259.8811	1351.7909	98.3170
296.5738	20.0079	700.8457	514.1132	1731.6791	535.2280
304.7970	8.8820	735.9925	447.3976	3753.5053	141.5715

Table 2

CAS# 375 -95-1 (Water Background)					
Frequency (cm^{-1})	Intensity ($M^{-1}cm^{-1}$)	Frequency (cm^{-1})	Intensity ($M^{-1}cm^{-1}$)	Frequency (cm^{-1})	Intensity ($M^{-1}cm^{-1}$)
26.5797	489.1194	307.5068	0.3010	871.2451	60.5531
30.2990	53.2596	310.6171	1.8263	916.3337	1037.1830
37.6731	69.1813	321.7410	0.5865	964.2359	1112.1241
43.8225	163.0534	334.3401	16.7265	1000.7733	386.7391
48.6815	37.3687	347.3221	11.9732	1021.2214	90.0670
61.1915	15.1970	352.4408	40.9862	1034.5577	319.2493
84.1342	15.9416	358.2465	41.9456	1048.6261	2169.9008
92.0932	6.5325	385.7612	3.3776	1056.7168	832.1455
120.4215	48.8846	417.1148	232.1468	1063.2292	222.8501
131.2560	6.9359	433.4556	212.5881	1077.0113	207.4406
137.1276	62.2814	447.4541	21.5628	1080.8817	161.1635
138.1247	73.6650	470.6984	51.5716	1087.8478	686.4143
148.8754	38.4080	476.1397	34.9992	1092.5374	1417.5306
166.9775	50.0438	483.8499	120.5815	1097.9432	507.4373
179.5291	12.1818	533.6049	607.9835	1105.5411	1485.5054
197.5045	801.5234	539.1852	76.1854	1111.2826	1317.6310
216.8301	255.5197	568.4732	71.6287	1147.4167	67.8257
238.7746	19.6868	575.5681	647.9311	1167.8088	27.3387
246.0370	25.0273	584.5346	428.0169	1182.1117	16.0091
255.6755	16.4194	588.6310	251.0396	1194.0675	116.6996
261.4865	0.4607	605.3782	120.4948	1202.7504	43.8013
265.3963	21.0190	616.4282	10.4041	1212.5603	15.5686
277.0584	19.9169	619.5841	3.0668	1226.6552	5.7913
286.2817	2.8874	664.6558	1051.1006	1257.2303	168.3988
290.6893	35.0331	677.8156	247.2916	1357.6301	170.1698
293.8878	34.4102	735.5113	199.0090	1709.3744	1012.1372
304.6373	2.6453	824.9639	2461.9030	3720.9505	263.4559

Table 2 (continued)

CAS# 375 -95-1 (Isolated Molecule)					
Frequency (cm^{-1})	Intensity ($M^{-1}cm^{-1}$)	Frequency (cm^{-1})	Intensity ($M^{-1}cm^{-1}$)	Frequency (cm^{-1})	Intensity ($M^{-1}cm^{-1}$)
27.5389	46.4145	310.6375	0.2838	879.0457	23.7377
31.4201	82.0478	314.4325	0.9325	924.0087	611.5857
38.7780	38.3220	324.5666	0.7461	974.9642	552.3505
46.4515	28.5389	336.7472	12.0175	1010.8255	237.5100
50.2169	138.8113	349.5386	2.1434	1031.2211	52.2855
61.9071	14.1707	353.0207	30.9561	1042.3343	200.7118
84.3494	9.4971	359.5999	18.8032	1059.9123	1553.4030
93.3671	5.4649	386.6068	2.2949	1066.0658	234.9543
121.4439	32.0088	419.1222	117.0704	1074.4468	86.5402
131.1939	3.0925	436.2000	99.0572	1087.8743	179.6126
136.9437	30.9000	449.9688	10.7083	1093.0818	51.2922
138.9143	34.1950	472.1165	21.9388	1099.2109	380.4030
149.3743	28.0321	479.2735	23.7562	1107.1966	572.0609
167.5308	24.4368	486.4485	68.3010	1113.5431	373.0625
180.1909	7.6139	539.6878	83.7652	1132.2770	957.6221
201.2904	516.8567	543.7815	212.1224	1137.8003	1335.4292
220.2108	200.0344	571.3269	23.4828	1155.5920	21.6387
241.5961	12.6041	580.6628	226.4332	1170.2623	34.7695
244.7278	12.3515	588.4381	331.6402	1185.0297	19.0119
257.1458	8.4180	593.2243	342.7406	1197.9241	87.7670
262.2100	0.1476	607.1731	59.0151	1206.4778	36.2819
266.9689	9.4666	617.8430	7.9266	1215.0006	14.8537
278.1726	15.2493	620.6767	1.7849	1229.3649	4.7038
287.0539	1.8790	666.5604	762.7952	1262.3724	139.0625
292.5622	15.1142	680.3924	166.3692	1349.3725	109.9495
296.3553	16.4177	739.0949	134.2435	1734.8733	519.2156
307.6208	1.3552	833.9375	1834.2983	3754.1906	150.3646

