Table S1 Unsplit rotational transitions of succinic anhydride/MHz

$J'_{K-,K+} \leftarrow J''_{K-,K+}$	ν_{obs}	$\nu_{obs-cal}$	$J'_{K-'K+} \leftarrow J''_{K-,K+}$	ν_{obs}	$\nu_{obs-cal}$
$3_{1,2} \leftarrow 3_{0,3}$	6119.81822	-0.0002	$6_{3,3} \leftarrow 6_{2,4}$	16828.68165	0.00242
$1_{1,1} \leftarrow 0_{0,0}$	7660.93401	0.002	$7_{1,6} \leftarrow 7_{0,7}$	17008.68613	-0.00370
$4_{1,3} \leftarrow 4_{0,4}$	7929.39046	-0.00016	$4_{1,4} \leftarrow 3_{0,3}$	17273.59277	-0.00044
$6_{2,4} \leftarrow 5_{3,3}$	8473.28654	0.00060	$5_{0,5} \leftarrow 4_{1,4}$	17546.65900	0.00076
$3_{0,3} \leftarrow 2_{1,2}$	8960.56240	-0.00006	$5_{3,2} \leftarrow 5_{2,3}$	17842.51776	0.00087
$5_{2,3} \leftarrow 5_{1,4}$	9675.28696	0.00100	$12_{3,9} \leftarrow 12_{2,10}$	18283.28521	-0.00018
$4_{2,2} \leftarrow 4_{1,3}$	9743.72100	0.00045	$6_{1,5} \leftarrow 5_{2,4}$	18373.70993	-0.00189
$6_{2,4} \leftarrow 6_{1,5}$	10159.70306	-0.00099	$4_{3,1} \leftarrow 4_{2,2}$	18627.34325	0.00030
$3_{2,1} \leftarrow 3_{1,2}$	10187.04214	-0.00074	$3_{3,0} \leftarrow 3_{2,1}$	19106.16474	-0.00469
$2_{2,0} \leftarrow 2_{1,1}$	10785.49689	-0.00366	$13_{4,9} \leftarrow 13_{3,10}$	19334.98685	-0.00059
$2_{1,2} \leftarrow 1_{0,1}$	11117.50860	-0.00401	$3_{3,1} \leftarrow 3_{2,2}$	19479.94700	0.00089
$7_{2,5} \leftarrow 7_{1,6}$	11327.48039	0.00190	$2_{2,1} \leftarrow 1_{1,0}$	19526.18679	-0.00020
$2_{2,1} \leftarrow 2_{1,2}$	12613.02947	0.00075	$14_{4,10} \leftarrow 14_{3,11}$	19628.79601	-0.00121
$5_{1,4} \leftarrow 4_{2,3}$	12990.71956	0.00108	$4_{3,2} \leftarrow 4_{2,3}$	19678.92210	0.00312
$8_{2,6} \leftarrow 8_{1,7}$	13261.80368	-0.00080	$5_{3,3} \leftarrow 5_{2,4}$	20060.13008	0.00015
$4_{0,4} \leftarrow 3_{1,3}$	13336.79834	-0.00040	$5_{1,5} \leftarrow 4_{0,4}$	20208.74598	0.00098
$11_{4,7} \leftarrow 10_{5,6}$	13538.97817	-0.00086	$2_{2,0} \leftarrow 1_{1,1}$	20238.58007	-0.00380
$3_{2,2} \leftarrow 3_{1,3}$	13611.24297	-0.00190	$8_{2,6} \leftarrow 7_{3,5}$	20404.70040	0.00269
$3_{1,3} \leftarrow 2_{0,2}$	14288.25250	0.00081	$6_{3,4} \leftarrow 6_{2.5}$	20684.88300	0.00186
$9_{3,6} \leftarrow 9_{2,7}$	14639.95440	0.00061	$8_{1,7} \leftarrow 8_{0,8}$	20756.90665	-0.00027
$8_{3,5} \leftarrow 8_{2,6}$	14967.09567	0.00050	$7_{2,6} \leftarrow 7_{1,7}$	21035.37603	0.00313
$10_{3,7} \leftarrow 10_{2,8}$	15004.88317	0.00084	$6_{0,6} \leftarrow 5_{1,5}$	21545.84690	0.00065
$7_{3,4} \leftarrow 7_{2,5}$	15782.67793	0.00120	$7_{3,5} \leftarrow 7_{2,6}$	21605.12106	0.00250
$9_{2,7} \leftarrow 9_{1,8}$	15968.82285	-0.00026	$10_{4,6} \leftarrow 10_{3,7}$	22410.20227	-0.00034
$11_{3,8} \leftarrow 11_{2,9}$	16197.77576	0.00068	$8_{3,6} \leftarrow 8_{2,7}$	22857.53869	0.00119
$5_{2,4} \leftarrow 5_{1,5}$	16657.41244	0.00086	$3_{2,2} \leftarrow 2_{1,1}$	22982.74632	-0.00530

