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

Supporting Information for:

Absorption Spectra of Pyruvic Acid in Water: Insights from Calculations for Small Hydrates and Comparison to Experiment

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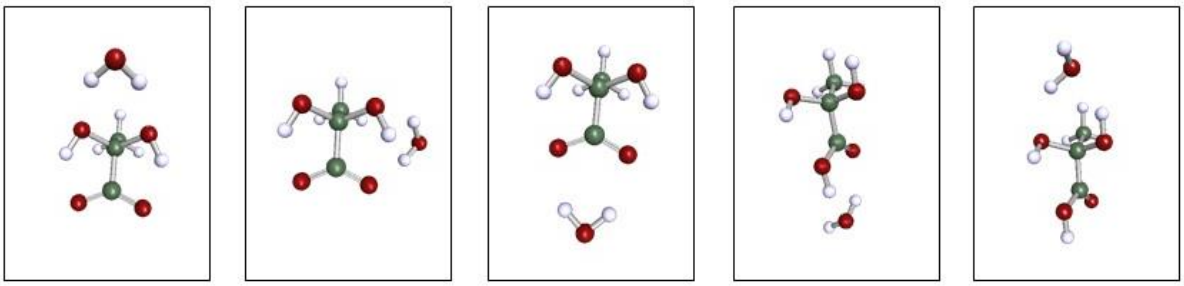
1. Effect of hydration on the vertical excitation energies to the first excited singlet state of the two diol forms (anionic and ketone)



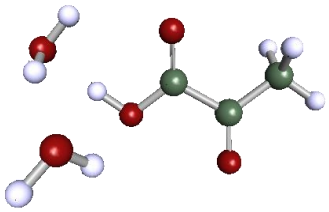
Anion diol + H_2O Conformer 1 | Anion diol + H_2O Conformer 2 | Anion diol + H_2O Conformer 3 | Ketone diol + H_2O Conformer 1 | Ketone diol + H_2O Conformer 2

Geometry	Energy (eV)	Energy (nm)	Description	Oscillator strength	Dipole moment (Debye)
Anion diol + H_2O	6.11	203	$n\pi^*$	0.00010469	1.70

Conformer 1					
Anion diol + H_2O Conformer 2	6.03	206	nπ*	0.00037199	2.18
Anion diol + H_2O Conformer 3	6.20	200	nπ*	0.00007862	1.84
Ketone diol + H_2O Conformer 1	5.77	215	nπ*	0.00166720	2.72
Ketone diol + H_2O Conformer 2	5.70	218	nπ*	0.00111908	1.81

The first excited state of the anion diol is at 213 nm, see Table 4 in the manuscript. Hydration of the anion diol was simulated by adding the water molecule at three different locations of the anion diol. The calculated vertical excitation energies are shifted only slightly, and do therefore not fall above 290 nm, the experimentally and atmospherically relevant region. The same is true for the ketone diol. The first excited state of the ketone diol is at 218 nm. The hydration affects the vertical excitation energies even less than for the anion diol. The monohydrated ketone diol absorbs at 215 nm or 218 nm depending on the location of the water molecule.

2. <u>Tt conformer with two water molecules</u>



State	Energy (eV)	Energy (nm)	Description	Oscillator strength	Dipole moment (Debye)
S1	3.42	362	nπ*	0.00000340	2.06
S2	5.24	237	nπ*	0.00020717	3.24

The Tt conformer with two water molecules is lower in energy by about 0.2 eV than the Tc conformer with two water molecules. However, to be consistent with the other clusters sizes we have depicted in the manuscript the Tc conformer. The excitation energy for the first excited state is tabulated here, and the difference in excitation energy is only 3 nm (359 nm vs. 362 nm) between the two different conformers.

