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

Supporting Information for

Hydration of the simplest α-keto acid: a rotational spectroscopic and *ab initio* study of the pyruvic acid-water complex

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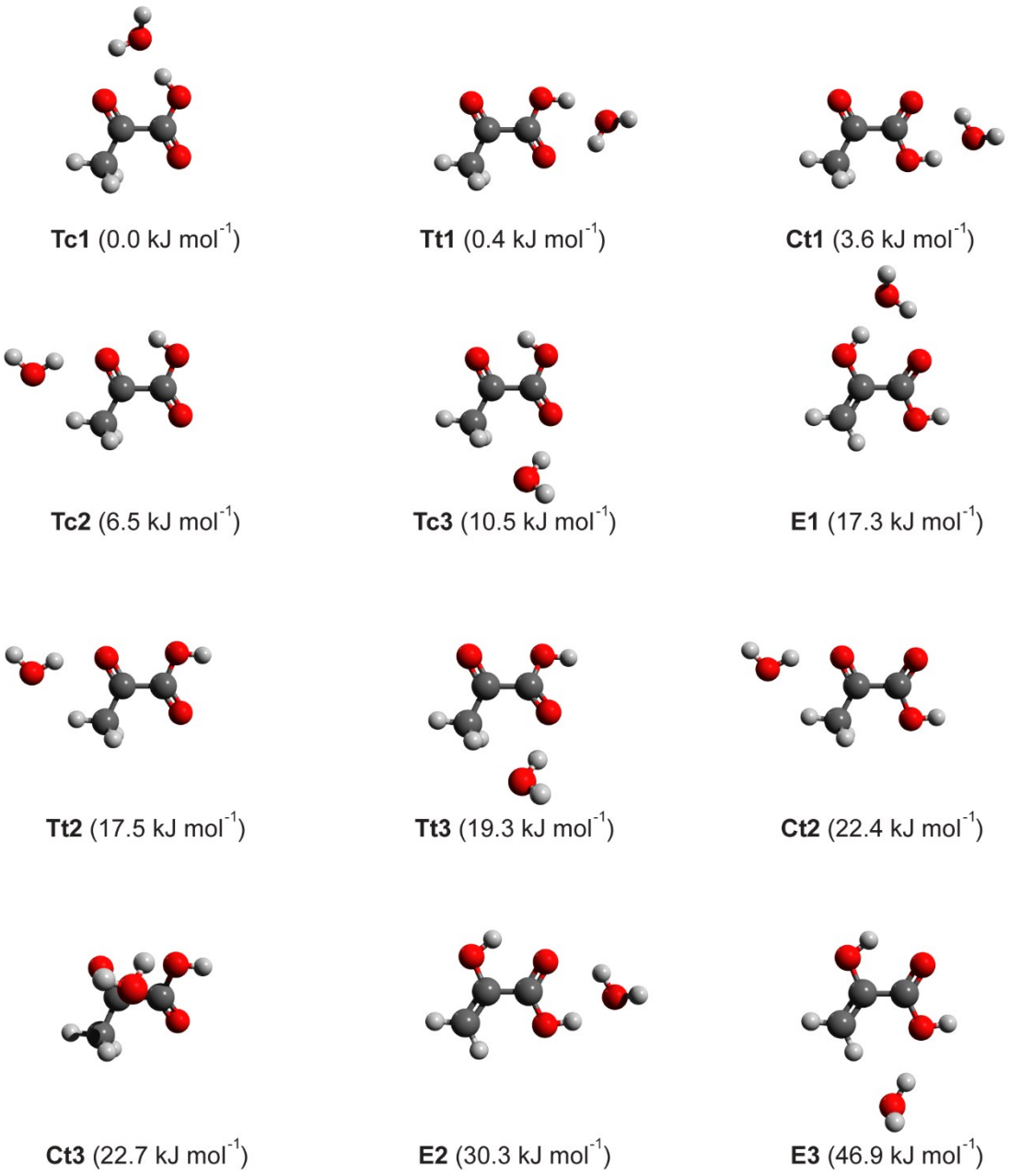

Fig. S1 Geometries of twelve isomers of the pyruvic acid monohydrate, calculated at the B3LYP-D3BJ/6-311++G(d,p) level of theory and arranged in order of increasing relative energy. Zero-point- and counterpoise-corrected energies relative to *Tc1* are given in parentheses. At this level of theory, each of *Tt2* and *Ct2* exhibits a single imaginary frequency corresponding to a large-amplitude motion with a negligible effect on the zero-point energy, likely due to the choice of integration grid ("Grid=FineGrid" in Gaussian); at the MP2/6-311++G(d,p) level of theory, neither isomer exhibits an imaginary frequency.

