Orientation and Polarization Dependence of Ground and Excited-State FSRS in Crystalline Betaine-30

Supporting Information

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Optical images of betaine-30 crystals

An optical image of the crystal used to obtain the data seen in Figures 2 and 4 can be seen in the main text, while the crystal used to obtain the data from Figure 3 can be seen below (Figure S1). The bottom edge of the crystal shows where it was cut for crystallographic studies.

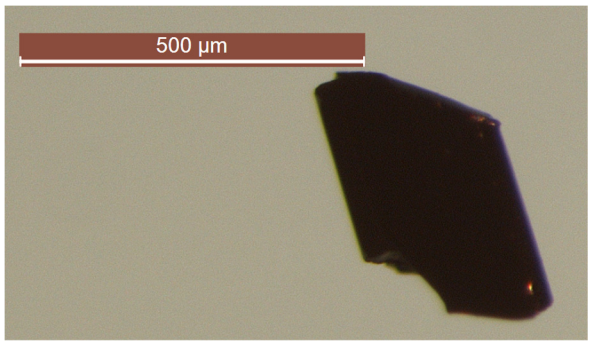

Figure S1. Optical image of the betaine-30 crystal used to collect the data for Figure 3 in the main text.

Polarization characterization

To ensure that the Raman pump and Raman probe polarizations were maintained as they traveled through the microscope setup to reach the crystal, we measured the power of the Raman pump and probe through an analyzer at the sample position while rotating the Raman pump and Raman probe polarizations. We see a sinusoidal function representing the amount of horizontally polarized power reaching the sample position, indicating that our polarizations are well-maintained through the microscope setup.

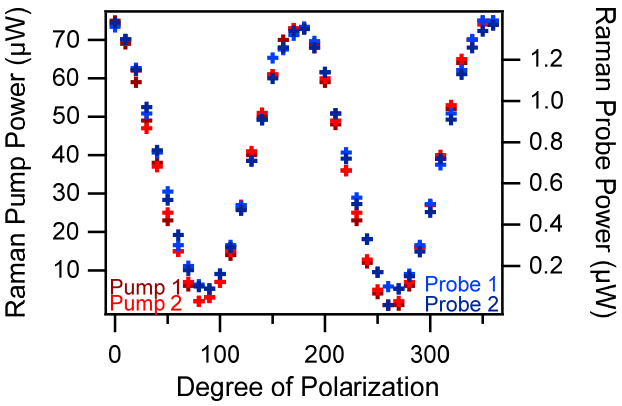

Figure S2. Raman pump and Raman probe power dependence. Initial values at 0 degrees polarization through the microscope without the analyzer: Raman pump 102 μW, Raman probe 2.8 μW, 60 nW background.

Raman pump pulse power dependence

We conducted a Raman pump pulse power dependence study, changing the power from 0.31 to 0.85 mW. The Raman gain of the 1350 cm^{-1} mode in crystalline betaine-30 is plotted as a function of Raman pump power, seen in Figure S3 below. The linear fit has an r^2 value of 0.956, showing that we are in the linear regime with respect to Raman pump power.

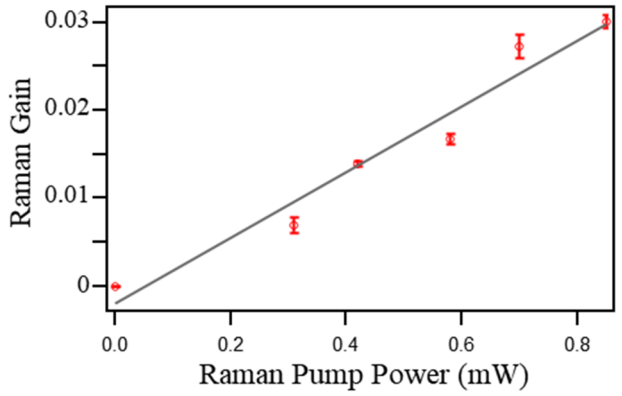

Figure S3. Raman pump pulse power dependence of the Raman gain of the 1350 cm^{-1} peak of crystalline betaine-30, fit to a linear function.

Excited state Raman spectra of a vertical betaine-30 crystal probed at 90°

In addition to the 0° and 45° data shown in the main text, excited state Raman spectra were taken for the 90° laser polarization for the vertical crystal orientation. As seen below in Figure S4, the signal magnitude is extremely poor using 90° probing pulse polarization and no kinetics could be obtained from these spectra.

