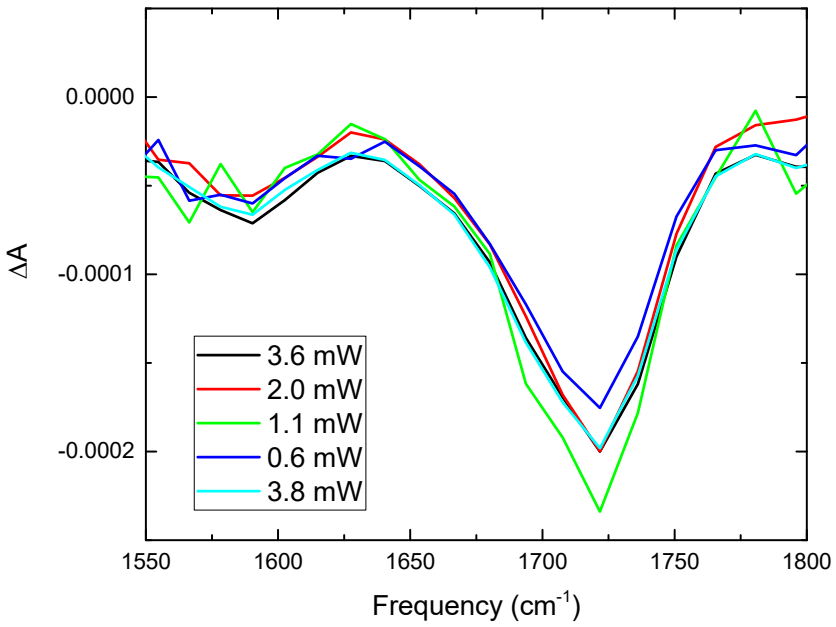
Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

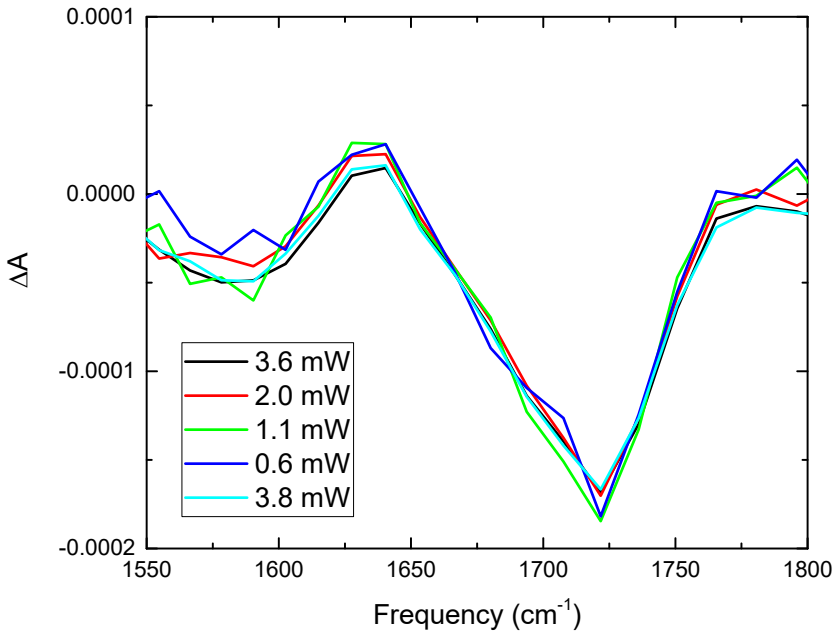
Supplementary information to lactic acid

Two-photon dissociation and ionization of water is an ever-present component in femtosecond UV-pump-probe experiments. In particular when the extinction coefficient of the solute is as low as that of lactic acid. The trick is to keep the pump pulse intensity low enough to prevent two-photon processes in water or solute from influencing the measured photochemistry, while still achieving an acceptable signal from one-photon excitation of the solute. This balance is relatively easy to achieve at short pump-probe delays of, say, t< 10 ps as diffusion times even for the ionization products of water normally prevents bi-molecular reactions from becoming significant. However, the potential effect of bi-molecular reactions increase with increasing delays. The best way to ascertain the influence of two-photon excitation is to measure the pump-pulse intensity dependence of the measured transient absorption. The intensity dependence of the lactate ground state excitation and the CO_2^- formation are shown below for a 0.3 M lactic acid solution at delays of t = 10 ps, t = 100 ps and t = 300 ps. At each delay, the spectra are normalized linearly according to the average pulse power used in the measurements. The spectra are identical within the experimental uncertainty. The measurements shown in the manuscript were recorded at P 2.5 mW. The graphs show a linear intensity thus verifying that the transient absorption dynamics reported in the manuscript are solely due to one-photon excitation of lactic acid.

