Supplementary Information

Methods

Time-resolved spectroscopy

We study the photo-dynamics of aqueous pyruvic acid with UV pump-IR probe femtosecond transient absorption spectroscopy. The 340 nm femtosecond pulses used for exciting the pyruvic acid sample accurately define when the excited state is populated, and the infrared femtosecond pulses used for probing the vibrational transitions of the reaction intermediates and products map the reaction dynamics in real time. The high time resolution enables the detection of the primary photo-dynamics without interference from reactions with other molecules than the surrounding water. The beam of 340 nm pump pulses is generated by frequency quadrupling a beam of 1360 nm femtosecond laser pulses from an Optical parametric amplifier (OPA) in two consecutive β-barium borate crystals. The OPA is pumped by an amplified Titanium:Sapphire laser. Pump pulses with an energy of 5 μJ are sent via a scanning delay line and through a half-wave plate before they are focused to a spot-size of 0.2 mm on the sample by a concave mirror. A mechanical chopper modulates the beam of pump pulses such that every second pump pulse excites the sample, while the rest are blocked. The beam of infrared probe pulses is generated by difference frequency mixing the signal and idler pulses from an optical parametric amplifier pumped by the amplified Titanium:Sapphire laser. The beam of probe pulses is divided into a signal and reference beam by a beam splitter and focused onto the sample by an off-axis paraboloidal mirror. The pulses in the signal beam probes the sample inside the volume excited by the pump pulses, while the reference beam passes through the sample outside the volume excited by the pump beam. A second off-axis paraboloidal mirror recollimates the signal and reference beams, and the probe pulses are subsequently analyzed and detected by a spectrometer equipped with a dual array HgCdTe detector. The spectrum of the signal pulses is normalized to that of the reference pulses and the induced transient absorption spectrum is obtained by subtracting the normalized probe spectrum recorded with pump pulse excitation from the normalized probe spectrum recorded without pump pulse excitation. The transient absorption measurements are recorded with pump and probe polarizations at the magic angle (54.7°). The data measured for $-0.5 < t < 0.5$ ps are obscured by the $t = 0$ coherence signal, and the transient absorption spectra therefore only shows data after $t > 0.5$ ps. The spectral resolution of the transient absorption spectrometer is ~10 cm^{-1} in the spectral range 1000 – 2000 cm^{-1} and ~4 cm^{-1} in the range 2200 – 2400 cm^{-1}. The linear pump-induced water solvent background signal has been subtracted from all transient absorption data.

Sample preparation

The samples used for transient absorption spectroscopy consist of a constantly flowing wire guided film of aqueous pyruvic acid. The flow ensures a fresh sample for every probe pulse and frequent replacement of the sample minimizes the buildup of permanent photoproducts. The transient absorption measurements use H_2O as solvent except for measurements recorded in the spectral range 1500 – 1750 cm^{-1}, where the absorption associated with the H_2O bending transition renders the sample opaque. D_2O is used as solvent in the 1500 – 1750 cm^{-1} range.

Steady-state spectroscopy

The UV-Vis steady-state spectra of aqueous fumarate and maleate are recorded by a Shimadzu UV-3600 spectrometer. The steady-state IR spectra of aqueous pyruvic acid and acetaldehyde

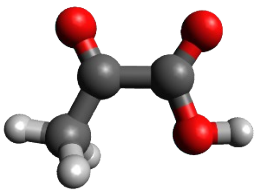
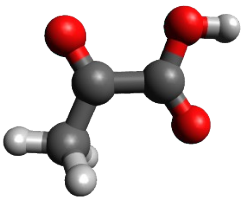
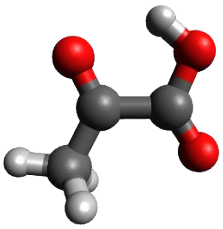
are recorded by ATR FTIR with the resolution set to $\Delta\nu = 4$ cm^{-1} on a Nicolet 380 spectrometer from Thermo Fisher.

Computational details

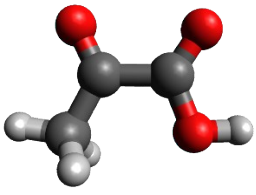
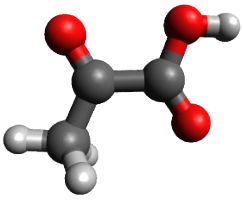
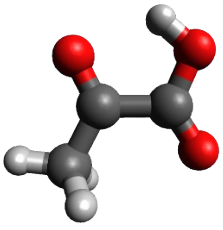
All calculations have been done using the ωB97X-D functional[1] and the aug-pcseg-1 basis set[2] and the IEFPCM implicit solvent model[3]. The ωB97X-D includes a range-separated X-functional and empirical dispersion, with the former important to accurately describe possible charge-transfer character of the excited states and the latter important for describing the interaction with explicit water molecules. Excitation energies have been calculated within the TDDFT framework, where only the optical part of the dielectric constant in the IEFPCM model is included. The solvent effect has been probed by including up to four explicit water molecules to provide hydrogen bonding to the carboxyl oxygen atoms. Triplet states have been calculated using a (ground state) unrestricted formalism. All calculations have been performed using the Gaussian-16 software package.[4] The quoted vibrational frequencies and intensities for molecular species in the ground state are calculated using the anharmonic approximation[5] while the vibrational frequencies as well as transition intensities for molecules in the excited states are calculated in the harmonic approximation since the perturbation estimate of the anharmonicity often is unstable for excited states.[6]

Conformations and relative energies (kJ/mol). It should be noted that the microsolvated systems are only representative, as other hydrogen-bonded networks with similar structures can be found. For the present purpose, however, the interest is only in how the vibrational frequencies change upon microsolvation, and this in general is insensitive to the exact microsolvated structure and also to including microsolvation relative to implicit solvation.