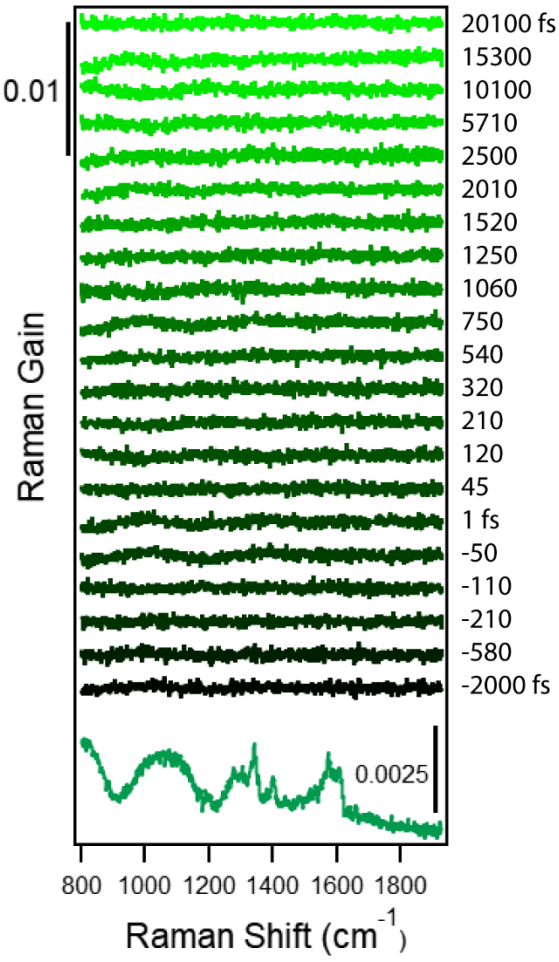

Figure S4. Representative excited state spectra for a vertical betaine-30 crystal probed at 90° polarization for the Raman and probe pulses. No transient features were observed.

Net dipole estimation and density functional theory calculations:

The ORTEP plot from the crystallization studies is shown below as Figure S5.

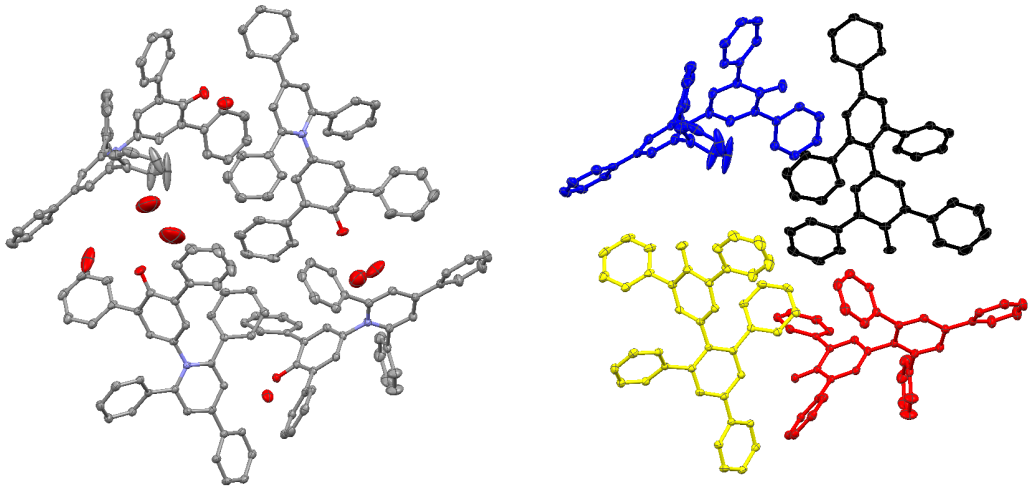

Figure S5. ORTEP plot of the betaine-30 unit cell showing minimal uncertainty in the atomic positions within the unit cell, with the exception of the water oxygen atoms. On the left is the original ellipsoid plot for the entire structure, while the right is color coordinated to match the main text with the oxygen atoms of the water molecules removed.

From this plot we can see that there is relatively little uncertainty with respect to the atomic positions in the betaine-30 unit cell. We used these positions to determine the net dipole of the unit cell seen in Figure 1 of the main text, as well as for Gaussian frequency calculations on non-geometry optimized structures.

The net dipole for the unit cell as depicted in Figure 1 of the main text did not include contributions from the water molecules, due to the significant uncertainty of the hydrogen atomic positions and thus the orientation of the water dipoles. In order to check the validity of the net dipole orientation, we also calculated the net dipole with inclusion of the water molecules, using the software-determined hydrogen positions. We find that inclusion of the 7 water dipoles changes

the relative magnitude of the net dipole from (-8.77, 1.02, -4.10) to (-6.36, 2.77, -4.14). Thus, the overall magnitude of the net dipole changes only slightly with the addition of the waters, as shown in Figure S6, and does not impact the interpretation of our results in the main text.