$6_{1,6} \leftarrow 5_{0,5}$	23210.74753	0.00054	$8_{7,1} \leftarrow 8_{6,2}$	50270.08000	0.04376
$8_{2,7} \leftarrow 8_{1,8}$	23644.23025	-0.00033	$8_{7,2} \leftarrow 8_{6,3}$	50270.08000	-0.06154
$7_{1,6} \leftarrow 6_{25}$	23672.29881	0.00074	$7_{7,0} \leftarrow 7_{6,1}$	50321.86200	0.03325
$9_{4,5} \leftarrow 9_{36}$	23861.43718	0.00034	$7_{7,1} \leftarrow 7_{6,2}$	50321.86200	0.01805
$16_{7,9} \leftarrow 16_{6,10}$	48105.71100	-0.02589	$20_{4,17} \leftarrow 20_{3,18}$	50554.98100	0.01003
$17_{7,11} \leftarrow 17_{6,12}$	48342.74900	0.00824	$7_{3,4} \leftarrow 6_{2,5}$	50782.51000	0.05670
$16_{7,10} \leftarrow 16_{6,11}$	48676.46400	-0.02421	$10_{3,8} \leftarrow 9_{2,7}$	51642.97700	0.03926
$15_{7,8} \leftarrow 15_{6,9}$	48729.67700	-0.02823	$6_{4,3} \leftarrow 5_{3,2}$	51692.00100	0.02039
$16_{1,15} \leftarrow 16_{0,16}$	48743.27200	0.00566	$6_{4,2} \leftarrow 5_{3,3}$	51871.23700	0.00275
$16_{2,15} \leftarrow 16_{1,16}$	48780.10000	-0.05736	$17_{1,16} \leftarrow 17_{0,17}$	52043.90400	0.00934
$15_{7,9} \leftarrow 15_{6,10}$	49006.37500	-0.02039	$17_{2,16} \leftarrow 17_{1,17}$	52063.18300	-0.00307
$14_{7,8} \leftarrow 14_{6,9}$	49308.40500	-0.01982	$14_{1,13} \leftarrow 13_{2,12}$	53151.99700	-0.00219
$13_{7,6} \leftarrow 13_{6,7}$	49517.83800	-0.03758	$11_{3,9} \leftarrow 10_{2,8}$	53357.37500	0.01271
$13_{1,12} \leftarrow 12_{2,11}$	49556.35500	0.00248	$15_{0,15} \leftarrow 14_{1,14}$	53482.35100	0.00339
$13_{7,7} \leftarrow 13_{6,8}$	49569.93900	-0.02617	$15_{1,15} \leftarrow 14_{0,14}$	53487.43300	-0.00062
$13_{2,11} \leftarrow 12_{3,10}$	49611.68900	-0.03178	$14_{2,13} \leftarrow 13_{1,12}$	53527.55300	0.01236
$18_{2,16} \leftarrow 18_{1,17}$	49621.55000	-0.05282	$7_{2,5} \leftarrow 6_{1,6}$	53692.12700	0.01555
$20_{3,17} \leftarrow 20_{2,18}$	49666.03800	-0.02396	$15_{3,12} \leftarrow 14_{4,11}$	54118.26200	-0.05237
$9_{3,7} \leftarrow 8_{2,6}$	49812.26300	-0.00568	$14_{2,12} \leftarrow 13_{3,11}$	54354.35800	-0.05717
$18_{3,16} \leftarrow 18_{2,17}$	49837.56000	-0.00128	$19_{2,17} \leftarrow 19_{1,18}$	53020.20000	0.00880
$14_{0,14} \leftarrow 13_{1,13}$	50023.85500	-0.00619	$19_{3,17} \leftarrow 19_{2,18}$	53140.51100	-0.00859
$14_{1,14} \leftarrow 13_{0,13}$	50034.19000	0.00430			
$10_{7,3} \leftarrow 10_{6,4}$	50093.10200	0.01948			
$10_{7,4} \leftarrow 10_{6,5}$	50095.12005	-0.00539			
$9_{7,2} \leftarrow 9_{6,3}$	50195.85800	-0.02419			
$9_{7,3} \leftarrow 9_{6,4}$	50196.37800	-0.02370			
$13_{2,12} \leftarrow 12_{1,11}$	50233.33300	0.02248			