Table 3

CAS 335-67-1 (Water Background)					
Frequency (cm^{-1})	Intensity (M^{-1}cm^{-1})	Frequency (cm^{-1})	Intensity (M^{-1}cm^{-1})	Frequency (cm^{-1})	Intensity (M^{-1}cm^{-1})
22.3956	369.7509	310.2458	0.2816	883.4417	274.4489
31.5516	227.4157	316.9228	7.3463	936.6261	1180.4088
32.9576	185.8183	333.4393	6.9214	987.1563	805.2486
45.9426	4.3765	346.4850	8.6320	1015.2415	54.2441
52.6540	52.4530	355.3098	56.0869	1033.0720	311.8785
79.8514	17.7759	358.6708	41.3799	1048.2249	2070.7662
91.9472	13.3201	396.4995	31.1012	1056.3263	731.2531
118.5732	31.1351	425.0916	271.2243	1066.7436	422.1453
132.4343	31.6870	441.3285	95.6734	1076.7433	104.6112
138.1118	52.1206	466.0511	27.9510	1081.7064	340.9349
141.3688	57.9098	477.7596	89.4325	1089.7970	1092.2402
163.3871	52.1788	483.7876	97.7353	1097.4064	710.5975
177.8441	56.8225	536.0903	43.8946	1104.9224	1706.8732
198.3303	554.1639	543.5935	352.5852	1111.4677	1102.0353
218.4593	294.9198	571.2779	129.9387	1145.6000	63.0204
244.2646	10.0672	579.4206	180.6174	1170.0328	11.6675
246.2465	21.9230	587.2669	1128.0815	1186.7547	83.4229
260.1738	23.4604	597.2628	164.2428	1198.2177	83.9219
262.6885	2.8764	616.0034	14.2782	1208.8620	20.9139
272.2421	16.2878	616.4928	42.4246	1224.1581	2.4667
285.0322	28.4321	662.2828	1099.4470	1256.9880	170.4403
290.4247	29.3273	677.5201	202.9928	1356.0470	176.8574
299.9090	6.8053	734.0190	202.3540	1709.1335	1011.4214
302.2376	12.0855	830.9424	2052.3891	3725.2498	258.8508

Table 3 (continued)

