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

Supporting information for the manuscript

Excited state structural evolution during charge-transfer reactions in Betaine-30

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Optimized DFT geometries as a function of central dihedral angle

As described in the main text, DFT geometry optimization and Raman frequency calculations were performed as a function of rotation around betaine-30's central dihedral angle, to mimic the planarization seen upon photoexcitation. These calculations included a conductor-like polarizable continuum model to mimic solvent environment. The optimized geometric coordinates are listed Table S1, following the numbering convention shown in Figure S1.

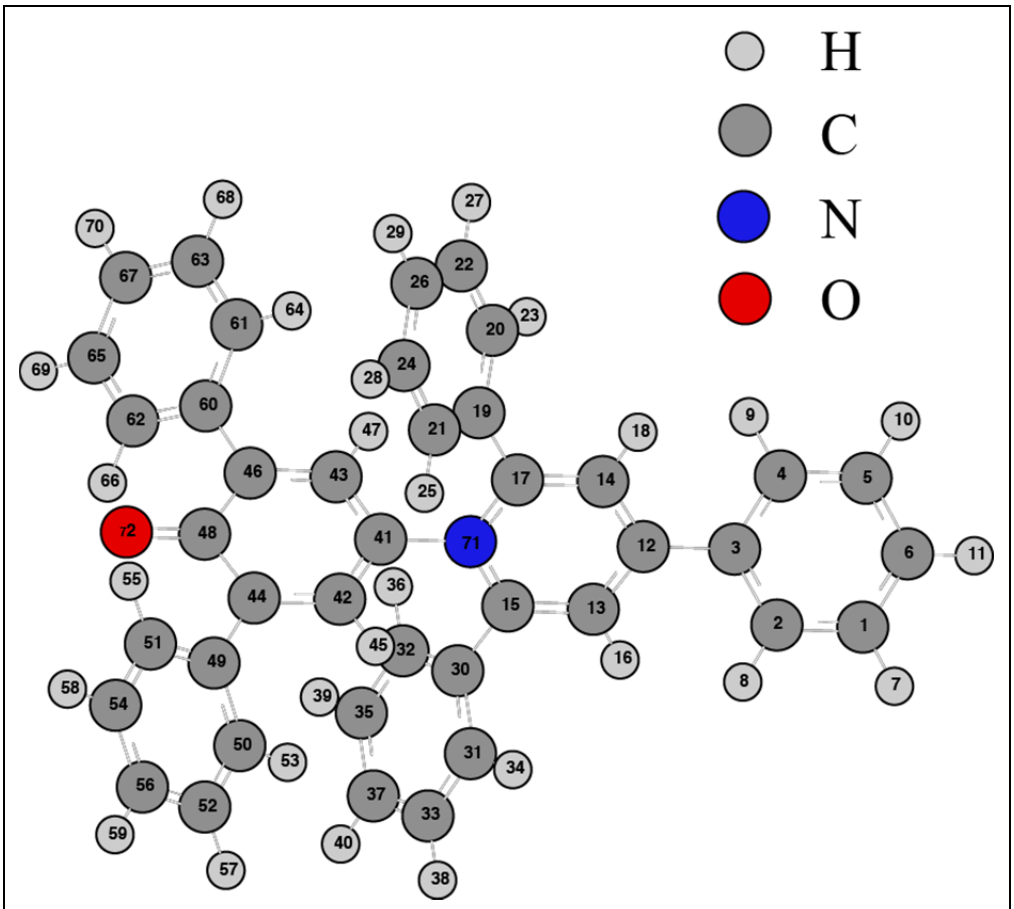

Figure S1. Optimized geometry of betaine-30. The dihedral angle scan was performed by rotation around the dihedral consisting of atoms 42, 41, 71, and 15. The equilibrium geometry is at a 66° dihedral angle.

Table S1: Cartesian coordinates of betaine-30, shown in figure S1, for central dihedral angles of 96, 86, 76, 66, 51, 36, 21, and 6°.

Dihedral angle of 96°

Atomic Number	X	Y	Z
1	-7.429834	-0.364339	-1.30259
2	-6.039217	-0.354118	-1.25826
3	-5.365977	-0.096261	-0.053035
4	-6.121507	0.144685	1.105926
5	-7.511995	0.121619	1.060464
6	-8.170167	-0.12977	-0.143604
7	-7.935076	-0.551381	-2.242845
8	-5.477809	-0.519134	-2.170019

9	-5.623931	0.321923	2.051772
10	-8.081163	0.295436	1.966094
11	-9.253338	-0.143058	-0.17852
12	-3.889781	-0.07928	-0.005607
13	-3.120265	-0.912814	-0.826887
14	-3.192644	0.767827	0.862558
15	-1.737428	-0.885623	-0.793175
16	-3.591664	-1.601951	-1.513141
17	-1.808388	0.772459	0.915627
18	-3.721778	1.444457	1.518504
19	-1.113837	1.679825	1.868343
20	-0.354159	1.178143	2.932917
21	-1.302167	3.061986	1.747263
22	0.219151	2.051647	3.852593
23	-0.223062	0.110387	3.051171
24	-0.715413	3.932857	2.663895
25	-1.89343	3.456344	0.928963
26	0.046171	3.429907	3.717096
27	0.798537	1.654418	4.677863
28	-0.856223	5.001706	2.553399
29	0.49888	4.106758	4.432465
30	-0.962611	-1.786009	-1.693028
31	-0.269003	-1.286785	-2.801513
32	-1.009562	-3.167299	-1.471734
33	0.384523	-2.161312	-3.666025
34	-0.248179	-0.221872	-2.9946
35	-0.34574	-4.037579	-2.334967
36	-1.553581	-3.55915	-0.620047
37	0.353252	-3.536444	-3.431747
38	0.91529	-1.767267	-4.524874
39	-0.378117	-5.104852	-2.149362
40	0.866344	-4.213587	-4.104845
41	0.36957	0.018959	0.079329
42	1.002757	1.031335	-0.63502
43	1.116406	-0.971524	0.708883
44	2.391417	1.103872	-0.70067
45	0.402171	1.789522	-1.126159
46	2.506917	-0.958296	0.665108
47	0.603843	-1.774399	1.227669
48	3.220058	0.098139	-0.044542
49	3.012985	2.216818	-1.465109
50	2.479495	2.626557	-2.699853
51	4.126225	2.921527	-0.972157
52	3.021125	3.700622	-3.405703
53	1.637489	2.08854	-3.121329