3. Comparison of vertical excitation energy and properties using different basis sets

Tc conformer of pyruvic acid, MP2/def-SV(P) optimization, ADC(2)/def-SV(P) excitation

State	Energy (eV)	Energy (nm)	Description	Oscillator strength	Dipole moment (Debye)
S1	3.53	351	npi*	0.00000355	2.03
S2	5.37	231	npi*	0.00055507	1.33

Tc conformer of pyruvic acid, MP2/cc-pVDZ optimization, ADC(2)/cc-pVDZ excitation

State	Energy (eV)	Energy (nm)	Description	Oscillator strength	Dipole moment (Debye)
S1	3.47	357	npi*	0.00000035	1.86
S2	5.28	235	npi*	0.00044061	1.33

Anion, MP2/def-SV(P) optimization, ADC(2)/def-SV(P) excitation

State	Energy (eV)	Energy (nm)	Description	Oscillator strength	Dipole moment (Debye)
S1	3.25	382	npi*	0.00004174	12.78
S2	3.89	319	npi*	0.00000669	9.35

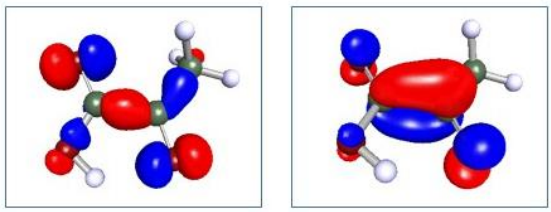
Anion, MP2/cc-pVDZ optimization, ADC(2)/cc-pVDZ excitation

State	Energy (eV)	Energy (nm)	Description	Oscillator strength	Dipole moment (Debye)
S1	3.18	390	nπ*	0.00000638	12.58
S2	3.80	327	nπ*	0.00000407	9.22

The different basis sets predict similarly the first two excitation energies, differing only by maximal 10 nanometers. The excited states have the same descriptions in terms of orbital transitions, and the oscillator strengths and dipole moments show the same trend.

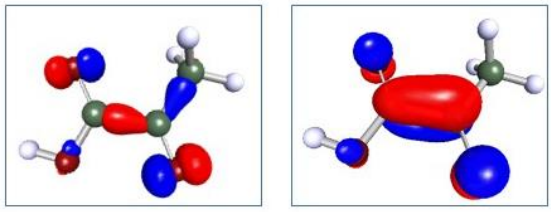
4. Molecular orbitals

Tc conformer



HOMO LUMO

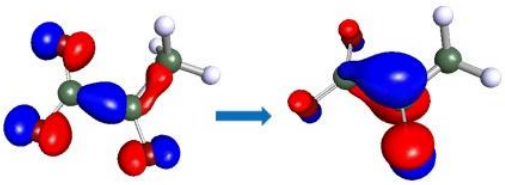
Tt conformer



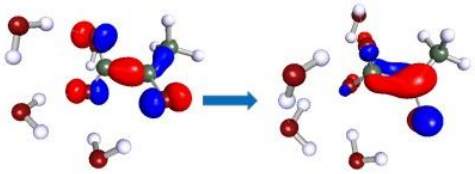
HOMO LUMO

Highest occupied molecular orbital (HOMO) and lowest occupied molecular orbital (LUMO) for the Tc and the Tt conformer of pyruvic acid.

Anion



Anion + 4 Water molecules



Orbitals involved in the first excitation transition of the anion and the anion cluster with 4 water molecules.

5. Cartesian coordinates

Tc conformer

C	1.3917787	-0.0000013	-0.5770865
C	0.0363784	-0.0000118	0.0659895
O	-1.0344907	-0.0000312	-0.5350214
C	0.0014661	0.0000047	1.6101654
O	-1.2509833	-0.0000101	2.0884458
O	1.0033181	0.0000420	2.2936445
H	-1.8118524	-0.0000067	1.2843745
H	1.2914039	0.0000117	-1.6703250
H	1.9569699	0.8824061	-0.2362773
H	1.9569603	-0.8824245	-0.2362996

Tt conformer

C	0.0112009	0.0000087	0.0526507
C	0.0074840	0.0000106	1.5944285
C	1.3886314	-0.0000060	-0.5618872
O	-1.0354403	0.0000197	-0.5740340
O	1.0264243	0.0000432	2.2606029
O	-1.2402505	-0.0000250	2.0954888