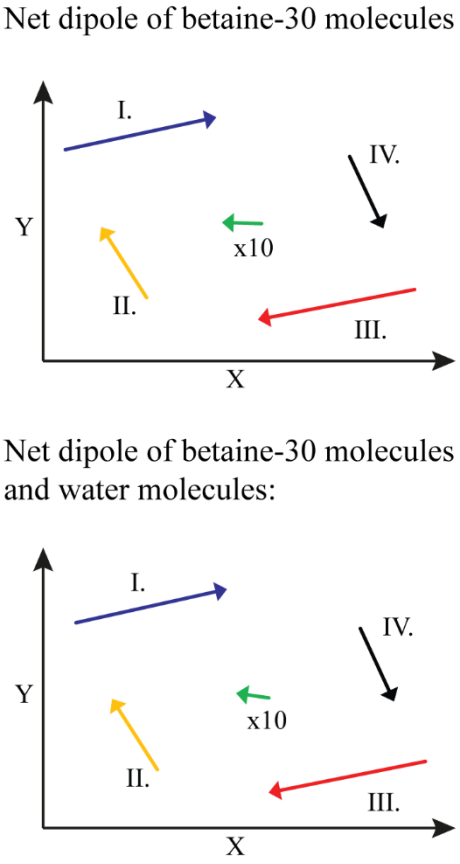

Figure S6. Difference in the net dipole moment between four betaine-30 molecules and four betaine-30 molecules with included dipoles from water. Arrows labeled I through IV represent the four betaine molecules, with the green arrow representing the resulting net dipole which has been scaled by a factor of 10.

In order to assign vibrational modes, we performed DFT calculations using Gaussian 09 using the two approaches detailed in the main text. All calculations were done at with a triple-split-valence basis set 6-311+G(d,p) and B3LYP functions due to the accuracy in vibrational

frequencies obtained with this level of theory. Frequency calculations for each of the four molecules in the betaine-30 unit cell were performed without geometry optimization from the crystal structure geometry, resulting in the spectra for each of the four molecules shown in Figure S7.

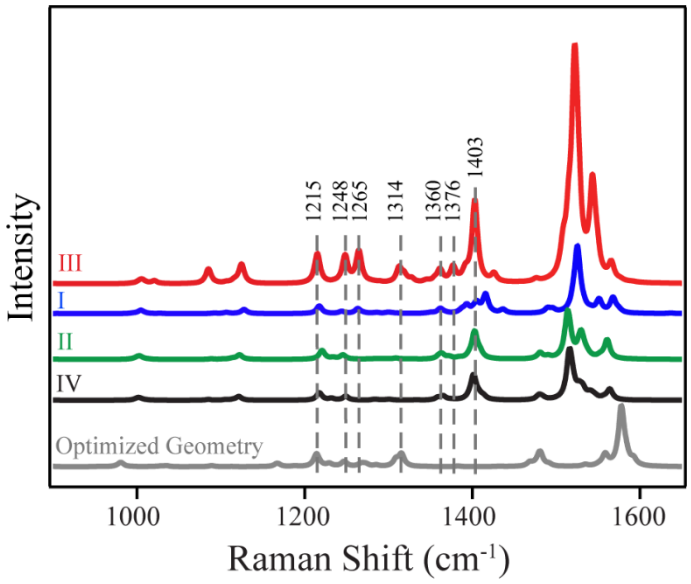

Figure S7. Scaled frequency spectra for the four betaine-30 molecules with unit cell geometries compared to that of the optimized geometry.

These frequency calculations showed relatively good agreement with experiment and were used to assign the vibrational spectra in the main text, with the molecule-specific frequencies shown in Table S1.

Table S1. Comparison of vibrational mode experimental frequencies and calculated frequencies for each molecule.

	Calculated Frequency (cm^{-1})			
Experimental Frequency (cm^{-1})	Molecule I	Molecule II	Molecule III	Molecule IV
1200	1217	1221	1215	1217
1290	1263	1246	1265	1249
1350	1402	1384	1377	1408
1415	1393	1403	1403	1401

The frequency calculations of the crystal structure geometries had multiple negative high frequency modes, and the complete frequency results and Raman activity values for all four geometries are reported in Table S2. To address this, we performed additional DFT calculations to obtain the optimized molecular geometry followed by Raman frequency calculations. These were calculated with a triple-split-valence basis set 6-311+G(d,p) and B3LYP functions. The scaled frequency values can be seen above in Figure S7 and in Figure 2 in the main text while the coordinates of the optimized geometry are shown below in Table S3. These frequencies were in very poor agreement with experiment and no mode assignments could be confidently assigned based solely on this optimized geometry.

Table S2. Scaled frequency and Raman activity values for each of the four betaine-30 molecules with unit-cell geometry.