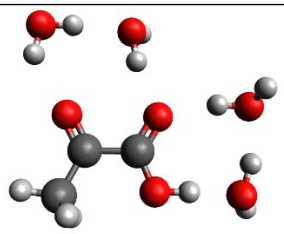
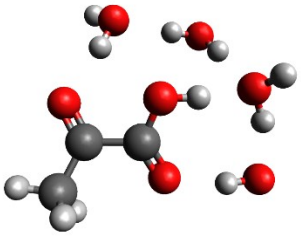
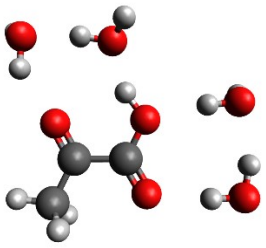
Gas-phase:

Conf 1	Conf 2	Conf 3
		
19.2	11.9	0.0

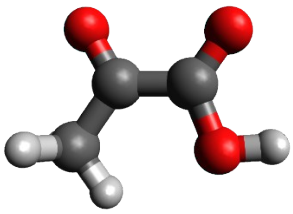
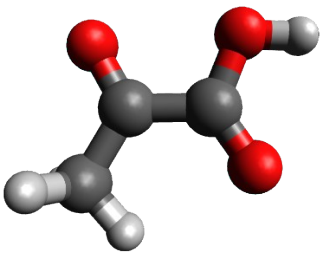
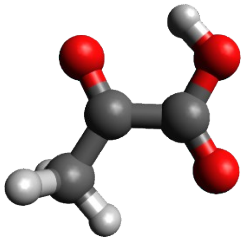
Implicit water:

		
10.3	8.5	0.0

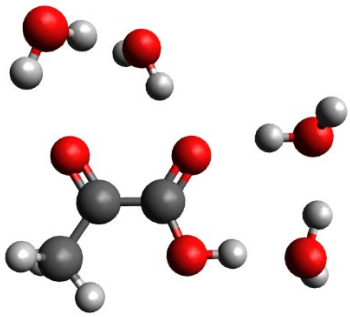
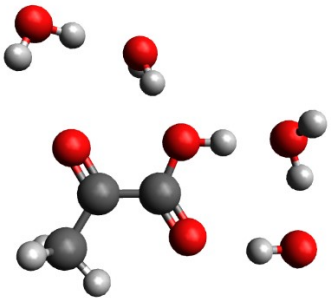
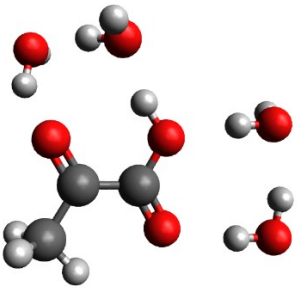
Implicit water and microsolvation:

		
-8.4	-15.6	0.0

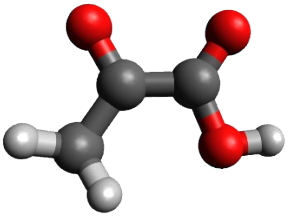
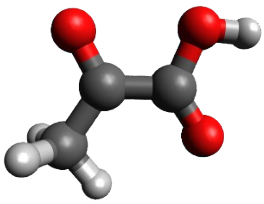
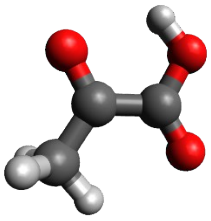
Singlet excited, Implicit water:

		
12.0	-6.7	0.0

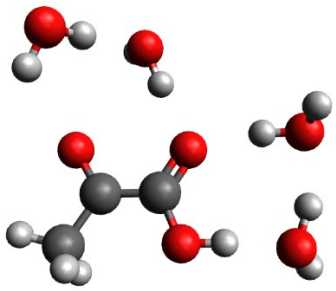
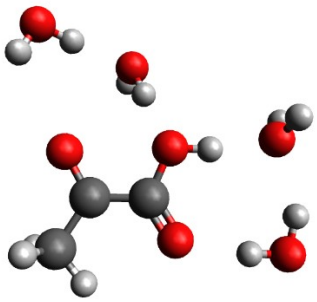
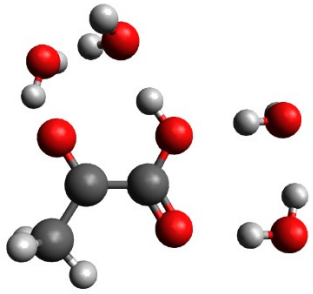
Singlet excited, Implicit water and microsolvation:

		
-6.1	-10.2	0.0

Triplet, Implicit water:

		
0.3	-11.8	0.0

Triplet, Implicit water and microsolvation:

		
-11.6	-12.2	0.0

Ground state geometries:
conf1_w4
Energy = -647.9183173000

C	-0.761758	2.994752	-0.046031
C	-0.866357	1.507286	-0.016963
C	0.450160	0.684034	0.001910
O	1.515590	1.427034	0.010285
O	-1.901993	0.888688	-0.008109
O	0.421027	-0.534623	0.007851
O	3.759681	0.135640	0.031715
O	2.600145	-2.306165	-0.081617
O	-4.144112	-1.030876	-0.024107
O	-1.699342	-2.416965	0.035764
H	-0.191504	3.305402	-0.929355
H	-1.758989	3.436922	-0.059763
H	-0.199871	3.341271	0.829154
H	2.375709	0.888207	0.034022
H	-1.546584	-2.864445	0.874188
H	-1.065359	-1.678233	0.029542
H	3.527430	-0.819632	-0.010056
H	4.244802	0.255400	0.855385
H	1.755394	-1.822052	-0.076461
H	2.639152	-2.740369	-0.940277
H	-3.780489	-0.138656	-0.024788
H	-3.339929	-1.582108	0.010657

conf1
Energy = -342.2598128310

C	-0.737886	-0.257810	-0.000035
O	-1.141554	-1.394029	-0.000056
C	0.802038	-0.052419	-0.000066
O	1.585456	-0.964837	0.000111
O	1.131626	1.236084	-0.000093
C	-1.609074	0.955278	0.000111
H	-1.387046	1.570544	-0.879918
H	-2.658964	0.657419	0.000259
H	-1.386711	1.570913	0.879752
H	2.098018	1.313093	0.000154

conf2_w4
Energy = -647.9210835990

C	-3.110218	-1.421915	-0.187831
C	-2.138789	-0.313628	0.024119
O	-2.424694	0.863665	0.028382
C	-0.659598	-0.717595	0.206146
O	-0.237171	-1.759010	-0.258268
O	0.018111	0.182642	0.861424
O	2.615216	-0.120496	0.788662
O	2.464214	-2.479174	-0.476300
O	-0.494819	3.013020	-0.040330
O	2.152007	2.295739	-0.787422
H	-3.058272	-2.119507	0.656902
H	-4.119627	-1.022484	-0.294611
H	-2.822363	-1.987679	-1.081624
H	0.998615	-0.026367	0.903642
H	-0.927448	3.595537	-0.672348
H	-1.084288	2.243932	0.039281
H	2.772721	-0.983202	0.337839
H	3.103805	-0.139681	1.617931
H	2.389084	1.509955	-0.275631
H	1.233474	2.498349	-0.533422
H	1.497628	-2.352080	-0.478654
H	2.725388	-2.469040	-1.403087

conf2
Energy = -342.2605130410

C	1.762551	0.765831	-0.000290
C	0.711076	-0.293617	0.000411
C	-0.749261	0.219536	0.000479
O	-1.628236	-0.772004	-0.000303
O	0.922129	-1.481633	0.000047
O	-1.025614	1.393710	0.000062
H	1.638578	1.408229	0.879512
H	2.752186	0.306453	-0.000897
H	1.637484	1.408242	-0.879926
H	-2.520675	-0.394003	-0.000742

conf3_w4
Energy = -647.9151172820

C	-0.976841	2.940426	0.067490
C	-0.950655	1.453795	0.008997
O	-1.925350	0.740191	-0.021921
C	0.448148	0.786962	-0.014085
O	1.451707	1.465090	-0.018185
O	0.475078	-0.522699	-0.030064
O	-1.441753	-2.254926	0.013078
O	-3.977433	-1.192551	-0.077494
O	4.106738	0.319371	-0.084206
O	2.815972	-2.227410	0.041655
H	-0.434869	3.349496	-0.792873
H	-2.008329	3.294543	0.076723
H	-0.444176	3.278087	0.964215
H	-0.412126	-1.004621	-0.030427
H	-2.377855	-1.963117	-0.018918
H	-1.326819	-2.852576	-0.733147
H	1.981579	-1.734236	0.032262

H	2.862714	-2.612306	0.923022
H	3.248764	0.769474	-0.063100
H	3.858081	-0.618158	-0.025925
H	-3.615837	-0.297190	-0.015026
H	-4.494705	-1.313021	0.725882

conf3
Energy = -342.2637449850

C	1.791676	0.714855	0.000014
C	0.683877	-0.275106	-0.000063
O	0.809591	-1.480203	0.000013
C	-0.764939	0.274189	-0.000030
O	-1.027004	1.449114	0.000007
O	-1.682846	-0.678603	0.000021
H	1.699468	1.362979	0.879664
H	2.755099	0.203229	-0.000081
H	1.699401	1.363230	-0.879439
H	-1.215587	-1.535526	-0.000001

Singlet excited state geometries:
conf1_w4
Total Energy, E(TD-HF/TD-DFT) = -647.791269679

C	-1.105380	2.859723	0.018350
C	-0.921317	1.367965	0.239119
C	0.351128	0.683919	0.119171
O	1.348084	1.480797	-0.214291
O	-1.988278	0.757557	0.556813
O	0.463892	-0.536215	0.322566
O	3.679125	0.308999	-0.425860
O	2.678339	-2.171419	0.008407
O	-3.469963	-1.366752	-1.230612
O	-1.677408	-2.204024	0.756706
H	-0.133911	3.261693	-0.275713
H	-1.848971	3.028146	-0.767757
H	-1.455650	3.328871	0.944156
H	2.220188	0.984132	-0.266389
H	-2.003942	-2.037479	1.646684
H	-0.901383	-1.619086	0.655569
H	3.510363	-0.651015	-0.296455
H	4.278817	0.568389	0.281829
H	1.829429	-1.702128	0.116975
H	2.571893	-2.710604	-0.782140
H	-3.416578	-0.407156	-1.183480
H	-2.867164	-1.664932	-0.522967

conf1
Total Energy, E(TD-HF/TD-DFT) = -342.131948825

C	0.652394	0.215829	-0.000094
O	1.189818	1.364578	-0.000102
C	-0.792389	0.057617	-0.000017
O	-1.585201	0.987582	0.000148
O	-1.164867	-1.239905	-0.000120
C	1.640115	-0.941424	0.000117
H	1.063518	-1.867720	-0.000428
H	2.275260	-0.882870	-0.890531