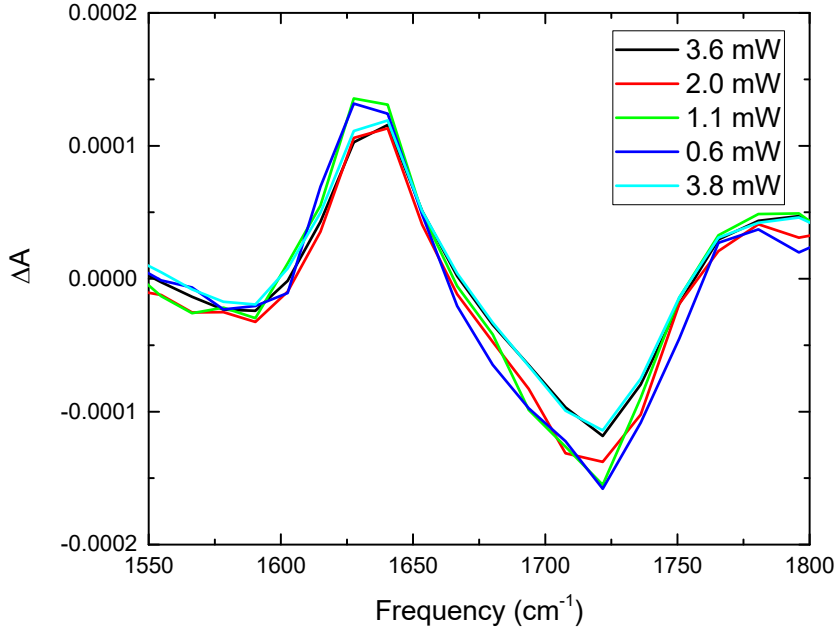
Delay: 10 ps



Delay: 100 ps


0.0001
0.0000
-0.0001
-0.0002
ΔA
1550
1600
1650
1700
1750
1800
Frequency (cm-1)
3.6 mW
2.0 mW
1.1 mW
0.6 mW
3.8 mW

Delay: 300 ps


0.0002
0.0001
0.0000
-0.0001
-0.0002
ΔA
1550
1600
1650
1700
1750
1800
Frequency (cm-1)
3.6 mW
2.0 mW
1.1 mW
0.6 mW
3.8 mW

The solvent signal is a result of pump-induced heating of the water. Photo-excitation deposits 6.2 eV in the solute. A significant fraction is transferred to the water shortly after the excitation. As the absorption spectrum of water depends on temperature, the pump-induced heating results in a time-dependent induced absorption background.

For every time delay, the background subtraction routine identifies and excludes the absorptions associated with vibrational transitions by use of the Matlab function “isoutlier”. The remaning data points are then fitted by a linear slope by use of the Matlab function “poly1”. The fitted line is then subtracted from the data as background.