Molecule I		Molecule II		Molecule III		Molecule IV	
Scaled Frequency	Raman Activity	Scaled Frequency	Raman Activity	Scaled Frequency	Raman Activity	Scaled Frequency	Raman Activity
-1158.14	30.6467	-1157.73	28.9077	-1161.41	164.0709	-1159.42	14.5926
-1153.98	27.1463	-1155.09	17.5939	-1160.31	228.2172	-1154.79	14.2877
-1153.69	8.6714	-1153.52	31.3431	-1155.24	17.5206	-1153.26	53.2022
-1152.26	39.9295	-1151.99	15.8624	-1149.33	692.6013	-1147.5	43.8149
-1145.63	98.1227	-1147.33	56.8755	-1147.97	1321.7329	-1145.06	11.5377
-1062.53	46.1993	-1061.06	53.067	-1068.14	204.3852	-1058.59	64.1937
-1059.73	104.6558	-1059.52	33.1219	-1064.71	94.0312	-1056.8	29.4264
-1059.14	15.4133	-1056.63	28.287	-1063.3	76.4097	-1055.46	69.7437
-1055.91	58.6302	-1053.53	85.1987	-1058.57	261.3471	-1053.49	23.4684
-1052.18	19.4982	-1045.79	35.15	-1055.93	62.3198	-1052.31	54.0269
-1041.33	9.1679	-1027.46	36.1307	-1050.48	55.4759	-1033.78	27.3605
-1018.59	3.005	-1016.03	31.0131	-1047.11	5.0146	-1016.78	108.9335
-1014.5	27.5578	-1014.19	8.2431	-1013.05	40.1848	-1002.91	12.579
-1000.67	35.5122	-1001.92	12.6704	-1012.5	254.6051	-1000.22	7.4481
-998.75	9.2489	-998.12	25.4702	-1007.8	75.1819	-998.12	6.6008
-991.76	23.1368	-993.41	7.1511	-990.51	8.8588	-993.08	25.6762
-991.24	14.3899	-988.51	81.5464	-988.42	472.6248	-991.42	15.4757
-981.72	110.4718	-985.42	10.7213	-986.86	272.4697	-990.23	42.1015
-978.62	15.3539	-982.86	23.976	-980.05	701.1007	-982.79	12.6952
-938.17	6.4272	-941.96	1.7096	-943.44	41.0636	-932.01	0.3186
-935.05	2.0612	-931.92	1.7076	-938.4	54.5918	-930.37	19.7962
-934.79	12.0097	-928.93	40.7002	-937.13	7.5901	-927.22	3.7208
-928.42	28.4848	-927.92	7.9715	-935.36	0.1959	-926.64	3.4252
-926.3	8.9355	-917.77	33.9116	-929.21	0.4736	-926.11	23.2809
-864.03	22.3082	-866.87	14.5672	-870.33	138.8851	-861.91	12.5456
-861.04	14.9894	-855.73	25.648	-867.14	213.2865	-857.81	17.3113
-855.1	4.0746	-854.57	10.5958	-855.15	5.4002	-857.71	0.5529
-851.23	11.8824	-853.49	4.3666	-847.7	47.451	-846.61	7.5685
-833.95	6.7718	-846.52	17.186	-842.21	44.7517	-843.24	2.8495
-455.45	0.0246	-455.35	0.1874	-456.19	1.4724	-462.27	0.0282
-447.33	1.9279	-450.97	0.5553	-454.21	3.9866	-449.17	0.2637
-443.45	0.1048	-445.74	1.1826	-449.01	29.9417	-442.25	0.601
-441.01	0.6365	-438.48	0.7704	-446.44	3.1977	-437.23	0.5061
-433.83	0.4168	-437.35	1.7049	-443.19	1.811	-433.56	0.2236
-424.69	0.6396	-434.45	2.9478	-437.36	0.9367	-432.94	2.2093
-419.69	18.236	-425.41	1.2677	-435.45	250.4317	-425.75	2.5019
-417.86	9.5594	-421.79	8.7889	-427.53	6.8368	-421.94	7.5794