54	4.666194	3.996721	-1.674642
55	4.565225	2.618284	-0.031642
56	4.118495	4.393848	-2.896176
57	2.589058	3.989057	-4.358085
58	5.518969	4.528453	-1.265559
59	4.543739	5.227703	-3.443649
60	3.252076	-2.037814	1.363378
61	2.862877	-2.465412	2.644634
62	4.339519	-2.694425	0.759966
63	3.519289	-3.512174	3.292043
64	2.044069	-1.962528	3.14774
65	4.994153	-3.742013	1.40382
66	4.665869	-2.377977	-0.221381
67	4.589465	-4.157876	2.674158
68	3.198369	-3.81595	4.282792
69	5.823927	-4.237959	0.911042
70	5.103992	-4.970296	3.175308
71	-1.091135	-0.054366	0.087617
72	4.488124	0.136976	-0.090473

Dihedral angle of 86°

Atomic Number	X	Y	Z
1	-7.500119	-1.135285	0.200058
2	-6.109167	-1.171324	0.205581
3	-5.364736	-0.010583	-0.059831
4	-6.049257	1.18687	-0.324153
5	-7.440122	1.222029	-0.31715
6	-8.16944	0.061218	-0.058167
7	-8.061078	-2.042131	0.393113
8	-5.602653	-2.111292	0.388933
9	-5.495869	2.100068	-0.507444
10	-7.954132	2.156459	-0.509429
11	-9.252905	0.08894	-0.057576
12	-3.888342	-0.047246	-0.059061
13	-3.175409	-0.901216	0.791426
14	-3.13418	0.771701	-0.907175
15	-1.791713	-0.916295	0.806471
16	-3.691441	-1.536037	1.497728
17	-1.74966	0.733752	-0.91143
18	-3.619146	1.427725	-1.615943
19	-0.997144	1.605985	-1.853359
20	-1.137844	2.994978	-1.743979
21	-0.234731	1.071028	-2.899571

22	-0.501616	3.838873	-2.652524
23	-1.73279	3.414757	-0.941141
24	0.388559	1.918238	-3.811604
25	-0.140328	-0.001174	-3.011291
26	0.262887	3.302454	-3.687078
27	-0.606548	4.91273	-2.550952
28	0.969439	1.495409	-4.623007
29	0.753983	3.95817	-4.396808
30	-1.076162	-1.821159	1.749196
31	-1.18579	-3.204853	1.56771
32	-0.377463	-1.323178	2.855727
33	-0.579737	-4.080084	2.467875
34	-1.73366	-3.595551	0.717999
35	0.216628	-2.201946	3.757639
36	-0.306739	-0.255472	3.01866
37	0.122815	-3.580589	3.562917
38	-0.660362	-5.149601	2.31236
39	0.750377	-1.808344	4.614827
40	0.59054	-4.261085	4.265077
41	0.371378	-0.071761	0.023532
42	1.132275	-1.009508	-0.666534
43	0.99091	0.966265	0.713527
44	2.52314	-0.95255	-0.660338
45	0.630525	-1.790909	-1.227057
46	2.377454	1.063902	0.7678
47	0.381624	1.693883	1.239063
48	3.220838	0.101339	0.06802
49	3.281646	-1.990599	-1.404857
50	2.889685	-3.339781	-1.34938
51	4.385698	-1.666046	-2.213604
52	3.558968	-4.321788	-2.079406
53	2.058416	-3.626217	-0.71434
54	5.053092	-2.645524	-2.945887
55	4.715121	-0.637276	-2.264956
56	4.645435	-3.979726	-2.883795
57	3.235269	-5.354993	-2.011644
58	5.895649	-2.365861	-3.569761
59	5.170125	-4.740944	-3.450504
60	2.985025	2.174678	1.545369
61	2.462094	3.47688	1.465584
62	4.072177	1.960106	2.410932
63	2.991424	4.519454	2.226165
64	1.639213	3.679187	0.788555
65	4.600023	2.999672	3.173451
66	4.499286	0.968979	2.48152

67	4.06411	4.286414	3.086026
68	2.569742	5.515207	2.139179
69	5.433333	2.804689	3.840431
70	4.479972	5.095369	3.676402
71	-1.088391	-0.111179	-0.054752
72	4.487749	0.179348	0.090567