COOH

harmonic														anharmonic													
cis		trans		cis_w2		cis_w2a		trans_w2		cis_w4		trans_w4		cis		trans		cis_w2		cis_w2a		trans_w2		cis_w4		trans_w4	
freq	int	freq	int	freq	int	freq	int	freq	int	freq	int	freq	int	freq	int	freq	int	freq	int	freq	int	freq	int	freq	int	freq	int
				30	2	40	2	29	7	17	0	19	1					30	2	40	2	29	7	17	0	19	1
				38	7	118	1	45	11	22	8	20	6					38	7	118	1	45	11	22	8	20	6
				54	118	175	15	58	112	22	9	27	1					54	118	175	15	58	112	22	9	27	1
				76	11	241	55	111	54	32	1	39	2					76	11	241	55	111	54	32	1	39	2
				105	51	255	11	114	6	46	5	58	3					105	51	255	11	114	6	46	5	58	3
				164	16	286	146	153	10	63	118	68	123					164	16	286	146	153	10	63	118	68	123
				235	4	309	79	175	2	70	122	75	32					235	4	309	79	175	2	70	122	75	32
				280	59	320	84	269	41	96	0	81	27					280	59	320	84	269	41	96	0	81	27
				370	85	404	24	344	92	123	2	118	2					370	85	404	24	344	92	123	2	118	2
				392	181	510	110	369	206	147	21	147	13					392	181	510	110	369	206	147	21	147	13
				443	1	568	144	419	8	193	4	162	3					443	1	568	144	419	8	193	4	162	3
				530	106	689	21	500	104	235	110	194	2					530	106	689	21	500	104	235	110	194	2
606	45	635	3	687	41	902	103	686	6	249	6	198	15	606	45	635	3	687	41	902	103	686	6	249	6	198	15
										273	13	253	83											273	13	253	83
										299	19	288	95											299	19	288	95
										319	78	300	44											319	78	300	44
										338	141	336	86											338	141	336	86
										349	94	376	29											349	94	376	29
										428	153	388	179											428	153	388	179
										481	104	417	52											481	104	417	52
										498	32	431	25											498	32	431	25
										505	228	485	105											505	228	485	105
										569	79	549	201											569	79	549	201
										712	16	628	151											712	16	628	151
										899	106	697	5											899	106	697	5
576	**116**	**565**	**88**	**1001**	**127**	**1052**	**130**	**1050**	**92**	**1112**	**133**	**1078**	**94**	**576**	**116**	**565**	**88**	**1001**	**127**	**1052**	**130**	**1050**	**92**	**1103**	**47**	**1083**	**75**
1125	**212**	**1158**	**36**	**1242**	**216**	**1256**	**204**	**1249**	**64**	**1285**	**203**	**1251**	**65**	**1070**	**167**	**1158**	**84**	**1209**	**161**	**1221**	**199**	**1218**	**23**	**1280**	**197**	**1225**	**18**
1313	**2**	**1243**	**337**	**1446**	**8**	**1484**	**23**	**1380**	**370**	**1514**	**37**	**1395**	**381**	**1291**	**1**	**1244**	**283**	**1351**	**5**	**1395**	**6**	**1284**	**304**	**1477**	**51**	**1353**	**379**
				1627	77	1620	96	1628	77	1616	86	1625	101					1627	77	1620	96	1628	77	1616	86	1625	101
				1639	65	1642	39	1634	65	1633	58	1628	81					1639	65	1642	39	1634	65	1633	58	1628	81
										1638	66	1638	66											1638	66	1638	66
										1658	53	1667	99											1658	53	1667	99
1870	**433**	**1901**	**336**	**1812**	**617**	**1807**	**569**	**1858**	**544**	**1782**	**812**	**1857**	**561**	**1838**	**373**	**1869**	**304**	**1771**	**553**	**1750**	**464**	**1815**	**532**	**1656**	**2083**	**1804**	**634**
3647	**73**	**3806**	**194**	**2892**	**1669**	**2606**	**1929**	**3044**	**1891**	**2228**	**2426**	**2877**	**2246**	**3647**	**73**	**3806**	**194**	**2892**	**1669**	**2606**	**1929**	**3044**	**1891**	**971**	**232**	**2252**	**965**
				3761	334	3441	732	3761	331	3388	813	3663	390					3761	334	3441	732	3761	331	3388	813	3663	390
				3823	36	3719	357	3831	34	3747	290	3779	381					3823	36	3719	357	3831	34	3747	290	3779	381
				3917	135	3884	112	3919	129	3775	341	3783	102					3917	135	3884	112	3919	129	3775	341	3783	102
				3920	125	3903	130	3925	132	3796	201	3828	39					3920	125	3903	130	3925	132	3796	201	3828	39
										3877	109	3842	232											3877	109	3842	232
										3901	160	3911	148											3901	160	3911	148
										3921	174	3921	135											3921	174	3921	135
										3923	103	3921	138											3923	103	3921	138

ωB97x-D/aug-pcseg-1 optimized geometries for the species in Tables 1 and 2.

CH3CHOHCOOH, ground state:
Energy = -496.3099451190

C	1.434108	-1.430956	1.062433
C	0.940982	-1.051338	-0.334073
C	-0.410745	-0.355330	-0.213062
O	-0.552388	0.857583	-0.138292
O	1.866848	-0.272854	-1.044648
O	-1.419454	-1.200830	-0.154081
H	0.780638	-1.960428	-0.923172
H	0.711671	-2.076566	1.573228
H	2.383078	-1.967783	0.971854
H	1.593536	-0.532615	1.670782

H	2.048788	0.546732	-0.549461
H	-2.259236	-0.686859	-0.021788
O	-3.392565	0.572485	0.242375
H	-4.001398	0.722577	-0.489632
H	-2.689073	1.229774	0.129074
O	1.834047	2.233574	0.240235
H	0.901909	1.950214	0.206056
H	2.052119	2.281033	1.176569