Table S2 Microwave rotational transitions in succinic anhydride isotopologues/MHz

Transition	^{13}CH isotope		^{13}CO isotope		^{18}OCO isotope		^{18}OCOC isotope	
$J'_{K'K+} \leftarrow J''_{K-,K+}$	ν_{obs}	$\nu_{obs-cal}$	ν_{obs}	$\nu_{obs-cal}$	ν_{obs}	$\nu_{obs-cal}$	ν_{obs}	$\nu_{obs-cal}$
$1_{1,1} \leftarrow 0_{0,0}$	7530.52229	-0.00134	7651.96950	-0.00224				
$3_{0,3} \leftarrow 2_{1,2}$	8999.79565	-0.00136	8883.75464	-0.00021	8423.22881	-0.00464		
$2_{1,2} \leftarrow 1_{0,1}$	10960.21065	-0.00124	11093.11417	-0.00083				
$4_{0,4} \leftarrow 3_{1,3}$	13337.11583	-0.00052	13242.19145	-0.00081	12656.01363	-0.00726		
$3_{2,2} \leftarrow 3_{1,3}$	13313.43168	0.00136	13619.92051	0.00133				
$3_{1,3} \leftarrow 2_{0,2}$	14102.25641	-0.00569	14250.92302	-0.00131	13953.04970	-0.00605	14119.04618	0.01671
$4_{1,4} \leftarrow 3_{0,3}$	17062.03407	0.00203	17223.60101	-0.00147			17084.62604	0.00387
$5_{0,5} \leftarrow 4_{1,4}$	17498.04788	0.00109	17438.67775	0.00034	16750.34784	-0.00879		
$5_{1,5} \leftarrow 4_{0,4}$	19979.28718	0.00213	20143.97210	0.00072	19662.09552	-0.01178	20008.75807	-0.01285
$6_{0,6} \leftarrow 5_{1,5}$	21444.71340	0.00069	21427.21329	0.00037	20652.96390	-0.01157	21498.42780	0.00103
$6_{1,6} \leftarrow 5_{0,5}$	22970.76381	0.00021	23128.29642	0.00214	22534.47361	-0.01275		
$9_{3,7} \leftarrow 8_{2,6}$	48938.59800	-0.03342	49758.71100	-0.00855	49109.06600	-0.01539		
$7_{3,4} \leftarrow 6_{2,5}$					49382.53500	0.00263		
$13_{7,6} \leftarrow 13_{6,7}$					50073.03900	-0.00695		

$10_{3,8} \leftarrow 9_{2,7}$	50737.15200	0.00401	51587.16400	0.00836	50915.43000	-0.00010		
$6_{4,3} \leftarrow 5_{3,2}$	50816.26200	0.00497	51631.11700	-0.01059	50940.16800	-0.03503	50842.82800	-0.16770
$6_{4,2} \leftarrow 5_{3,3}$	51012.46900	0.00236	51803.98000	0.00051	51082.25000	0.01129	51042.41000	-0.15410
$14_{1,13} \leftarrow 13_{2,12}$	52771.21900	0.01310	52904.62100	-0.00863	51229.19100	-0.02282		
$11_{3,9} \leftarrow 10_{2,8}$	52442.31600	-0.00541	53292.99200	-0.01793	52571.51200	-0.00088		
$15_{0,15} \leftarrow 14_{1,14}$					51616.85900	-0.00938		
$15_{1,15} \leftarrow 14_{0,14}$	53071.99600	-0.03497	53249.02300	-0.03678	51624.66400	0.02467		
$14_{2,13} \leftarrow 13_{1,12}$					51750.77000	-0.00385		
$12_{3,10} \leftarrow 11_{2,9}$	54208.39800	-0.00138	55020.27700	-0.01258	54203.23000	0.01973	54247.13300	0.01979
$14_{2,12} \leftarrow 13_{3,11}$	54253.27000	-0.01151	54000.16800	0.00158				
$15_{11,4} \leftarrow 14_{2,13}$					54669.55100	0.01160		
$7_{4,4} \leftarrow 6_{3,3}$	54648.10500	-0.00138	55486.53500	-0.00942	54688.44900	-0.01120	54681.06600	-0.14979
$16_{0,16} \leftarrow 15_{1,15}$					54954.12500	0.00359	56613.82000	0.01381
$16_{1,16} \leftarrow 15_{0,15}$					54958.04700	0.00031	56615.70000	0.04099
$7_{4,3} \leftarrow 6_{3,4}$	55230.96900	0.03778	56001.10900	0.00970	55112.30900	0.02229	55273.77700	-0.08232
$13_{3,11} \leftarrow 12_{2,10}$	56182.01200	0.00322	56915.11300	0.01359	55946.59000	0.02247	56235.50400	0.03970
$9_{8,1} \leftarrow 9_{7,2}$							56335.40600	0.14871
$8_{4,5} \leftarrow 7_{3,4}$							58231.57500	-0.08229