Dihedral angle of 76°

Atomic Number	X	Y	Z
1	-7.485749	-1.169676	0.07321
2	-6.094433	-1.186574	0.08504
3	-5.365688	0.008299	-0.02960
4	-6.066283	1.219345	-0.15012
5	-7.457638	1.233856	-0.14976
6	-8.17127	0.039984	-0.04117
7	-8.034268	-2.101191	0.14917
8	-5.575075	-2.134778	0.15528
9	-5.525084	2.155579	-0.21591
10	-7.98432	2.177526	-0.23016
11	-9.255018	0.052247	-0.04564
12	-3.888941	-0.008416	-0.02384
13	-3.16872	-0.94469	0.72748
14	-3.141961	0.91147	-0.76853
15	-1.784469	-0.944609	0.75082
16	-3.680365	-1.655745	1.36038
17	-1.75736	0.881723	-0.78115
18	-3.632837	1.635747	-1.40291
19	-1.014266	1.834697	-1.64888
20	-1.179229	3.209645	-1.44237
21	-0.234	1.387837	-2.72330
22	-0.550485	4.126197	-2.28360
23	-1.785661	3.562055	-0.61600
24	0.381629	2.307396	-3.56745
25	-0.118127	0.327443	-2.90706
26	0.231129	3.677371	-3.34643
27	-0.67404	5.188284	-2.10679
28	0.976563	1.952985	-4.40113
29	0.717053	4.389916	-4.00295
30	-1.0673	-1.912672	1.62466
31	-1.23247	-3.283761	1.39547
32	-0.311385	-1.48301	2.72310
33	-0.627344	-4.213939	2.23934
34	-1.820827	-3.62237	0.55045

35	0.280363	-2.416128	3.56954
36	-0.19527	-0.425454	2.92283
37	0.130039	-3.782447	3.32657
38	-0.750733	-5.273107	2.04561
39	0.856947	-2.075137	4.42151
40	0.597354	-4.505677	3.98492
41	0.370822	-0.03559	0.02015
42	1.086181	-1.022381	-0.65189
43	1.038145	0.991014	0.68211
44	2.477107	-1.01512	-0.66892
45	0.546918	-1.794495	-1.18991
46	2.427724	1.0381	0.71670
47	0.462437	1.747054	1.20493
48	3.2236	0.025995	0.02997
49	3.188593	-2.089017	-1.40886
50	2.750009	-3.422622	-1.33354
51	4.293331	-1.811975	-2.23411
52	3.375787	-4.43518	-2.06049
53	1.916708	-3.672837	-0.68602
54	4.917115	-2.821863	-2.96332
55	4.657142	-0.795808	-2.30070
56	4.463698	-4.140169	-2.88138
57	3.016936	-5.455596	-1.97778
58	5.761113	-2.578602	-3.60035
59	4.954275	-4.925404	-3.44587
60	3.087749	2.143315	1.45823
61	2.598249	3.458233	1.36961
62	4.193458	1.914417	2.29660
63	3.176573	4.498775	2.09626
64	1.762847	3.671784	0.71168
65	4.769961	2.952313	3.02548
66	4.595625	0.913571	2.37315
67	4.266468	4.251402	2.93022
68	2.779392	5.503996	2.00315
69	5.61613	2.746065	3.67260
70	4.720179	5.058662	3.49448
71	-1.087619	-0.043572	-0.01746
72	4.491863	0.051127	0.03876

Dihedral angle of 66° (ground state equilibrium)

Atomic Number	X	Y	Z
1	1.107256	0.405194	-7.533685
2	1.142449	0.399021	-6.144914

3	0	0	-5.402441
4	-1.142449	-0.399021	-6.144914
5	-1.107256	-0.405194	-7.533685
6	0	0	-8.206194
7	1.999329	0.674175	-8.093783
8	2.069783	0.644322	-5.630915
9	-2.069783	-0.644322	-5.630915
10	-1.999329	-0.674175	-8.093783
11	0	0	-9.292867
12	0	0	-3.934224
13	0.403045	-1.107991	-3.212802
14	-0.403045	1.107991	-3.212802
15	0.453099	-1.114213	-1.830805
16	0.754558	-1.997733	-3.728646
17	-0.453099	1.114213	-1.830805
18	-0.754558	1.997733	-3.728646
19	-0.827495	2.324477	-1.065197
20	-2.191407	2.490949	-0.790798
21	0.071421	3.328602	-0.695312
22	-2.637286	3.640163	-0.154052
23	-2.901267	1.711105	-1.058406
24	-0.379512	4.476576	-0.048685
25	1.134692	3.195821	-0.890374
26	-1.733807	4.633539	0.223837
27	-3.69654	3.755778	0.059408
28	0.332461	5.242161	0.249519
29	-2.087968	5.524031	0.736874
30	0.827495	-2.324477	-1.065197
31	2.191407	-2.490949	-0.790798
32	-0.071421	-3.328602	-0.695312
33	2.637286	-3.640163	-0.154052
34	2.901267	-1.711105	-1.058406
35	0.379512	-4.476576	-0.048685
36	-1.134692	-3.195821	-0.890374
37	1.733807	-4.633539	0.223837
38	3.69654	-3.755778	0.059408
39	-0.332461	-5.242161	0.249519
40	2.087968	-5.524031	0.736874
41	0	0	0.304619
42	1.149344	0.353397	1.043582
43	-1.149344	-0.353397	1.043582
44	1.151363	0.304077	2.42249
45	2.054688	0.658513	0.517154
46	-1.151363	-0.304077	2.42249
47	-2.054688	-0.658513	0.517154