-416.06	7.4225	-417.55	1.3213	-422.96	133.0561	-418.59	0.9919
-411.15	2.804	-413.13	0.3408	-415.93	54.6318	-413.84	4.368
-408.59	0.7045	-409.07	0.6723	-410.79	38.818	-408.41	9.9917
-405.96	0.2796	-405.55	3.7503	-407.96	45.9122	-405.23	1.0049
-401.46	7.0356	-400.05	5.6775	-402.12	21.2538	-404.22	1.216
-397.71	4.4522	-398.22	0.3995	-399.47	197.6256	-394.33	2.3737
-370.18	0.4254	-382.11	2.0114	-393.99	1.768	-391.36	0.1286
-314.64	21.5704	-321.06	10.5738	-376.75	39.5277	-321.22	25.0657
-289.68	4.6759	-242.61	6.5711	-303.52	4.8061	-294.43	9.4596
-190.2	198.87	-184.59	152.0029	-278.26	1611.569	-154.66	102.3157
-53.43	1.6129	-110.27	1.8742	-131.62	1.82	-96.73	0.4136
-21.79	2.965	-35.54	1.815	-120.66	2.2343	-58.81	0.1465
45.23	10.829	58.25	9.1407	-80.49	59.3872	-49.92	24.1108
60.49	24.1118	62.28	6.5931	-16.54	783.114	-19.25	5.5923
69.86	31.1244	70.72	1.6965	27.65	8.2207	36.46	6.0145
77.5	1.3068	90.35	30.4302	51.38	96.3873	69.01	11.2224
89.1	19.6369	93.87	7.4097	67.12	126.6558	70.87	13.3986
100.1	6.1561	105.63	3.3355	77.1	51.8518	82.84	7.7657
103.16	3.6921	116.33	15.5031	85.33	175.8378	94.33	10.5186
117.04	13.2172	125.93	13.6697	90.34	27.6093	101.44	10.1272
120.46	17.166	135.03	6.4184	96.27	7.3809	118.92	30.6227
131.58	6.826	139.86	28.3853	121.69	178.8976	126.04	10.6149
144.97	6.2638	149.17	2.1238	134.49	222.7112	134.95	11.5234
163.21	14.7078	152.99	9.9664	142.22	14.8865	148.45	2.0215
186.72	10.8094	203.95	28.2939	187.81	35.5956	200.02	36.8982
202.06	12.576	205.7	4.2767	197.58	62.7167	202.09	2.6793
206.5	18.2295	208.08	62.6659	201.1	213.6915	209.59	109.0356
208.08	64.9332	208.72	17.606	203.58	59.4882	211.49	55.8208
209.2	80.3618	215.84	33.6308	207.27	266.9124	217.34	14.4014
210.79	33.3551	220.86	53.5545	210.92	48.2449	222.6	6.113
227.61	36.6929	226.35	8.0449	220.73	526.8878	230.77	16.5284
234.37	1.2844	238.66	63.1926	224.82	410.2892	233.64	7.7166
236.64	48.3973	253.73	41.0603	240.74	3131.5949	243.48	78.2693
248.83	43.6997	257.55	9.5313	251.54	550.0617	253.98	14.5268
267.14	14.3248	265.67	52.7048	262.85	282.1833	263.64	10.1967
289.03	10.1737	284.26	135.4595	283.64	4732.8493	291.58	16.4377
295.42	30.4678	293.93	48.6802	292.68	11.474	296.4	47.2042
305.55	95.6447	311.79	12.6331	305.37	4.1224	310.85	128.3476
310.55	58.3073	318.39	48.3904	309.91	51.1199	312.66	14.5279
318.34	9.1357	326.42	18.6284	313	30.0885	323.86	9.877
323.94	19.5977	327.72	57.2287	323.53	24.8009	328.03	7.2588