$15_{2,14} \leftarrow 14_{1,13}$	56430.18000	-0.01512	56643.73000	-0.00753	54962.90600	-0.03381		
$8_{4,5} \leftarrow 7_{3,4}$	58195.98400	0.02208	59084.25000	-0.04427	58217.44500	-0.01447		
$14_{3,12} \leftarrow 13_{2,11}$					57918.48800	-0.01452		
$16_{1,15} \leftarrow 15_{2,14}$					58063.68400	0.00874		
$16_{2,15} \leftarrow 15_{1,14}$					58225.86300	0.00543		
$17_{0,17} \leftarrow 16_{1,16}$					58290.51600	0.00793		
$17_{1,17} \leftarrow 16_{0,16}$					58292.45700	-0.02025		
$6_{5,2} \leftarrow 5_{4,1}$	58481.40200	-0.05198	59517.71100	0.00827				
$6_{5,1} \leftarrow 5_{4,2}$	58485.65200	0.06306	59521.14500	-0.01394				
$8_{4,4} \leftarrow 7_{3,5}$	59613.68800	-0.02303	60340.86700	-0.04003	59257.12500	-0.00808	59672.35200	-0.19423
$9_{4,6} \leftarrow 8_{3,5}$	61329.10900	0.00024	62297.86700	0.00065	61412.00000	0.01153	61362.61700	-0.14867
$17_{1,16} \leftarrow 16_{2,15}$					61430.84400	0.01525		
$17_{2,16} \leftarrow 16_{1,15}$					61519.16400	-0.00692		
$8_{5,4} \leftarrow 7_{4,3}$					66687.23400	-0.05301		
$9_{4,5} \leftarrow 8_{3,6}$	64295.67600	-0.01078	64942.94600	0.02268	63615.45300	0.03540	64375.67200	-0.03293
$8_{5,4} \leftarrow 7_{4,3}$					66687.23400	-0.05301		
$8_{5,3} \leftarrow 7_{4,4}$					66736.18800	0.02240		
$10_{4,6} \leftarrow 9_{3,7}$							69570.99200	0.03461

Table S3. Semi-experimental equilibrium rotational constants and residuals of the fits (in MHz).

Isotopologue	Axis g	B_g	Exp – calc [a]	Exp – calc [b]	d_{HH} [c]
Parent	*a*	5974.315	0.078	0.078	1.7576
	b	2377.984	-0.005	-0.005	
	c	1737.358	-0.002	-0.002	
^{13}CH	*a*	5856.019	0.000	0.001	1.7577
	b	2371.493	0.010	0.010	
	c	1723.790	0.005	0.005	
^{13}CO	*a*	5972.668	-0.031	-0.031	1.7576
	b	2363.613	0.019	0.019	
	c	1729.535	0.000	0.001	
^{18}0CO	*a*	5922.761	-0.003	-0.003	1.7580
	b	2273.315	0.006	0.006	
	c	1676.717	0.003	0.003	
^{18}OCOC	*a*	5856.913	0.001	0.001	1.7577
	b	2377.959	-0.030	-0.030	

c	1727.292	-0.006	-0.006

[a] Fit with three predicates (mean of CCSD(T)_AE/wCVQZ values): C-H = 1.0872(20) Å, C-C-H = 108.32(30)°, O-C-C-H = 121.73(30)°

[b] Fit with an additional fourth predicate: C-C = 1512(2) Å (CBS value).

[c] Non-bonded distance between the two out-of-plane hydrogen atoms derived from P_c.