H	2.274274	-0.883300	0.891507
H	-2.131772	-1.256271	0.000010

conf2_w4
Total Energy, E(TD-HF/TD-DFT) = -647.793125215

C	-0.576433	3.003771	0.143512
C	-0.669591	1.514646	-0.050895
C	0.526968	0.686689	-0.111608
O	0.257688	-0.605027	-0.290114
O	-1.814331	0.992028	-0.177808
O	1.661643	1.152655	-0.001664
O	2.359228	-2.143704	-0.412536
O	4.099787	-0.171327	0.258333
O	-1.964288	-2.160637	0.681928
H	-1.030574	3.530271	-0.698396
H	-1.099596	3.295721	1.065914
H	0.490699	3.236351	0.220670
H	1.096455	-1.159242	-0.351055
H	-1.928775	-2.145453	1.643333
H	-1.223089	-1.604398	0.395715
H	3.123324	-1.571169	-0.178960
H	2.531861	-2.467658	-1.302892
H	3.324553	0.418406	0.234506
H	4.382245	-0.182638	1.178814
H	-4.079651	-0.042179	-0.428956
O	-4.321316	-0.960719	-0.274512
H	-3.500396	-1.364791	0.066237

conf2
Total Energy, E(TD-HF/TD-DFT) = -342.139078562

C	1.801442	0.736081	-0.000031
C	0.655152	-0.236142	0.000059
C	-0.723611	0.231355	0.000026
O	-1.598442	-0.791991	0.000012
O	0.890982	-1.477756	0.000004
O	-1.056667	1.409422	0.000036
H	2.424364	0.590927	0.890193
H	2.424140	0.591017	-0.890445
H	1.361435	1.739181	-0.000038
H	-2.494823	-0.426287	-0.000449

conf3_w4
Total Energy, E(TD-HF/TD-DFT) = -647.789253970

C	-1.108839	2.871681	-0.005960
C	-0.956512	1.384789	-0.203021
O	-1.991090	0.714123	-0.479660
C	0.366459	0.758714	-0.087006
O	1.359673	1.436824	0.169834
O	0.461597	-0.551391	-0.270489
O	-1.521180	-2.155843	-0.694057
O	-3.558563	-1.306926	0.923356
O	4.055056	0.419696	0.290677
O	2.835107	-2.145970	0.034648
H	-0.105185	3.250195	0.215855

H	-1.508369	3.334860	-0.915183
H	-1.794781	3.075770	0.823964
H	-0.395224	-1.044766	-0.460150
H	-2.294436	-1.964406	-0.119386
H	-1.860232	-2.161725	-1.595526
H	1.989383	-1.679838	-0.058564
H	2.773265	-2.599122	0.881879
H	3.188579	0.852306	0.262505
H	3.823289	-0.522670	0.233395
H	-3.286789	-0.381216	0.858221
H	-3.460946	-1.534600	1.854430

conf3
Total Energy, E(TD-HF/TD-DFT) = -342.136531080

C	1.804623	-0.704463	0.000091
C	0.642594	0.247363	0.000191
O	0.822844	1.494845	-0.000260
C	-0.736974	-0.260731	0.000120
O	-1.007776	-1.454980	-0.000053
O	-1.711638	0.656336	-0.000238
H	1.384013	-1.715968	-0.001525
H	2.424647	-0.545021	-0.889760
H	2.423475	-0.546635	0.890998
H	-1.321029	1.545004	0.002286

Triplet state geometries:
conf1_w4
Energy = -647.8138381960

C	-1.030861	2.887327	-0.010701
C	-0.879271	1.409061	0.244347
C	0.361187	0.687243	0.137970
O	1.370041	1.462293	-0.213749
O	-1.966913	0.803240	0.598409
O	0.457240	-0.532599	0.359936
O	3.689318	0.247395	-0.452005
O	2.630978	-2.204220	0.014304
O	-3.553600	-1.337052	-1.201579
O	-1.693022	-2.210361	0.698239
H	-0.642388	3.112931	-1.009308
H	-2.081025	3.181325	0.047004
H	-0.455215	3.442791	0.738126
H	2.232128	0.953120	-0.273235
H	-1.998560	-2.125689	1.606884
H	-0.919479	-1.616687	0.630669
H	3.499464	-0.707079	-0.313114
H	4.303832	0.497159	0.246238
H	1.796480	-1.710475	0.132663
H	2.498090	-2.745080	-0.770992
H	-3.490970	-0.377555	-1.172660
H	-2.921028	-1.636108	-0.520401

conf1
Energy = -342.1552389670

C	-1.656215	0.926219	0.003607
C	-0.649024	-0.192924	-0.016444

C	0.784933	-0.049031	-0.002553
O	1.164490	1.246339	0.000807
O	-1.157297	-1.387069	0.003274
O	1.578439	-0.981372	0.004196
H	-2.566523	0.632393	-0.526618
H	-1.916251	1.181799	1.038321
H	-1.212000	1.796093	-0.486545
H	2.131559	1.260946	0.000963