352.03	2.149	351.67	8.2438	347.73	33.9423	354.18	7.7987
369.46	2.859	369.92	8.9184	363.64	18.7419	372.92	2.2098
376.52	12.6749	379.57	8.6991	367.38	2.5708	374.44	1.1985
397.61	21.5311	393.68	12.2072	390.51	240.5902	397.92	16.6318
406.03	50.5594	411.77	14.0185	395.63	26.8988	402.81	11.1207
416.26	12.8858	419.49	10.1998	408.84	11.1573	406.61	3.0898
426.68	65.1058	430.73	25.8049	410.28	109.9795	427.73	11.0461
450.11	14.2019	450.84	38.4317	421.98	94.5577	443.12	23.0796
471.3	99.5615	475.72	9.1064	470.04	9.5306	471.44	17.9719
498.76	42.6055	501.49	70.5773	489.33	192.0178	497.26	63.6425
510.24	61.2692	520.43	17.5849	511.59	1214.0046	516.95	454.9456
514.43	474.0097	521.29	239.5638	512.85	452.1051	519.02	27.4813
516.75	21.6526	522.83	26.6827	518.78	37.8133	522.47	18.8133
519.96	10.5715	524.24	13.8404	519.69	38.4001	523.04	20.9144
521.75	30.9001	524.98	8.0832	522.08	25.6735	525.05	24.6661
522.13	25.8863	528.47	7.3957	524.54	304.6146	526.35	9.5156
523.76	25.7807	530	7.9695	527.68	63.1245	527.61	9.1883
531.53	14.2131	538.32	6.8087	530.79	22.3813	533.56	31.0513
561.72	3.6633	564.27	22.0484	556.25	9.7067	573.45	10.0198
576.44	3.0392	571.64	209.4581	575.73	141.1228	576.09	19.4978
587.59	109.7848	580.02	7.7453	592.9	698.1155	579.34	6.4963
618.02	21.3159	628.25	105.4596	607.96	270.3451	615.9	57.3119
627.89	5.0019	630.74	11.3025	631.06	26.9349	632.86	8.8401
643.4	37.6574	650.03	29.6612	636.02	383.8096	648.36	45.3893
649.81	60.519	655.22	142.9074	648.52	77.5054	650.59	32.9048
685.56	78.3619	683.36	98.3707	679.76	1807.9793	680.62	85.2745
687.25	160.8671	687.37	101.1368	686.82	25.1433	685.23	56.9331
696.84	14.9468	691.99	16.3242	694.89	42.3969	695.38	12.1231
718.14	11.4636	715.97	11.6454	714.69	24.4095	714.73	5.3472
721.19	17.8521	719.96	10.658	720.36	8.0498	719.28	3.9854
723.36	2.8843	723.46	9.6027	724.24	8.212	725.14	4.9455
735.14	24.8023	730.48	4.6621	727.87	3.4843	732.31	3.3666
737.05	17.2666	731.41	10.7424	734.8	18.2961	732.64	2.4479
741.03	16.3902	733.08	18.4117	741.7	223.7239	737.09	23.7618
742.12	7.2763	744.49	0.94	743.54	260.2498	739.83	1.6777
748.11	7.6016	756.7	13.7417	752.19	212.4995	754.9	32.2347
755.55	43.5655	758.54	16.9496	757.45	83.4243	755.69	11.7687
759.44	10.2865	760.14	43.1922	760.87	48.522	759.18	3.5498
777.05	27.4204	771.38	59.8562	768.53	22.2953	769.05	43.1119
782.86	31.679	775.31	13.2212	789.47	77.4854	780.45	10.6656
794	202.4101	794.9	10.1773	798.03	39.2901	794.32	5.6939

800.09	10.0932	803.61	132.8983	800.24	862.7003	801.83	138.4275
804.39	349.5142	810.26	30.447	804.07	318.6949	806.95	183.5519
816.99	5.295	812.49	116.8068	813.76	1018.7536	811.64	39.9653
819.59	44.8051	815.73	90.6753	814.96	219.5775	815.22	56.0967
822.51	7.1501	818.55	60.6229	819.81	47.9412	818.88	25.8197
827.22	3.2247	822.36	8.701	821.96	17.16	823.61	6.9147
829.83	37.2971	828.18	16.6807	824.47	22.025	827.15	11.4505
830.81	22.7673	830.93	44.4594	827.27	29.3055	830.47	21.8683
831.8	10.8756	832.64	6.6403	831.68	70.8568	833.53	20.2188
868.43	4.6908	870.99	11.3459	869.64	12.2395	869.69	8.667
883.05	240.0504	873.72	13.8267	877.3	262.1805	875.53	32.7206
884.63	49.7486	881.91	277.76	881.93	1345.3727	881.3	203.5012
904.91	60.0984	903.22	77.3204	897.7	53.3158	903.68	47.6107
995.52	161.8772	993.55	47.6795	994.01	126.2603	995.11	18.7265
1002.65	185.0281	999.68	443.5041	1001.99	167.9879	998.86	214.0056
1004.63	998.7698	1001.98	12.2306	1002.83	350.8602	1001.63	814.6761
1006.81	170.8943	1002.59	188.6968	1005.29	968.4062	1003.92	150.6012
1008.04	66.9764	1003.46	906.5026	1007.44	599.5135	1005.38	95.3455
1015.59	5.5831	1006.96	48.0462	1013.32	61.8948	1008.5	118.5256
1027.79	113.8829	1012.57	89.4986	1020.8	1055.1788	1014.15	72.054
1092.22	189.1905	1088.53	175.3687	1085.27	5791.3987	1085.13	330.664
1106.52	464.6952	1102.72	93.3442	1106.52	376.3497	1105.21	250.0257
1122.85	65.7709	1113.7	343.3933	1115.96	967.6967	1114.64	203.3875
1127.81	1642.6263	1122.27	1784.2676	1124.7	7708.8346	1121.48	1513.6979
1217.42	3099.3313	1220.71	3570.5091	1215.15	12208.0536	1217.49	3084.4257
1244.22	883.056	1234.02	555.3376	1235.96	196.04	1231.97	717.5793
1263.36	1986.9551	1245.64	1726.6096	1248.25	11127.9962	1248.98	1659.7149
1269.95	203.2754	1261.65	30.3952	1260.82	402.4602	1260.52	33.6755
1278.91	113.2299	1271.98	37.3657	1264.67	12882.0431	1271.17	9.0441
1284.33	145.3817	1274.25	28.6925	1277.23	170.9245	1281.72	158.557
1287.06	257.3177	1279.07	50.7388	1279.38	99.1231	1284.07	176.3275
1296.97	106.9825	1284.63	152.91	1282.75	188.0769	1286.63	16.7642
1299.79	337.3836	1286.31	30.248	1289.03	376.9941	1287.02	115.1155
1301.54	90.2601	1290.54	156.742	1298.02	19.6516	1293.54	57.993
1305.53	183.0009	1298.21	80.2299	1302.8	70.1163	1296.54	84.1444
1310.21	9.8749	1300.35	143.9427	1312.59	6068.2518	1301.1	329.9731