48	0	0	3.150208
49	2.350197	0.75998	3.150869
50	3.410052	-0.104515	3.464749
51	2.462968	2.105588	3.536677
52	4.54659	0.371283	4.109457
53	3.322795	-1.155153	3.207137
54	3.599155	2.579019	4.18326
55	1.630348	2.785291	3.351741
56	4.651278	1.712993	4.469768
57	5.358487	-0.316588	4.336963
58	3.655669	3.625224	4.477998
59	5.539904	2.077923	4.980398
60	-2.350197	-0.75998	3.150869
61	-3.410052	0.104515	3.464749
62	-2.462968	-2.105588	3.536677
63	-4.54659	-0.371283	4.109457
64	-3.322795	1.155153	3.207137
65	-3.599155	-2.579019	4.18326
66	-1.630348	-2.785291	3.351741
67	-4.651278	-1.712993	4.469768
68	-5.358487	0.316588	4.336963
69	-3.655669	-3.625224	4.477998
70	-5.539904	-2.077923	4.980398
71	0	0	-1.123621
72	0	0	4.389378

Dihedral angle of 51°

Atomic Number	X	Y	Z
1	7.439774	-1.243554	0.104004
2	6.048425	-1.226587	0.101970
3	5.348836	-0.014737	-0.020749
4	6.08121	1.177359	-0.145605
5	7.47253	1.156073	-0.152209
6	8.156206	-0.053382	-0.025312
7	7.96448	-2.185624	0.212027
8	5.506477	-2.156901	0.223657
9	5.56465	2.12223	-0.265579
10	8.022604	2.083357	-0.261911
11	9.239934	-0.06836	-0.027147
12	3.872501	0.006159	-0.018902
13	3.119677	-1.049413	-0.542816
14	3.151724	1.084538	0.506961
15	1.735004	-1.015949	-0.577187

16	3.607873	-1.889091	-1.016123
17	1.768238	1.089059	0.543659
18	3.664827	1.908423	0.981967
19	1.079518	2.184284	1.279801
20	1.316455	3.512136	0.906278
21	0.292405	1.917048	2.408644
22	0.757352	4.559065	1.637877
23	1.925422	3.726661	0.035622
24	-0.252827	2.965513	3.142599
25	0.113561	0.894359	2.716137
26	-0.02726	4.288561	2.756969
27	0.937573	5.582942	1.331623
28	-0.852795	2.749232	4.01893
29	-0.458987	5.101993	3.328606
30	1.01718	-2.083469	-1.324191
31	1.264188	-3.425245	-1.009816
32	0.189645	-1.774461	-2.413101
33	0.677442	-4.443253	-1.759726
34	1.901521	-3.674007	-0.169075
35	-0.383709	-2.794167	-3.16575
36	0.001635	-0.741018	-2.675956
37	-0.14644	-4.130898	-2.839179
38	0.866136	-5.477965	-1.49828
39	-1.01425	-2.544429	-4.01117
40	-0.599777	-4.922145	-3.424994
41	-0.389217	0.045142	0.046286
42	-1.058712	-1.0467	0.599443
43	-1.117682	1.080498	-0.542413
44	-2.445642	-1.098801	0.638986
45	-0.485871	-1.844211	1.058111
46	-2.50526	1.068856	-0.560176
47	-0.588329	1.892309	-1.02771
48	-3.248205	-0.029741	0.051308
49	-3.099101	-2.267962	1.282674
50	-2.618315	-3.569338	1.056456
51	-4.186926	-2.117469	2.160721
52	-3.189992	-4.673822	1.687661
53	-1.795158	-3.72051	0.366723
54	-4.756806	-3.219627	2.794298
55	-4.580621	-1.127342	2.345619
56	-4.263459	-4.505071	2.561533
57	-2.80019	-5.666575	1.489351
58	-5.589556	-3.074373	3.474433
59	-4.711939	-5.36203	3.051788
60	-3.22162	2.195091	-1.212974

61	-2.802748	3.521522	-1.011299
62	-4.308582	1.977928	-2.078026
63	-3.432934	4.586833	-1.654367
64	-1.982091	3.72309	-0.331519
65	-4.936752	3.040646	-2.723425
66	-4.656048	0.966982	-2.242702
67	-4.504233	4.352132	-2.515399
68	-3.09022	5.60039	-1.475308
69	-5.767398	2.844397	-3.393242
70	-4.998193	5.178341	-3.014642
71	1.059366	0.052883	-0.027719
72	-4.51402	-0.054886	0.067719

Dihedral angle of 36°

Atomic Number	X	Y	Z
1	-7.41349	-1.236713	-0.262289
2	-6.02256	-1.206667	-0.242263
3	-5.336828	-0.006428	0.007959
4	-6.083359	1.160358	0.241228
5	-7.474436	1.125463	0.228551
6	-8.144036	-0.071883	-0.025074
7	-7.926907	-2.168648	-0.468287
8	-5.469249	-2.115246	-0.448158
9	-5.578123	2.093466	0.460277
10	-8.035443	2.032325	0.421954
11	-9.227502	-0.097179	-0.037747
12	-3.861438	0.027625	0.025127
13	-3.10183	-1.066386	0.446573
14	-3.142178	1.15893	-0.378352
15	-1.717558	-1.026435	0.502556
16	-3.586486	-1.950288	0.835279
17	-1.759834	1.17259	-0.414302
18	-3.656274	2.022575	-0.775495
19	-1.094924	2.325584	-1.084438
20	-1.304798	3.619116	-0.594049
21	-0.368616	2.148227	-2.27013
22	-0.775771	4.720336	-1.266644
23	-1.869651	3.764272	0.319712
24	0.147006	3.25084	-2.943749
25	-0.212518	1.152842	-2.667482
26	-0.04931	4.539005	-2.441451
27	-0.934444	5.716752	-0.870916
28	0.700181	3.104276	-3.864219