conf2_w4
Energy = -647.8140929920

C	-0.530947	3.044085	0.159158
C	-0.614054	1.561907	-0.059647
C	0.546760	0.701372	-0.101430
O	0.239656	-0.583497	-0.296194
O	-1.785333	1.050362	-0.218530
O	1.691386	1.133751	0.025588
O	2.296248	-2.199638	-0.415007
O	4.076171	-0.254796	0.214619
O	-1.969312	-2.051511	0.798180
H	-0.967986	3.583211	-0.688215
H	-1.065250	3.328811	1.072166
H	0.530137	3.290323	0.253333
H	1.060833	-1.161154	-0.353522
H	-1.955235	-1.930652	1.753206
H	-1.217407	-1.533348	0.470247
H	3.078860	-1.645276	-0.197718
H	2.450360	-2.536549	-1.304039
H	3.298215	0.335120	0.203388
H	4.376705	-0.263343	1.129205
H	-4.170105	-0.143173	-0.543160
O	-4.338928	-1.067825	-0.339719
H	-3.508787	-1.382926	0.065128

conf2
Energy = -342.1598715440

C	1.813730	0.727860	0.000154
C	0.647497	-0.214309	-0.000265
C	-0.727042	0.234514	-0.000043
O	-1.596414	-0.797238	0.000176
O	0.891275	-1.479232	-0.000079
O	-1.067747	1.407853	-0.000114
H	2.431218	0.578440	0.892960
H	2.436193	0.573183	-0.888242
H	1.403285	1.741813	-0.003891
H	-2.492728	-0.432891	0.000231

conf3_w4
Energy = -647.8094387870

C	-1.083938	2.888742	0.037777
C	-0.898356	1.415629	-0.205439
O	-1.958761	0.760108	-0.528996
C	0.400909	0.772692	-0.097714
O	1.400816	1.423573	0.195703
O	0.487066	-0.536565	-0.329121

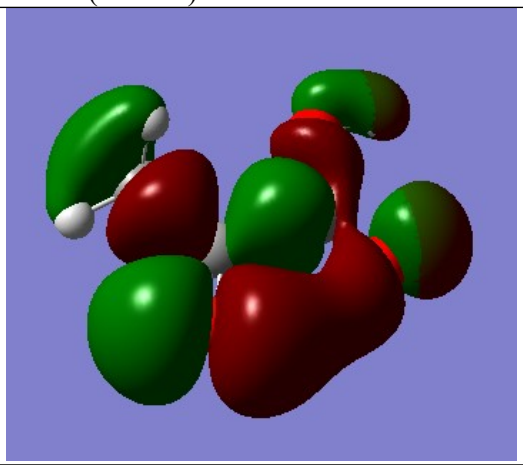
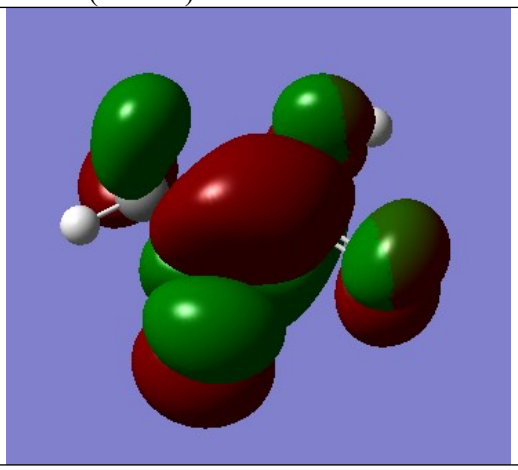
O	-1.606164	-1.994208	-0.804902
O	-3.549563	-1.401752	1.016576
O	4.034373	0.342188	0.360054
O	2.791486	-2.205778	-0.000450
H	-1.469344	3.380155	-0.862097
H	-1.787362	3.055988	0.860636
H	-0.099571	3.289000	0.294866
H	-0.376215	-1.004126	-0.534517
H	-2.333507	-1.834651	-0.163185
H	-2.000300	-1.901043	-1.678732
H	1.968014	-1.701380	-0.100376
H	2.691270	-2.676873	0.833103
H	3.163495	0.769156	0.313274
H	3.811887	-0.599474	0.272964
H	-3.400425	-0.472775	1.228269
H	-3.473670	-1.866882	1.857132

conf3

Energy = -342.1553619350

C	1.811514	0.702035	0.000497
C	0.633718	-0.228287	-0.000579
O	0.848658	-1.492544	-0.000443
C	-0.740634	0.259038	-0.000082
O	-1.014990	1.447054	-0.000447
O	-1.724041	-0.659173	0.000525
H	2.423430	0.545684	0.895866
H	2.433220	0.535638	-0.886145
H	1.407759	1.718780	-0.007129
H	-1.369010	-1.559508	0.001317

Natural transition orbitals for the three conformations:

Conf	NTO1 (HOMO)	NTO2 (LUMO)
1		

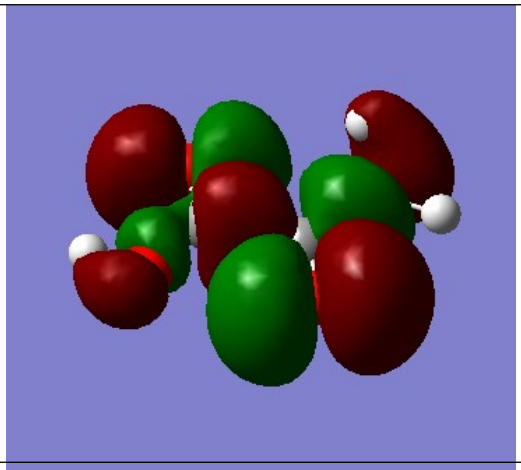
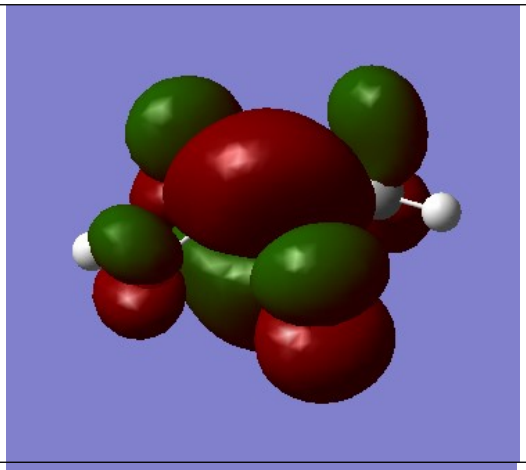
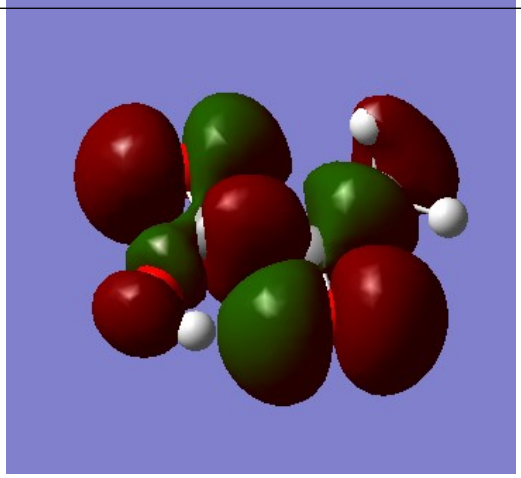
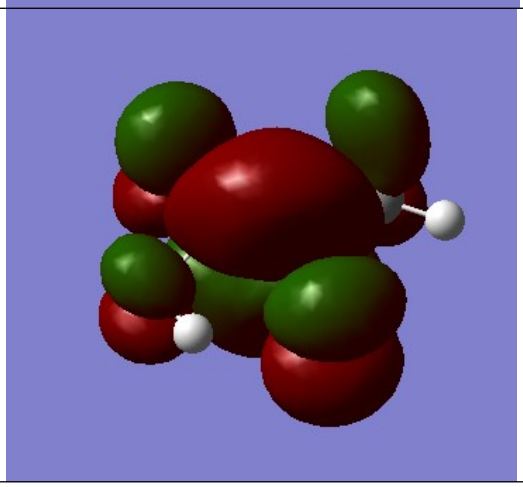
2		
3		

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Fig. SI1. Steady-state IR absorption of pyruvic acid in H_2O and D_2O measured against H_2O and D_2O references.

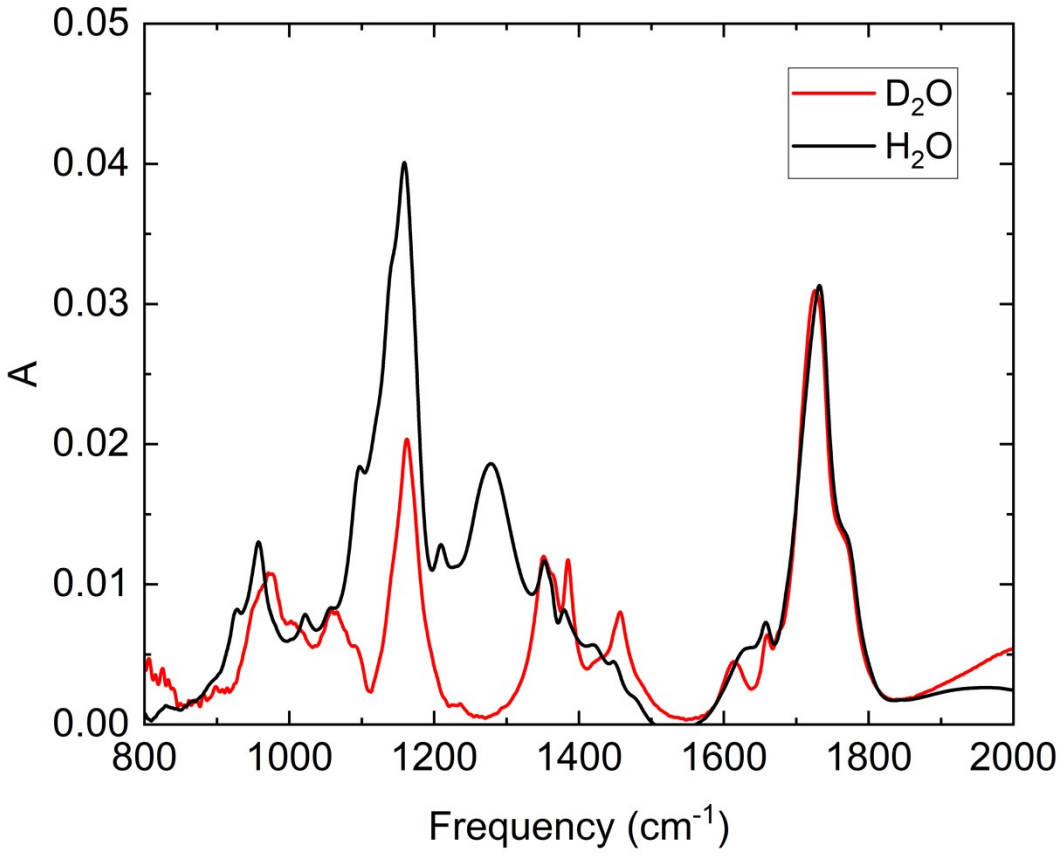

Fig. SI2. UV pump- IR probe transient absorption spectrum of pyruvic acid after excitation at 340 nm. The spectral range 1500 – 1750 cm^{-1} is measured using D_2O as solvent, all the other spectra are recorded in H_2O.