CH3CHOHCOOH, singlet excited state:
Energy = -496.120461577

C	1.370611	-1.349595	1.137849
C	0.937488	-1.058239	-0.295659
C	-0.369804	-0.256832	-0.360710
O	-0.442959	0.829257	0.381775
O	1.953743	-0.453760	-1.053818
O	-1.480144	-1.051410	-0.242578
H	0.679297	-1.993924	-0.809975
H	0.555895	-1.822935	1.697446
H	2.230204	-2.027868	1.129007
H	1.656838	-0.426107	1.653094
H	2.162053	0.410628	-0.652570
H	-2.281459	-0.481717	-0.145702
O	-3.659361	0.516078	0.072444
H	-4.046797	0.795828	-0.764864
H	-3.425818	1.335452	0.523881
O	2.049390	2.127716	0.023704
H	1.095886	2.266416	0.101266
H	2.378787	2.189171	0.927332

CH3CHOHCOOH, triplet excited state:
Energy = -496.1460181830

C	0.706359	-2.398859	-0.079863
C	0.921998	-0.900989	-0.157692
C	-0.364975	-0.151635	0.146924
O	-0.256633	1.178000	0.382982
O	1.940059	-0.531506	0.749033
O	-1.332036	-0.285014	-0.811601
H	1.219423	-0.624968	-1.187161
H	-0.116438	-2.705394	-0.733721
H	1.616492	-2.919244	-0.395786
H	0.467276	-2.691941	0.948686
H	2.274886	0.340822	0.477338
H	-2.197694	0.029460	-0.449637
O	-3.701900	0.495162	0.184964
H	-3.798602	1.453609	0.222442

H -3.803063 0.200037 1.097274
O 2.413431 1.990199 -0.401982
H 1.459539 2.153212 -0.390196
H 2.794517 2.698579 0.127377

CH3CHOH radical conformation 1:
Energy = -154.3167531290
C 1.206456 -0.181168 0.019662
C -0.091809 0.527135 -0.118573
O -1.256126 -0.177485 0.046358
H -0.206720 1.561851 0.199259
H 2.032970 0.503104 -0.199227
H 1.357935 -0.579285 1.039090
H 1.278273 -1.031116 -0.674838
H -1.101331 -1.110473 -0.141681

CH3CHOH radical conformation 2:
Energy = -154.3171325340
C 1.226209 -0.162747 0.013826
C -0.091710 0.504515 -0.105858
O -1.165194 -0.340513 0.016932
H -0.241486 1.526158 0.247190
H 2.030987 0.552757 -0.184394
H 1.389513 -0.583406 1.022098
H 1.316474 -0.991966 -0.701077
H -1.980937 0.169955 0.032918

CH3CHOH anion conformation 1:
Energy = -154.4000085300
C 1.175616 -0.211459 -0.004436
C -0.064544 0.656772 -0.151039
O -1.245579 -0.228028 -0.081221
H -0.107376 1.282932 0.766597
H 2.071815 0.417585 0.118063
H 1.142615 -0.895116 0.879606
H 1.353124 -0.855529 -0.880663
H -1.161973 -0.797523 0.699017

CH3CHOH anion conformation 2:
Energy = -154.3997844840
C 1.199297 -0.213771 0.002665
C -0.060337 0.617696 -0.204250
O -1.208516 -0.273634 0.133368
H -0.063171 1.359007 0.622078
H 2.088087 0.437463 -0.026583
H 1.228219 -0.755726 0.975141

H	1.340117	-0.976461	-0.780377
H	-1.758887	-0.298766	-0.647692

CH3CH2OH anti conformation:

Energy = -154.9783435110

C	-1.220900	-0.221565	-0.000023
C	0.081948	0.544574	0.000018
O	1.152701	-0.395537	0.000043
H	0.144369	1.189977	-0.888659
H	-2.066960	0.475035	0.000463
H	-1.297458	-0.856994	-0.890328
H	-1.297035	-0.857700	0.889820
H	1.984857	0.085962	-0.000317
H	0.144338	1.189965	0.888707

CH3CH2OH gauche conformation:

Energy = -154.9783671950

C	-1.209419	-0.242134	0.021634
C	0.078349	0.555477	-0.047100
O	1.237485	-0.256313	0.109124
H	0.132819	1.113770	-0.993648
H	-2.074603	0.425559	-0.074371
H	-1.259002	-0.977066	-0.792271
H	-1.286921	-0.775507	0.976370
H	1.252851	-0.901936	-0.604833
H	0.121401	1.285627	0.768553

CH3CH2O anion:

Energy = -154.4652368080

C	-1.174040	-0.209714	0.000014
C	0.192314	0.493303	0.000001
O	1.259523	-0.360485	-0.000011
H	0.185803	1.186904	-0.882410
H	-2.008497	0.509946	-0.000471
H	-1.274413	-0.851081	-0.887941
H	-1.274790	-0.850370	0.888437
H	0.186067	1.186951	0.882386