29	0.35907	5.394771	-2.966541
30	-1.019863	-2.12589	1.222998
31	-1.294992	-3.457741	0.889743
32	-0.190518	-1.851921	2.320583
33	-0.738804	-4.498938	1.630741
34	-1.931017	-3.681858	0.041081
35	0.353222	-2.89449	3.063589
36	0.021246	-0.826717	2.598459
37	0.08511	-4.220991	2.719702
38	-0.95048	-5.525283	1.3543
39	0.98466	-2.670365	3.915522
40	0.514977	-5.0303	3.298419
41	0.402479	0.07284	-0.097255
42	1.048806	-1.075483	-0.564535
43	1.17052	1.108424	0.450745
44	2.432083	-1.161063	-0.617139
45	0.46064	-1.885405	-0.978222
46	2.555373	1.065134	0.4621
47	0.670547	1.950027	0.91377
48	3.267022	-0.082378	-0.095552
49	3.053017	-2.374395	-1.210002
50	2.554835	-3.653707	-0.909458
51	4.126431	-2.28688	-2.113975
52	3.096418	-4.798302	-1.494208
53	1.74179	-3.756119	-0.199266
54	4.66612	-3.429259	-2.700914
55	4.533855	-1.314546	-2.355797
56	4.155977	-4.692469	-2.394442
57	2.69386	-5.772824	-1.239184
58	5.488362	-3.333012	-3.402167
59	4.580892	-5.580684	-2.848709
60	3.302674	2.203016	1.057641
61	2.907651	3.527811	0.803389
62	4.396572	2.001387	1.91799
63	3.566881	4.606804	1.392011
64	2.08264	3.716926	0.125472
65	5.053792	3.078219	2.508711
66	4.726738	0.992046	2.122673
67	4.644469	4.38795	2.249306
68	3.241843	5.618363	1.173166
69	5.889178	2.894322	3.176102
70	5.161148	5.224767	2.706054
71	-1.037007	0.096298	0.070303
72	4.529703	-0.141348	-0.119789

Dihedral angle of 21°

Atomic Number	X	Y	Z
1	-7.39741	-1.237948	-0.396225
2	-6.006691	-1.204769	-0.371
3	-5.325511	-0.031195	-0.006974
4	-6.077224	1.105606	0.333875
5	-7.468136	1.067156	0.314834
6	-8.132963	-0.103364	-0.051685
7	-7.906886	-2.148187	-0.69027
8	-5.449709	-2.087597	-0.661458
9	-5.575875	2.015731	0.641033
10	-8.032855	1.949826	0.59156
11	-9.216308	-0.131292	-0.068771
12	-3.851069	0.006928	0.017132
13	-3.083283	-1.115919	0.329161
14	-3.132701	1.173352	-0.269673
15	-1.699719	-1.073248	0.400978
16	-3.561141	-2.036752	0.630702
17	-1.751079	1.19582	-0.308461
18	-3.647823	2.067951	-0.589285
19	-1.121283	2.401158	-0.922414
20	-1.31942	3.656897	-0.338464
21	-0.459458	2.311723	-2.154527
22	-0.84198	4.8072	-0.96609
23	-1.836337	3.734564	0.611253
24	0.005448	3.463161	-2.782135
25	-0.313853	1.345812	-2.622716
26	-0.179127	4.713402	-2.187916
27	-0.991484	5.773585	-0.498747
28	0.508447	3.384533	-3.738999
29	0.188486	5.607491	-2.678054
30	-1.025767	-2.214227	1.081219
31	-1.307681	-3.528583	0.689379
32	-0.220549	-1.994505	2.208725
33	-0.784737	-4.604928	1.403768
34	-1.923604	-3.711753	-0.183589
35	0.291481	-3.072196	2.92385
36	-0.004714	-0.983483	2.532522
37	0.014492	-4.380754	2.52327
38	-1.002359	-5.616863	1.082435
39	0.904231	-2.889343	3.799
40	0.418634	-5.217516	3.081041
41	0.419567	0.077557	-0.154516
42	1.087347	-1.098854	-0.522788

43	1.192445	1.134295	0.362992
44	2.469838	-1.174488	-0.575967
45	0.517229	-1.940334	-0.893565
46	2.575033	1.103238	0.381118
47	0.694176	1.988198	0.80182
48	3.298258	-0.062049	-0.120884
49	3.101616	-2.412773	-1.103
50	2.636107	-3.678856	-0.71059
51	4.154125	-2.361411	-2.03364
52	3.189207	-4.847649	-1.233765
53	1.840377	-3.750978	0.022231
54	4.705092	-3.527989	-2.559114
55	4.536184	-1.398547	-2.345484
56	4.227311	-4.778636	-2.161991
57	2.812446	-5.811641	-0.90891
58	5.510403	-3.460822	-3.282993
59	4.660861	-5.685539	-2.568682
60	3.313212	2.267584	0.935737
61	2.924502	3.579218	0.615091
62	4.391246	2.103099	1.82335
63	3.575263	4.682951	1.166494
64	2.111372	3.737702	-0.084509
65	5.040149	3.204463	2.376459
66	4.715134	1.103585	2.080659
67	4.637339	4.501601	2.051243
68	3.255673	5.684026	0.897286
69	5.863342	3.050018	3.066047
70	5.147252	5.357554	2.479208
71	-1.011105	0.089923	0.092678
72	4.559587	-0.108974	-0.148825