CAS 335-67-1 (Isolated Molecule)					
Frequency $(M^{-1}cm^{-1})$	Intensity $(M^{-1}cm^{-1})$	Intensity $(M^{-1}cm^{-1})$	Intensity $(M^{-1}cm^{-1})$	Intensity $(M^{-1}cm^{-1})$	Intensity $(M^{-1}cm^{-1})$
28.6753	67.1965	313.7511	0.1818	891.7183	138.2092
33.7991	32.8249	320.0772	4.2913	945.7977	681.1468
43.3463	169.0232	336.4228	4.5322	999.0215	449.4544
46.9246	7.8981	348.6703	2.4073	1025.1247	37.3031
56.0477	61.9823	356.6637	40.9830	1040.6387	165.6704
82.3097	8.9230	359.5906	18.5441	1060.4214	1260.8205
92.3507	7.6850	397.8286	18.2619	1066.1629	328.9040
120.7377	21.0179	427.8284	133.3972	1081.9449	286.3925
132.5981	22.7062	444.1411	42.9101	1085.0923	48.3841
138.8143	23.4856	467.4239	16.4962	1094.6086	266.1482
142.2854	24.0258	478.6852	26.3982	1104.1479	477.7260
164.6364	34.3991	486.2466	65.5382	1111.0981	392.4212
179.1660	24.7648	538.2768	52.6908	1133.0857	1110.3150
202.8976	360.7429	545.2985	262.9139	1137.3804	1089.4455
222.8891	200.8900	573.9170	73.8472	1155.7920	28.3954
244.2341	15.3657	582.3087	68.5217	1173.0124	14.0355
247.6092	2.2556	589.8246	665.3264	1190.6720	77.0065
261.7820	12.6441	599.6437	100.9798	1203.0663	64.7918
263.8864	1.2230	617.2761	7.4155	1211.9025	17.1535
273.7841	8.0987	617.9981	22.6422	1227.3217	2.7356
287.6793	13.2684	666.3223	766.4326	1262.5046	141.5838
292.2910	14.6287	680.7364	130.2213	1349.3617	109.3636
303.1535	3.3939	739.0673	133.7617	1735.1531	521.1107
304.7818	6.8771	840.1908	1502.2515	3754.1497	149.6210

Table 4

CAS# 2706-90-3 (Water Background)					
Frequency (cm^{-1})	Intensity ($M^{-1}cm^{-1}$)	Frequency (cm^{-1})	Intensity ($M^{-1}cm^{-1}$)	Frequency (cm^{-1})	Intensity ($M^{-1}cm^{-1}$)
35.3914	150.9012	341.2846	2.4933	963.4112	619.2281
41.2470	268.7744	358.6903	43.9891	1027.5721	714.8957
54.2900	106.1684	388.7946	99.3905	1049.4395	1420.9182
92.7805	30.0859	437.1240	147.6534	1054.0031	1091.6893
116.3376	40.6081	469.8067	171.5298	1062.8201	237.2314
143.2621	49.4226	488.3560	56.9798	1089.6550	441.4743
171.6912	45.5609	528.5646	115.2248	1099.2822	1406.1375
205.6676	211.3356	549.3385	416.2016	1105.8013	1334.1741
235.5281	159.7754	576.9758	529.6406	1144.8319	56.0647
248.5112	20.3747	588.8538	675.1506	1188.8960	140.5985
268.4352	12.9103	609.0909	100.9134	1210.4704	12.1207
279.3347	12.3495	657.6329	1059.0920	1258.0938	170.4747
297.3264	11.1004	681.6684	65.1009	1357.3024	168.5811
302.1235	16.1782	735.9528	186.3401	1708.6938	1017.6745
330.9137	10.2883	869.6891	1234.4397	3720.4796	259.6304
CAS# 2706-90-3 (Isolated Molecule)					
Frequency (cm^{-1})	Intensity ($M^{-1}cm^{-1}$)	Frequency (cm^{-1})	Intensity ($M^{-1}cm^{-1}$)	Frequency (cm^{-1})	Intensity ($M^{-1}cm^{-1}$)
29.3329	43.3309	343.7723	0.3098	973.7051	328.3846
41.6659	175.5144	358.4320	20.7755	1038.4431	448.0291
52.2380	82.2654	389.2641	65.6215	1059.9024	487.4646
95.6663	13.7656	439.2099	74.0574	1066.5082	720.9132
116.7713	25.8657	471.6562	70.0599	1075.6484	283.7392
144.2638	19.1196	488.5487	49.6604	1103.0416	214.2725
172.8908	28.1557	531.0303	83.7605	1129.3933	1025.2176
210.7102	105.9193	552.6304	237.0392	1133.8789	983.3764
239.7934	95.7315	580.4434	251.2851	1154.7054	34.2157
244.5599	14.8461	594.4802	499.4831	1193.7325	132.3647
270.3305	7.0275	610.6311	52.6481	1214.0188	8.1781
280.1186	5.7651	662.1798	689.2837	1263.6269	136.6384
299.7862	5.1500	684.1114	43.2103	1349.2572	106.1613
305.0017	7.6714	739.3694	135.8901	1734.5640	541.3890
333.3629	4.8156	879.4047	880.0666	3754.0864	145.0214