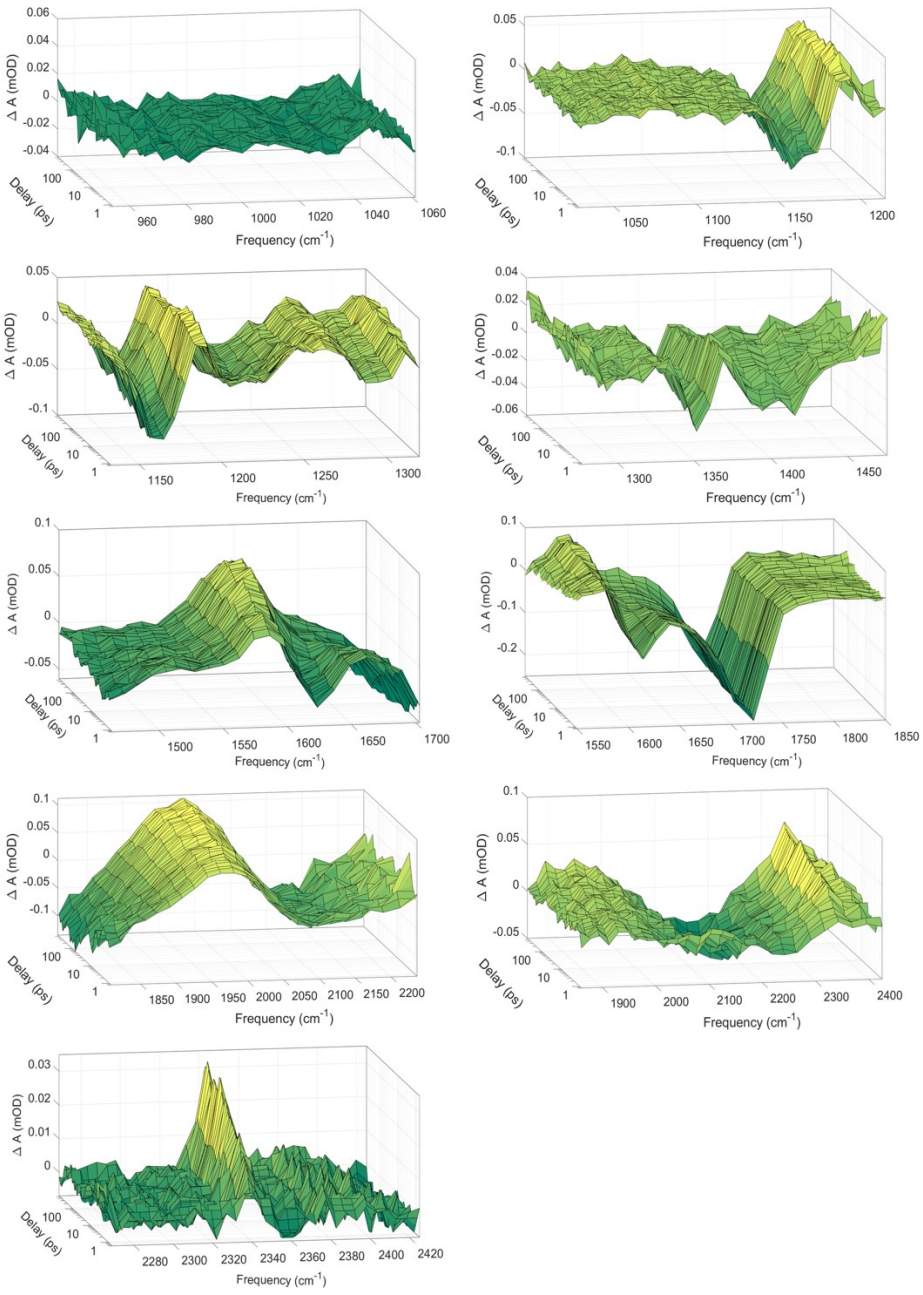

Fig. SI3. Steady-state IR spectrum of acetaldehyde in H_2O measured against an H_2O reference.