H	-1.1187265	-0.0000219	3.0628397
H	1.3028511	-0.0000046	-1.6566544
H	1.9507924	0.8831261	-0.2178721
H	1.9507732	-0.8831507	-0.2178728

Anion

C	0.0021935	0.0000060	0.0640691
C	0.0119912	0.0000144	1.5944708
O	1.0770557	0.0000094	2.2083258
C	-1.4111420	0.0000278	2.2711964
O	-1.4164704	0.0000551	3.5237334
O	-2.3530571	0.0000082	1.4270903
H	1.0352980	-0.0000042	-0.3232995
H	-0.5568022	-0.8777003	-0.2974421
H	-0.5567878	0.8777175	-0.2974522

Ketone diol

O	0.5897677	1.7460832	1.8338009
C	-0.0841570	0.8237784	1.4294224
O	-0.9756877	0.1436488	2.1946080
H	-0.9386554	0.5679333	3.0706778
C	-0.0637714	0.2470353	0.0040880
O	-0.0112170	-1.1583250	0.0391927
H	-0.7602911	-1.4252117	0.5963652
O	-1.2788608	0.7083367	-0.5554129
C	1.1510490	0.7276584	-0.7662500
H	2.0762130	0.3974388	-0.2722690
H	1.1207806	0.2977324	-1.7806562
H	1.1433985	1.8243156	-0.8250701
H	-1.2777894	0.3810959	-1.4685887

Anion diol

C	0.6862928	1.8437524	1.8352727
C	-0.2565258	0.7556449	1.3763841
O	-1.1880792	0.4905481	2.4273613
C	0.3947112	-0.6084982	0.9984257
O	-0.5136807	-1.4271271	0.6172643
O	1.6302436	-0.7574719	1.0975283
O	-0.9534465	1.2147016	0.2175498
H	-1.2421553	0.3497386	-0.1347973
H	1.4117675	2.0590328	1.0371554

H	0.1161056	2.7575457	2.0775821
H	1.2347968	1.5004358	2.7245206
H	-1.4949900	-0.3910146	2.1392351

Anion ketone + H_2O

C	1.4052394	0.0169782	-0.6353602
C	-0.0168970	-0.0052992	-0.0869626
O	-0.9856267	-0.0159048	-0.8393139
C	-0.1272686	-0.0132539	1.4736161
O	-1.2908864	-0.0311517	1.9443788
O	0.9993529	-0.0001840	2.0551479
H	1.3857681	0.0212392	-1.7363523
H	1.9339125	0.9002336	-0.2462904
H	1.9585635	-0.8542497	-0.2535172
O	-0.2471458	-0.0251946	4.6008168
H	0.4832281	-0.0135732	3.9538794
H	-0.9442901	-0.0326639	3.9196494

Anion + 2 H_2O

C	1.6054691	0.0505462	-0.6262841
C	0.1658758	-0.0743611	-0.1551026
O	-0.7521117	-0.1711924	-0.9659730
C	-0.0259036	-0.0679905	1.3972449
O	-1.2061785	-0.1692162	1.8293979
O	1.0598720	0.0410155	2.0307789
H	1.6431506	0.0371053	-1.7258332
H	2.0416400	0.9781279	-0.2265693
H	2.2020978	-0.7695126	-0.1997232
O	-0.2501137	-0.0361873	4.5574723
H	0.4843070	0.0192782	3.9194931
H	-0.9439712	-0.1109476	3.8807151
H	-2.8240169	-0.3323210	0.8834965
O	-3.4748920	-0.4036967	0.1587485
H	-2.8350858	-0.3563508	-0.5638807

Anion + 3 H_2O

C	1.6202467	0.1071964	-0.6474156
C	0.1902539	-0.0789907	-0.1767306
O	-0.6100660	-0.7521221	-0.8265109
C	-0.1426390	0.5500005	1.2003840