Dihedral angle of 6°

Atomic Number	X	Y	Z
1	-7.385394	-1.224633	-0.528439
2	-5.994864	-1.195139	-0.493855
3	-5.314796	-0.05969	-0.022144
4	-6.067824	1.042259	0.416718
5	-7.458585	1.007067	0.387454
6	-8.122152	-0.124988	-0.086575
7	-7.893954	-2.104125	-0.905825
8	-5.436774	-2.048757	-0.859886
9	-5.56716	1.920354	0.80701
10	-8.024263	1.861606	0.740104

11	-9.205414	-0.150313	-0.111329
12	-3.841347	-0.024135	0.011058
13	-3.069457	-1.168363	0.209876
14	-3.118504	1.161218	-0.156973
15	-1.687219	-1.13065	0.297233
16	-3.543388	-2.116655	0.417928
17	-1.736716	1.186766	-0.20068
18	-3.630736	2.082042	-0.396748
19	-1.14604	2.439119	-0.762958
20	-1.338158	3.655387	-0.099191
21	-0.551472	2.434414	-2.032005
22	-0.920291	4.85001	-0.684982
23	-1.805907	3.667634	0.878706
24	-0.145582	3.630044	-2.616928
25	-0.412383	1.50005	-2.562291
26	-0.323586	4.840636	-1.943956
27	-1.065194	5.784952	-0.156281
28	0.305519	3.616713	-3.602402
29	-0.002642	5.7692	-2.401673
30	-1.044792	-2.32225	0.922924
31	-1.317996	-3.607891	0.440444
32	-0.28926	-2.178113	2.095896
33	-0.836283	-4.729842	1.112682
34	-1.895485	-3.732691	-0.468455
35	0.182336	-3.301373	2.767728
36	-0.083789	-1.189766	2.489443
37	-0.087249	-4.581003	2.278603
38	-1.047284	-5.718723	0.722529
39	0.75625	-3.176847	3.678741
40	0.283607	-5.453567	2.803609
41	0.440251	0.063501	-0.198611
42	1.150605	-1.121	-0.46443
43	1.203449	1.151656	0.288283
44	2.53338	-1.164822	-0.527244
45	0.613459	-2.003102	-0.781692
46	2.584144	1.158493	0.300726
47	0.697367	2.006326	0.712469
48	3.336753	-0.003297	-0.161852
49	3.194691	-2.41956	-0.973598
50	2.768619	-3.667111	-0.488785
51	4.238393	-2.404036	-1.915277
52	3.35049	-4.853815	-0.934232
53	1.981986	-3.709296	0.255655
54	4.817892	-3.58902	-2.363394
55	4.589974	-1.455563	-2.298214

56	4.378869	-4.821405	-1.875228
57	3.004193	-5.802613	-0.538488
58	5.615216	-3.550439	-3.098107
59	4.834766	-5.742266	-2.221668
60	3.296929	2.356187	0.81701
61	2.889115	3.648269	0.44721
62	4.370934	2.240409	1.717114
63	3.517918	4.781446	0.963942
64	2.078481	3.768036	-0.262637
65	4.997729	3.370767	2.235539
66	4.709161	1.256054	2.012816
67	4.576056	4.64884	1.861629
68	3.18412	5.767033	0.65749
69	5.818145	3.254432	2.935791
70	5.068742	5.527587	2.262719
71	-0.983036	0.056134	0.118446
72	4.59609	-0.008295	-0.222853

Transient absorption signals

The assignment of the Raman features in figure 2 is based on comparison with transient absorption features, which are seen by comparing the transmission of the probe with and without the actinic pump. Figure S2 shows these spectra for four representative time delays. In red is the FSR spectrum, and in blue is the transient absorption spectrum. The transient absorption spectrum clearly shows oscillatory features around 700 and 1000 cm^{-1}, which also appear in the FSR spectrum. The FSR spectrum also shows the narrow vibrational features which probe the structural response to photoexcitation. These FSR spectra are the same as those shown in Figure 2.