1313.81	92.0037	1308.8	409.3711	1316.66	264.1486	1307.55	71.0206
1322.89	46.4167	1315.61	83.0321	1318.72	2648.0171	1321.32	13.6507
1344.58	96.3142	1322.45	23.4736	1327.49	1610.3857	1329.74	32.6978
1350.56	349.6843	1327.39	96.4553	1344.36	583.8767	1331.09	13.7862
1361.83	2041.4187	1331.1	58.1855	1346.87	390.4943	1333.77	146.3361
1367.68	229.3727	1360.53	1329.373	1355.14	1116.6845	1358.54	893.2262
1387.4	1171.4793	1364.27	1553.7745	1361.39	5316.3745	1365.01	1630.8929
1393.32	3032.0993	1372.54	780.0291	1377.05	6311.525	1374.09	233.886
1402.09	951.2388	1383.96	453.8651	1391.46	3559.1162	1397.87	1174.5754
1405.38	3577.9069	1397.03	849.9365	1392.17	538.5421	1401.49	9899.6078
1415.75	7869.662	1402.74	11311.7999	1402.98	35204.2491	1407.52	1343.1277
1436.57	1538.7817	1409.25	2055.6025	1425.83	3502.4877	1413.11	1255.935
1489.77	1869.6096	1480.66	2497.0081	1475.98	1138.9857	1479.4	1784.3785
1495.75	1396.6162	1490.25	930.2676	1508.18	11108.2409	1483.12	964.0618
1520.33	3083.0513	1513.43	17995.9489	1514.92	18327.669	1515.65	19240.6982
1525.25	27655.4436	1516.33	4071.1842	1521.69	74770.5356	1519.26	5086.8653
1530.57	1861.6034	1527.26	1106.3922	1523.68	14526.1586	1527.12	3425.6239
1533.72	535.4125	1528.39	3016.7922	1526.32	25481.2143	1531.48	3753.0144
1540.45	613.829	1530.32	7565.7376	1533.78	1254.3316	1536.83	202.3883
1542.94	194.2351	1534.9	220.7269	1539.52	748.6667	1539.05	937.4069
1549.72	355.4634	1535.83	1282.014	1543.2	39224.0644	1541.8	1653.5727
1551.25	5148.2264	1538.53	387.3897	1548.41	9563.0723	1545.67	832.1006
1567.71	6493.0197	1544.56	51.9438	1563.34	121.9124	1547.7	310.6598
1572.78	82.98	1552.34	882.2444	1565.68	7382.9038	1556.79	635.9446
1574.48	1111.2167	1555.88	144.006	1576.66	607.4858	1560.01	135.9522
1636.55	204.9379	1560.77	8196.1357	1590.5	181.372	1563.95	4527.5903