O	-1.2860520	1.0764861	1.3311405
O	0.7933257	0.4330559	2.0296621
H	1.7705080	-0.3855999	-1.6190499
H	1.8457746	1.1837978	-0.7242196
H	2.2936508	-0.3008016	0.1196770
O	-0.2119068	-0.9453598	4.3999869
H	0.2314697	-0.4256847	3.7083465
H	-1.1362257	-0.8568923	4.1124069
H	-2.7488735	0.2100128	0.6222742
O	-3.2674477	-0.5930525	0.4076334
H	-2.5547105	-1.0624218	-0.0530568
O	-2.7873311	-0.2050929	3.2720197
H	-3.0510823	-0.6533400	2.4493501
H	-2.2173128	0.4821108	2.8746281

Anion + 4 H_2O

C	1.3307845	0.2866572	-0.8741412
C	0.0633716	-0.2692164	-0.2611862
O	-0.5406683	-1.2258051	-0.7464882
C	-0.3588919	0.4475415	1.0332852
O	-1.5386825	0.9142640	1.0737092
O	0.5645014	0.5442762	1.8806076
H	1.5076054	-0.1486351	-1.8681384
H	1.2478661	1.3845995	-0.9155386
H	2.1655958	0.0587754	-0.1935706
O	-0.2764643	-0.4462717	4.5147664
H	0.1176490	-0.0407341	3.7255862
H	-1.1957403	-0.5402822	4.2131366
H	-2.8604360	-0.3367210	0.5444725
O	-3.1804048	-1.2588018	0.5033435
H	-2.3744568	-1.6484438	0.1272101
O	-2.8702547	-0.2839585	3.2315715
H	-3.0235408	-0.9026111	2.4955473
H	-2.4122689	0.4183410	2.7335578
O	0.2815060	3.2738782	0.7372936
H	0.7114694	2.6558153	1.3494361
H	-0.5995809	2.8672247	0.7333537

Anion + 5 H_2O

C	-1.1510909	0.7332814	0.9000277
H	-0.6585808	-0.1715139	0.5163835
H	-0.4448591	1.3325507	1.4977447

H	-1.9877746	0.4799723	1.5667613
C	-1.6783007	1.5683137	-0.2488523
O	-1.5881695	1.1817677	-1.4128699
C	-2.3748989	2.8914510	0.1608595
O	-2.1974012	3.8924367	-0.5823469
O	-3.0411117	2.7864911	1.2303278
O	-5.1731682	4.4964442	1.9079878
H	-5.6850788	3.7889793	1.4660649
H	-4.2942360	4.0699463	1.8624577
O	-5.8086912	2.1831036	0.4272963
H	-5.6860810	2.5958579	-0.4597638
H	-4.8855102	2.0991974	0.7162096
O	-5.3420460	3.5551493	-1.9147785
H	-4.5369261	3.3290717	-2.4197382
H	-5.0734033	4.3958549	-1.4825707
H	-2.4807621	2.2620708	-2.8837315
O	-2.7864611	3.1336900	-3.1833340
H	-2.4581739	3.6426682	-2.4161766
H	-3.4935541	5.2274759	-0.4455282
O	-4.3366438	5.7241522	-0.4657660
H	-4.7204597	5.4529125	0.3948318

Ketone + H_2O

C	1.3546229	-0.0347475	-0.5366834
C	-0.0357912	0.0095714	0.0327544
C	-0.1038423	0.0008624	1.5787266
O	0.9285426	-0.0868593	2.2180125
O	-1.0472426	0.0421790	-0.6612507
O	-1.3048353	0.0815221	2.1396681
H	-2.0390526	0.1618316	1.4778544
H	1.3065243	-0.0310827	-1.6327151
H	1.9300980	0.8277363	-0.1675866
H	1.8750277	-0.9316989	-0.1689207
O	-3.5212145	0.2777262	0.5940047
H	-3.0287016	0.2235316	-0.2398655
H	-4.0127724	-0.5543442	0.6161715

Ketone + 2 H_2O (Tc conformer)

C	-2.3026529	0.3518473	-0.0927808
C	-0.8499465	0.3618995	-0.4745509
O	-0.2535970	1.3616295	-0.8591441
C	-0.1323052	-1.0012127	-0.3391476