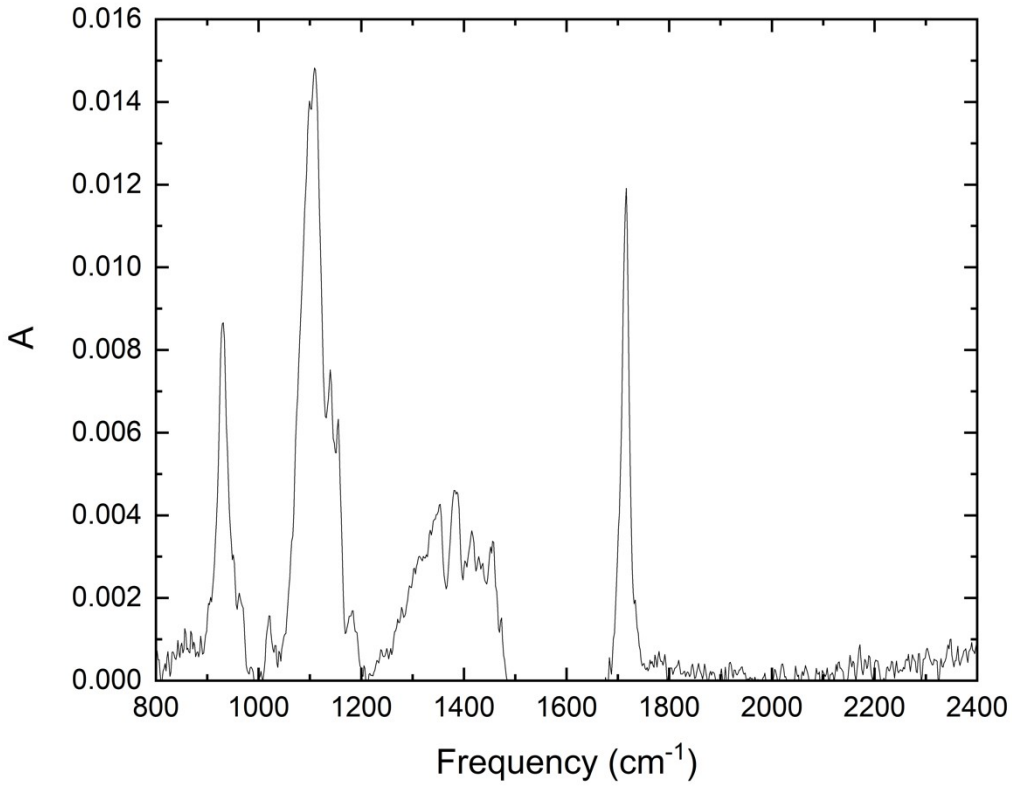

Table SI1. Calculated transition frequencies and intensities of methyl hydroxy carbene.

Singlet methyl hydroxy carbene:

E(harm) (cm^{-1})	E(anharm) (cm^{-1})	I(harm) (km/mol)	I(anharm) (km/mol)
1460	1407	11	19
1428	1379	21	21
1376	1326	47	76
1345	1304	15	70
1322	1275	257	183
1072	1046	72	79
976	937	39	55

Triplet state methyl hydroxy carbene:

E(harm) (cm^{-1})	E(anharm) (cm^{-1})	I(harm) (km/mol)	I(anharm) (km/mol)
1448	1401	1	1
1440	1410	7	3
1383	1349	50	62
1350	1316	46	10
1166	1187	146	144
1084	1054	4	2
1000	984	10	5
910	889	16	17

Table SI2 Singlet excited pyruvic acid, three configurations.

Conf. 1 with 4 H_2O

E(harm) (cm^{-1})	E(anharm) (cm^{-1})	I(harm) (km/mol)	I(anharm) (km/mol)
1721		85	
1532		103	
1483		13	
1437		10	
1420		15	
1346		206	
1246		722	
1003		3	

Conf. 2 with 4 H_2O:

E(harm) (cm^{-1})	E(anharm) (cm^{-1})	I(harm) (km/mol)	I(anharm) (km/mol)
1689		401	
1520		39	
1437		18	
1420		14	
1352		138	
1262		688	
1122		26	
1008		130	

Conf. 2 with 4 D_2O:

E(harm) (cm^{-1})	E(anharm) (cm^{-1})	I(harm) (km/mol)	I(anharm) (km/mol)
1677		510	
1519		45	
1437		18	

1421	14
1361	152
1289	318
1124	88
1078	163
1006	1

Table SI3 Triplet pyruvic acid, three configurations.

Conf. 1 with 4 H_2O:

E(harm) (cm^{-1})	E(anharm) (cm^{-1})	I(harm) (km/mol)	I(anharm) (km/mol)
1663	1627	341	8
1515	1461	105	101
1456	1507	5	53
1447	1204	1	50
1416	1313	9	72
1370	1332	107	25
1249	1214	453	501
1147	1115	21	9

Conf. 1 with 4 D_2O:

E(harm) (cm^{-1})	E(anharm) (cm^{-1})	I(harm) (km/mol)	I(anharm) (km/mol)
1650	1595	687	48
1515	1464	109	61
1455	1509	4	18
1447	1199	12	45
1416	1308	7	18
1370	1340	93	97
1249	1224	416	453
1147	1116	22	15

Conf. 2 with 4 H_2O:

E(harm) (cm^{-1})	E(anharm) (cm^{-1})	I(harm) (km/mol)	I(anharm) (km/mol)
1707	1645	504	122
1481	1520	19	17
1455	1236	5	241
1435	1425	11	10
1404	1351	3	15
1354	1276	175	76
1266	1146	354	314
1143	1108	113	112
1014	928	0	2

Conf. 2 with 4 D_2O:

E(harm) (cm^{-1})	E(anharm) (cm^{-1})
1701	1626
1481	1455
1455	1301
1435	1435
1404	1390
1354	1264
1267	1173
1014	1024

Conf. 3 with 4 H_2O:

E(harm) (cm^{-1})	E(anharm) (cm^{-1})	I(harm) (km/mol)	I(anharm) (km/mol)
1709	1725	317	197
1466	1462	37	379
1431	1391	10	74
1407	1346	330	573
1394	1501	227	101
1333	1998	99	2491
1261	1254	248	1610
1127	1099	34	117
1027	307	70	2689
1010	983	5	2

Conf. 3 with 4 D_2O:

E(harm) (cm^{-1})	E(anharm) (cm^{-1})	I(harm) (km/mol)	I(anharm) (km/mol)
1706	1716	501	93
1466	1342	34	563
1431	1387	10	51
1408	2027	341	2254
1395	1494	168	38
1336	1458	109	251
1262	1263	245	1215
1127	1089	33	15
1014	996	10	2