Table 5

CAS# 958445-44-8 (Water Background)					
Frequency (cm^{-1})	Intensity (M^{-1}cm^{-1})	Frequency (cm^{-1})	Intensity (M^{-1}cm^{-1})	Frequency (cm^{-1})	Intensity (M^{-1}cm^{-1})
17.9077	739.1247	352.5887	26.7194	964.6726	1577.2843
25.4505	59.9417	361.8769	86.9577	980.7554	331.0374
33.0140	13.2078	388.4782	14.3287	1001.7475	561.4724
39.8172	65.5762	398.9627	209.4919	1025.7535	2412.9341
45.0561	309.8647	441.4457	137.2982	1036.8400	357.7818
49.3986	53.3335	463.3159	93.3296	1043.9811	812.5418
73.6007	43.1295	474.4974	64.7404	1051.1147	2136.8122
80.7208	71.0147	485.6045	63.4568	1063.0100	3058.2707
95.5775	19.5301	524.1564	245.6911	1077.7558	332.3240
104.5047	73.1573	548.7835	146.3320	1102.0839	761.2820
135.3675	8.7470	550.3838	279.3603	1108.2589	1763.0417
165.7559	68.6248	565.5350	1727.6633	1115.1753	2118.1876
196.8032	25.6996	579.3249	94.4640	1130.2605	1978.0450
200.1130	94.0807	594.8519	52.4163	1138.2145	384.8184
202.7910	75.9455	604.8802	137.5401	1214.8051	116.9882
238.8526	10.3120	635.6600	53.5637	1273.9913	210.3181
241.6767	28.3445	652.0332	610.4030	1289.4026	391.4026
267.6399	58.6649	717.3674	221.7464	1312.3300	43.8608
281.6568	34.7401	737.3936	176.2253	1350.2410	137.7654
286.2667	22.5498	741.9804	413.6813	1388.8893	24.3057
295.5654	24.8368	806.6528	1024.3895	1719.8822	1029.4802
310.5434	32.6468	826.7841	162.5412	3197.5979	9.4063
324.7031	10.2296	904.1323	427.2589	3728.2290	246.0491

Table 5 (continued)

CAS# 958445-44-8 (Isolated Molecule)					
Frequency (cm^{-1})	Intensity ($M^{-1}cm^{-1}$)	Frequency (cm^{-1})	Intensity ($M^{-1}cm^{-1}$)	Frequency (cm^{-1})	Intensity ($M^{-1}cm^{-1}$)
16.6945	366.3808	352.6974	10.4390	984.5788	569.5342
21.0839	48.5148	367.6656	36.4602	1000.1045	210.2987
25.7129	12.8621	385.8515	5.0373	1014.9700	519.3693
36.5176	19.7080	404.1198	108.6167	1038.5149	268.7717
46.9260	136.4825	446.1207	61.4451	1046.9987	1547.9194
51.8393	142.5321	465.5650	48.9792	1057.3541	293.2731
68.8677	29.5261	480.0536	32.7518	1075.8763	1252.4321
79.4906	6.4842	487.2315	54.1760	1098.2623	112.2322
89.0983	22.0473	525.2901	152.3997	1102.8601	1105.9452
111.8512	53.9035	549.6319	132.3560	1118.5289	715.4340
131.3421	2.6304	552.5400	45.4852	1129.8669	1542.0230
168.4853	25.5486	570.8894	1007.5271	1134.5152	335.9843
196.9306	29.6575	581.8125	206.6481	1150.2127	1146.5461
204.1675	21.0659	600.0455	34.1094	1175.2872	2096.8227
209.8700	42.3005	605.4262	72.5777	1228.7983	111.7169
238.2462	7.6541	639.4023	49.4093	1277.2500	176.2072
244.3869	25.3366	652.5740	383.1802	1293.5921	372.0194
269.3129	24.6640	720.1957	116.8736	1326.1389	38.2491
284.4728	11.7323	738.2741	193.5382	1337.9405	64.4465
289.2649	18.8047	744.6336	192.2427	1385.4228	19.6322
300.2477	8.6432	811.4382	484.0547	1751.8990	534.0512
311.4256	13.9067	834.3717	78.4165	3189.5990	4.4945
325.5279	4.3261	921.5758	243.7782	3755.9583	129.1723