4440.62	51.4996	4445.59	74.0789	4443.78	71.8288	4446.11	70.9303
4446.5	46.5995	4451.89	53.0004	4449.43	67.6246	4450.29	19.0772
4451.28	10.852	4454.35	54.4375	4451.78	42.4941	4450.64	21.5337
4451.34	134.5449	4454.88	22.5222	4453.75	32.7272	4451.79	38.5859
4455.15	37.1094	4455.67	61.4354	4456.69	86.3334	4454.08	108.9557
4455.74	67.3176	4457.43	89.8308	4457.35	86.9981	4455.44	103.6063
4456.03	28.7045	4457.75	33.1848	4460.22	51.9496	4457.69	26.2593
4460.74	103.1794	4458.66	18.1346	4460.52	47.9185	4458.03	21.0056
4461.93	13.8636	4459.87	40.1246	4461.39	73.4574	4461.01	206.3134
4462.49	104.4082	4461.89	56.5603	4461.97	223.8639	4463.43	99.4261
4463.38	17.6271	4464.61	90.3134	4463.67	70.2118	4463.57	31.9528
4463.8	35.4936	4464.73	119.1468	4466.34	88.2094	4463.99	158.336
4464.68	21.5257	4466.09	47.4286	4466.99	135.6225	4464.25	36.5785
4466.85	26.8317	4466.63	55.4875	4467.28	224.5018	4466.18	141.3192
4467.43	52.6718	4467.29	140.284	4467.9	993.2733	4467.27	27.9776
4468.23	106.2808	4467.7	10.9053	4468.72	183.9293	4467.99	35.1257
4468.28	47.0845	4468.85	16.4616	4470.1	11.8606	4470.5	90.3945
4470.04	146.5409	4471.11	34.3851	4470.89	178.924	4471.08	61.8225
4470.65	77.9238	4471.47	37.8125	4471.36	20.2256	4471.32	91.3053
4471.73	34.6108	4471.95	42.2877	4471.41	169.6254	4473.93	24.2347
4472.3	33.8952	4473.64	147.8685	4473.11	82.0865	4474.89	22.3064
4472.51	24.5405	4475.04	163.4885	4473.17	131.1144	4475.43	40.1862
4473.23	93.0839	4475.9	46.7057	4475.49	313.1602	4476.13	62.5124
4476.02	140.0151	4476.97	126.9854	4476.05	153.4707	4477.48	116.3919
4476.94	127.6898	4478.88	160.1876	4477.99	106.079	4477.58	232.7775
4477.08	32.1583	4479.21	170.5582	4480.21	124.392	4481.14	21.1893
4481.84	359.5432	4482.56	144.985	4483.38	49.0113	4482.18	39.2447
4482.05	177.7009	4484.82	22.2803	4487.02	17.0859	4486.51	40.5251
4486.84	36.5878	4488.11	123.1076	4490.14	378.3036	4488.39	123.2429

Table S3. Optimized geometry of ground state betaine-30.

Atom	X	Y	Z
C	-1.196584	-0.141806	-7.460504
C	-1.197748	-0.140258	-6.069684
C	0	0	-5.348894
C	1.197748	0.140258	-6.069684
C	1.196584	0.141806	-7.460504
C	0	0	-8.162065
H	-2.130386	-0.262321	-7.997661
H	-2.132841	-0.278803	-5.539572
H	2.132841	0.278803	-5.539572
H	2.130386	0.262321	-7.997661
H	0	0	-9.245869
C	0	0	-3.874114
C	-1.07246	0.511615	-3.131942
C	1.07246	-0.511615	-3.131942
C	-1.062911	0.551426	-1.748367
H	-1.90277	0.989564	-3.633005
C	1.062911	-0.551426	-1.748367
H	1.90277	-0.989564	-3.633005
C	2.147734	-1.28938	-1.04809
C	3.482604	-0.979531	-1.336306
C	1.868351	-2.363911	-0.190754
C	4.51957	-1.721518	-0.77333
H	3.711799	-0.142039	-1.986017
C	2.905289	-3.107269	0.359693
H	0.843228	-2.614275	0.0509
C	4.233843	-2.787723	0.074615
H	5.548066	-1.460063	-0.994508
H	2.674891	-3.935947	1.01893
H	5.038495	-3.36381	0.516558
C	-2.147734	1.28938	-1.04809
C	-3.482604	0.979531	-1.336306
C	-1.868351	2.363911	-0.190754
C	-4.51957	1.721518	-0.77333
H	-3.711799	0.142039	-1.986017
C	-2.905289	3.107269	0.359693
H	-0.843228	2.614275	0.0509
C	-4.233843	2.787723	0.074615
H	-5.548066	1.460063	-0.994508
H	-2.674891	3.935947	1.01893
H	-5.038495	3.36381	0.516558
C	0	0	0.384582

C	-1.075006	-0.567577	1.085342
C	1.075006	0.567577	1.085342
C	-1.101995	-0.598127	2.464841
H	-1.877493	-1.038086	0.528187
C	1.101995	0.598127	2.464841
H	1.877493	1.038086	0.528187
C	0	0	3.242089
C	-2.244655	-1.238697	3.158383
C	-3.548873	-1.108865	2.649965
C	-2.067573	-2.011347	4.319386
C	-4.629333	-1.743493	3.257576
H	-3.72267	-0.479248	1.784217
C	-3.147939	-2.648415	4.922829
H	-1.079598	-2.097217	4.748467
C	-4.433627	-2.521765	4.397
H	-5.626377	-1.618068	2.848343
H	-2.984394	-3.244126	5.814621
H	-5.273278	-3.013677	4.875798
C	2.244655	1.238697	3.158383
C	3.548873	1.108865	2.649965
C	2.067573	2.011347	4.319386
C	4.629333	1.743493	3.257576
H	3.72267	0.479248	1.784217
C	3.147939	2.648415	4.922829
H	1.079598	2.097217	4.748467
C	4.433627	2.521765	4.397
H	5.626377	1.618068	2.848343
H	2.984394	3.244126	5.814621
H	5.273278	3.013677	4.875798
N	0	0	-1.047029
O	0	0	4.485889