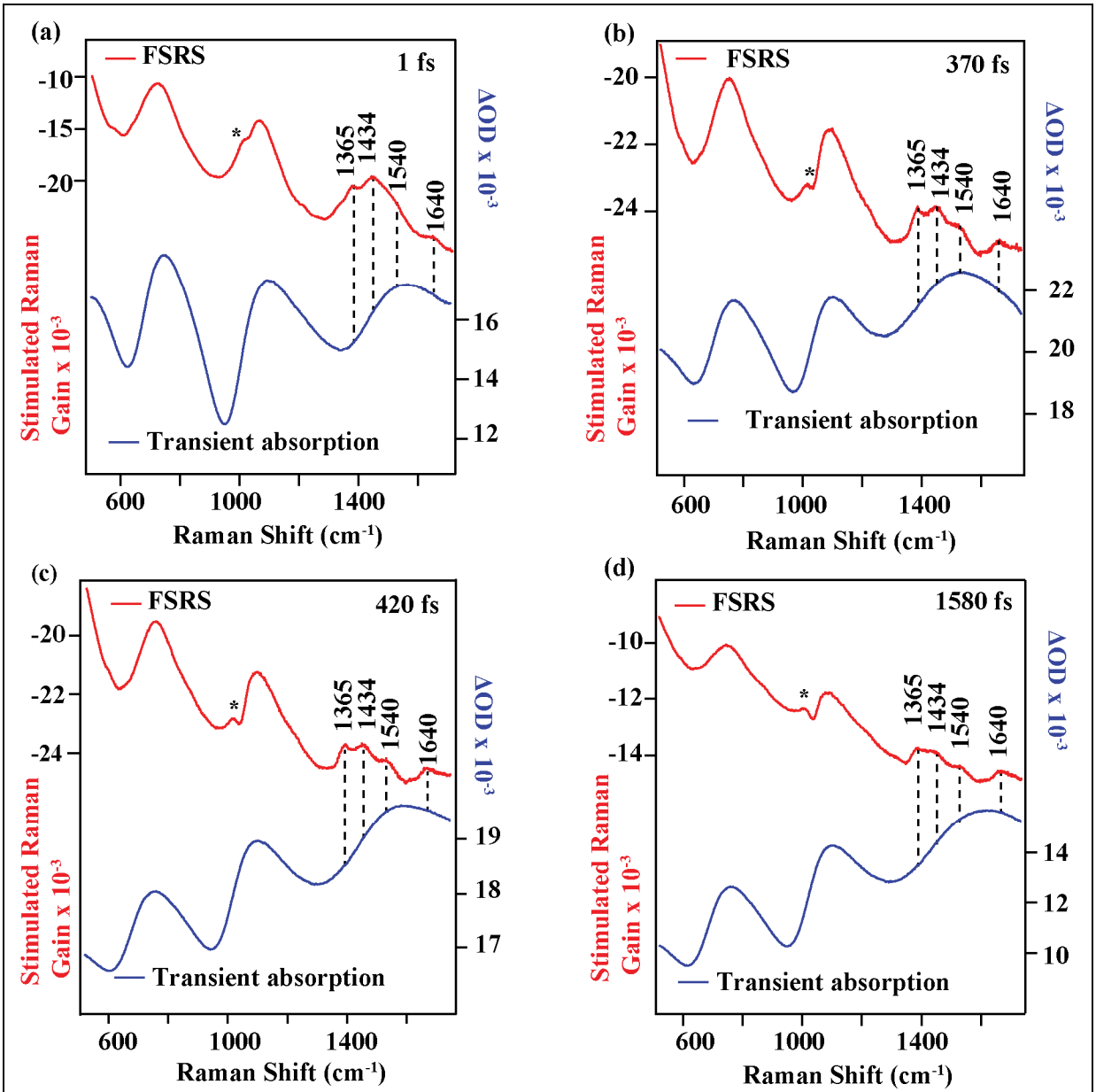

Figure S2: Femtosecond stimulated Raman spectrum (FSRS) and transient absorption (TA) spectrum, shown for four different time points. Panels a-d display time points of 1 fs, 370 fs, 420 fs, and 1580 fs after time zero, respectively. Broad oscillatory features are present in both FSRS and transient absorption spectra, and the narrowband Raman features are clearly present only in the FSR spectrum. The asterisks indicate a methanol artifact.

Transient absorption spectra across the entire spectral range probed by FSRS are shown in Figure S3. An excited state absorption feature is clearly visible after photoexcitation with a

532 nm pulse. Interesting, there is no prominent amplitude oscillation in the optical spectra as is seen in FSRS. The transient absorption feature decays with a time constant of 1.8 ps.

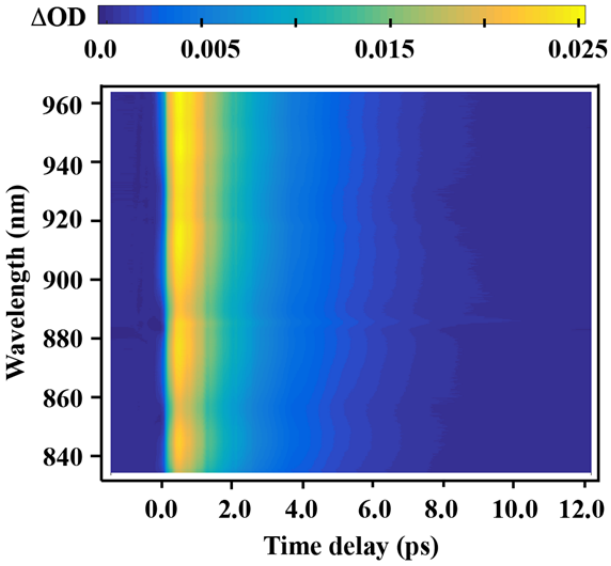

Figure S3: Transient absorption spectra of betaine-30 ranging from 834 nm to 963 nm. There is an excited state absorption which decays with a time constant of 1.8 ps.

Raman pump pulse effects on kinetics

In order to determine the effect of the Raman pump pulse on the observed kinetics, we examined the transient absorption signal with and without this pulse. In Figure S4, we show that the Raman pulse does not affect or slightly increases the excited state lifetime. The decay without the Raman pump present is 1600 ± 100 fs, and is 1800 ± 200 fs with the Raman pump on. The Raman pump is resonant with absorption from the charge-transferred state, and could also be resonant with a stimulated emission process back to a hot ground state. Either of those processes could serve to shorten the lifetime of the charge-transferred state. In the case of stimulated emission, we would expect to see dispersive lineshapes corresponding to ground state

features in our transient spectra, as has been observed in previous FSRS experiments.[1,2] As these are not observed, we attribute the different kinetics to an excited state absorption process. However, the timescale is changed by less than ~12 %, and thus is not expected to alter the dynamics. The transient absorption measurements shown in Figure 4 and 5, as well as in Table 1, were made with the Raman pump on, so as to facilitate comparison with the transient Raman features.