O	1.1417793	-1.0637969	-0.7043952
O	-0.7486430	-1.9590953	0.0984156
H	1.5030319	-0.2005715	-1.0493352
H	-2.7243014	1.3570136	-0.2159016
H	-2.8418692	-0.3771334	-0.7167140
H	-2.4084177	0.0064515	0.9466348
O	2.4010056	1.0870364	-1.6577261
H	3.0819613	1.4141533	-1.0543385
H	1.6792537	1.7263436	-1.5570612
O	1.4857005	-3.9878419	0.2112156
H	0.5915631	-3.6308759	0.2986275
H	1.9131706	-3.2450251	-0.2314133

Ketone + 2 H_2O (Tt conformer)

C	1.6925223	-0.3015947	-0.3220594
C	0.3667315	0.3987115	-0.1717993
O	-0.2359879	0.9509862	-1.0782139
C	-0.2281549	0.3499638	1.2481820
O	-1.2870790	1.1452179	1.3895384
O	0.2444906	-0.3706206	2.1178726
H	-1.6171135	0.9936168	2.3345109
H	2.0330155	-0.2289026	-1.3625590
H	2.4319723	0.1511833	0.3569930
H	1.5927391	-1.3545203	-0.0179172
O	-2.1976370	0.2950346	3.6773594
H	-1.4274246	-0.2866953	3.7774636
H	-2.8075437	-0.2468822	3.1367887
H	-3.1112438	-0.0919596	0.9215296
O	-3.5765081	-0.7250654	1.4897470
H	-4.5065267	-0.5230423	1.3253538

Ketone + 3 H_2O

C	-3.0681335	-0.4658624	0.4161748
C	-1.6229146	-0.2011241	0.1010146
C	-1.2279956	1.2893957	0.0281772
O	-1.9559922	2.1288107	0.5273499
O	-0.7852753	-1.0848175	-0.0467396
O	-0.0674042	1.5642357	-0.5504984
O	1.4468572	0.0315178	-1.8919728
O	1.9104989	-2.1408185	-0.2434305
O	2.6351940	2.4453550	-1.1167944
H	0.3765843	0.7728283	-1.0185205

H	-3.2458281	-1.5465607	0.4806554
H	-3.3326338	0.0362073	1.3583984
H	-3.7018153	-0.0153080	-0.3640128
H	2.1255480	0.7272465	-1.7945775
H	1.7976542	-0.7294649	-1.3858812
H	1.8048266	-2.9584997	-0.7475069
H	0.9999686	-1.9463540	0.0313605
H	3.0124500	2.3710236	-0.2303150
H	1.7132978	2.6787584	-0.9225672

Ketone + 4 H_2O

C	-2.7698378	1.2732242	-1.2241083
C	-1.3541667	1.7178903	-0.9912449
C	-1.1097043	3.2379932	-1.0638858
O	-1.9878633	4.0045484	-0.7091351
O	-0.4411228	0.9537784	-0.6836283
O	0.1026161	3.6203866	-1.4477179
O	1.6913802	2.0366592	-2.6041252
O	3.5948969	3.4423893	-1.3978659
O	2.2850284	1.3956510	0.1544021
O	1.9973097	5.6740609	-0.8636991
H	0.6669063	2.8708298	-1.8864874
H	-2.8562187	0.1890160	-1.0732682
H	-3.4350290	1.8266719	-0.5433221
H	-3.0716279	1.5436843	-2.2502795
H	3.3680662	2.9031457	-0.6216171
H	3.1755713	4.3047489	-1.1934697
H	2.4885149	2.5845877	-2.3582799
H	1.8484822	1.2513516	-2.0575580
H	2.4675031	0.6597164	0.7516687
H	1.3188704	1.3617235	0.0480460
H	1.8505043	5.8805855	0.0687141
H	1.1742664	5.2161413	-1.1091344

Anion diol + H_2O Conformer 1

C	-1.9718656	0.1336021	0.1484848
C	-0.4511496	0.0521079	0.0720844
O	0.0740973	1.3533997	-0.1397217
C	0.0497826	-0.8396677	-1.1104629
O	0.2541156	-0.2123036	-2.1851084
O	0.2236112	-2.0521246	-0.8106634
O	0.0438443	-0.5303591	1.2679213