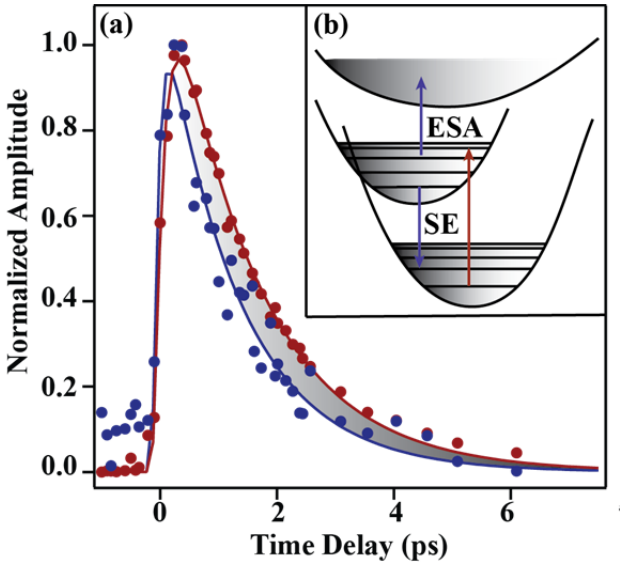

Figure S4. Figure 8: Transient absorption trace of betaine-30 with (blue dots) and without (red dots) Raman pump. Blue and red lines are the bi exponential fits. Insert shows a schematic of excited state absorption (ESA) and stimulated emission (SE) processes that can interfere FSR process after promoting betaine-30 to its charge transferred state from the excitation of the 532 nm actinic pump.

Reproducibility of amplitude oscillations

We compared the amplitude modulations of the modes observed in FSRS across multiple experiments in order to confirm the generality and accuracy of these results. The time delay points sampled were changed in order to eliminate artifacts associated with Fourier transformation. Figure S5 shows the amplitude components of oscillations observed for the 1434 cm^{-1} mode for two different experiments. These two experiments show very similar low frequencies which are coupled to the 1434 cm^{-1} mode through amplitude modulation. The amplitudes of the Fourier components are different between the experiments, which likely results from differences in the cross correlation values.

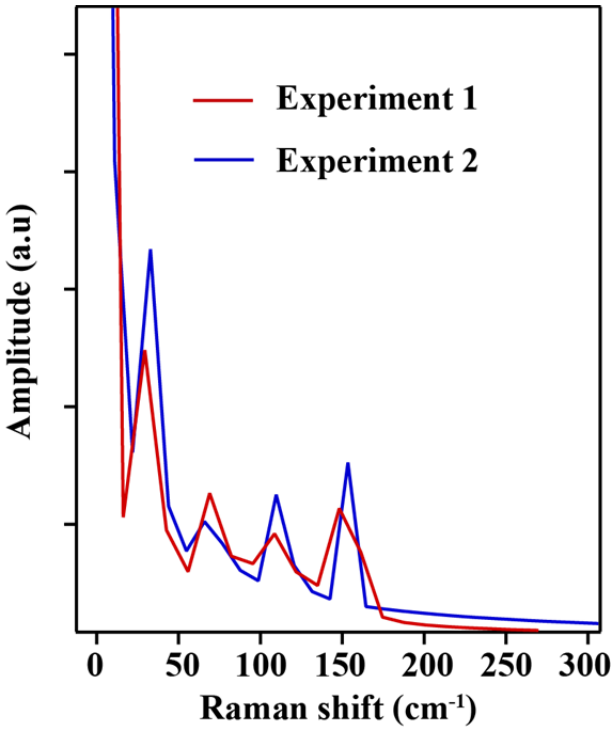

Figure S5: Comparison of low frequency amplitude modulations of the 1434 cm^{-1} across repeated experiments. The low frequency modes are observed by amplitude modulation of the 1434 cm^{-1} mode, which can be Fourier transformed to obtain the power spectrum shown here.

Ground State Spectrum of Betaine-30

We obtained the ground state Raman spectrum of betaine-30 with excitation at 785 nm (shown in Figure S6). Here we used ~ 1 OD betaine-30 in methanol in 2 mm thick glass cuvette and the reference spectrum of methanol was subtracted to eliminate instrument response.

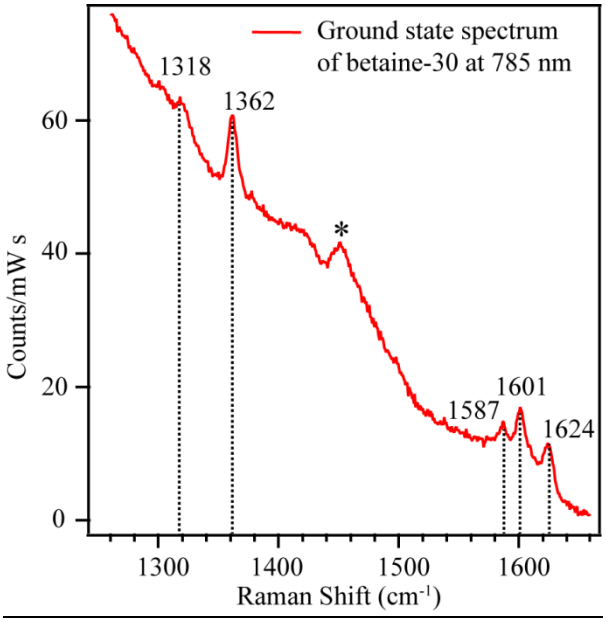

Figure S6. Ground state Raman spectrum of betaine-30 obtained at 785 nm. The asterisk indicates a solvent peak.

References

1. D. W. McCamant, P. Kukura, R. A., Mathies, *J. Phys. Chem. B*, 2005, **109**, 10449-10457

2. R. R. Frontiera, S. Shim, R. A. Mathies, *J. Chem. Phys.*, 2008, **129**, 064507