H	0.3118157	-1.4039248	0.8911471
H	-2.3915037	-0.8747991	0.2925806
H	-2.2612167	0.7735856	0.9987308
H	-2.3682356	0.5660934	-0.7840328
H	0.3546450	1.2338025	-1.0799061
O	1.5026036	1.6979289	2.3162527
H	1.1828728	1.9430431	1.4333144
H	1.1647842	0.7883478	2.2944633

Anion diol + H_2O Conformer 2

C	-1.6516361	0.2034358	0.4478872
C	-0.1942242	-0.0732804	0.8096322
O	0.5119945	1.1637716	0.8339510
C	0.5016448	-1.0136917	-0.2286013
O	1.0583682	-0.4289938	-1.2082998
O	0.4627816	-2.2357832	0.0608063
O	-0.1357827	-0.7106113	2.0670642
H	0.1076260	-1.6127556	1.7607236
H	-2.2053223	-0.7484383	0.4148296
H	-2.0962195	0.8469473	1.2261369
H	-1.7163680	0.7083315	-0.5267240
H	1.1691409	0.9993364	0.1288670
O	-0.1045595	2.0474333	-1.9281224
H	-0.1533017	2.2309288	-0.9791838
H	0.2910889	1.1522146	-1.8711468

Anion diol + H_2O Conformer 3

C	-1.9277616	0.6857313	0.9297494
C	-0.3987590	0.6576308	0.9141418
O	0.0914496	1.9709815	0.7438066
C	0.1315926	-0.2156491	-0.2610249
O	0.3378993	0.4094086	-1.3411014
O	0.3156609	-1.4351440	0.0195971
O	0.0711001	0.1010236	2.1240504
H	0.3497336	-0.7787743	1.7943090
H	-2.3203182	-0.3364337	1.0533270
H	-2.2680735	1.3108662	1.7718653
H	-2.3046606	1.1106088	-0.0145135
H	0.3802330	1.9106863	-0.1907782
O	1.2806361	-1.9672362	-2.6166523
H	1.0362298	-2.1781399	-1.6981693
H	1.0500609	-1.0237459	-2.5496589

Ketone diol + H_2O Conformer 1

O	-1.0890466	0.8878651	-0.2050594
C	0.0012193	0.4401343	0.1233940
O	1.0808005	1.1768961	0.3993527
H	0.8092170	2.1317038	0.2924984
C	0.3001648	-1.0590663	0.2814173
O	1.5648677	-1.3701143	-0.2442686
H	2.1683475	-0.7263019	0.1603764
O	0.2579363	-1.2479880	1.6834516
C	-0.7185743	-1.9136227	-0.4458005
H	-0.6996419	-1.7034462	-1.5241552
H	-0.4670256	-2.9745616	-0.2914428
H	-1.7222777	-1.7076210	-0.0536667
H	0.4468698	-2.1894594	1.8169334
O	-0.1311181	3.5076789	-0.0447169
H	0.0034062	3.8394661	-0.9430923
H	-0.8709120	2.8804650	-0.1550896

Ketone diol + H_2O Conformer 2

O	-2.3211791	1.1783204	0.0419124
C	-1.1182295	1.2598121	0.1513332
O	-0.4521623	2.4299624	0.3291691
H	-1.1413040	3.1170795	0.3546904
C	-0.1257995	0.0893683	0.1158392
O	0.9611824	0.4238934	-0.7510499
H	1.2770152	1.2829715	-0.4240058
O	0.3063228	-0.0494270	1.4407148
C	-0.7702315	-1.1648470	-0.4408193
H	-1.0996483	-1.0036433	-1.4766291
H	-0.0395810	-1.9858212	-0.4123057
H	-1.6388529	-1.4270499	0.1765373
H	0.9621382	-0.7767345	1.4078079
O	2.3020412	-1.7472441	0.5010032
H	3.2112637	-1.6228342	0.8010206
H	2.1922336	-1.0606345	-0.1813843