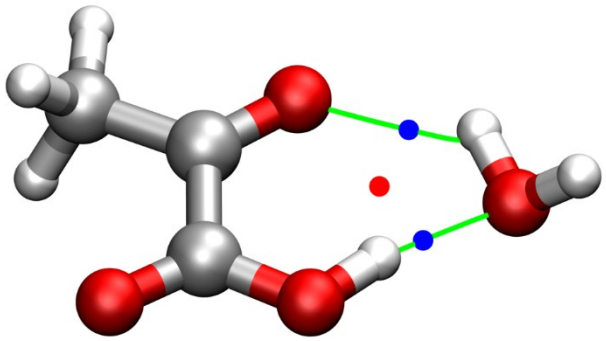

Fig. S2 Molecular graph of the observed pyruvic acid monohydrate, based on a topological atoms-in-molecules analysis of the wavefunction calculated at the MP2/aug-cc-pVTZ level of theory. Intermolecular bond critical points are shown in blue, the ring critical point is shown in red, and the intermolecular bond paths are shown in green. For clarity, the paths between the ring critical point and the surrounding bond critical points are omitted.

Table S1 Cartesian coordinates of the three most stable isomers of pyruvic acid-water complex, optimized at the MP2/aug-cc-pVTZ level of theory

	Tc1			*Tt1*			*Ct1*		
	x	*y*	*z*	*x*	*y*	*z*	*x*	*y*	*z*
C	-0.61162	-0.73801	-0.01182	1.434583	0.109984	0.00019	1.440862	-0.07826	0.000772
C	-0.56543	0.803584	-0.00724	-0.095443	-0.049291	-0.009293	-0.10109	-0.14527	0.005739
O	0.416108	-1.39375	-0.08243	1.936954	1.215204	-0.020309	2.060761	-1.12109	0.031844
O	0.631976	1.36834	-0.0051	-0.737182	1.104399	0.012975	-0.65157	1.06958	0.053158
O	-1.59938	1.436586	-0.01427	-0.616104	-1.156148	-0.036999	-0.71285	-1.19413	-0.02944
C	-1.97682	-1.33604	0.062974	2.201098	-1.17624	0.030554	2.072549	1.280262	-0.04297
H	-1.90372	-2.41872	0.055481	3.264591	-0.960563	0.038411	3.152554	1.172117	-0.05624
H	-2.57424	-0.97861	-0.77502	1.937196	-1.782282	-0.835574	1.756637	1.862962	0.821738
H	1.373847	0.717066	0.012745	-1.706569	0.900194	0.004628	-1.63546	0.946281	0.056483
H	-2.47661	-0.98501	0.965326	1.918392	-1.752499	0.91108	1.730381	1.819647	-0.92572
O	2.888984	-0.16043	0.094662	-3.173494	-0.041446	0.062552	-3.16137	0.127647	-0.05944
H	2.449407	-0.99762	-0.10486	-2.622399	-0.835551	-0.036034	-2.67182	-0.71156	-0.01994
H	3.583142	-0.06015	-0.56342	-3.841797	-0.093763	-0.627076	-3.84045	0.071487	0.619251

Table S2 Measured transition frequencies of the 0^- and 0^+ states of the pyruvic acid-water complex

0^-									0^+								
J'	K_a'	K_c'	J''	K_a''	K_c''	Sym.	Frequency/MHz	Residual[a]/MHz	J'	K_a'	K_c'	J''	K_a''	K_c''	Sym.	Frequency/ MHz	Residual[a]/MHz
3	0	3	2	1	2	A	7096.4221	0.0041	3	0	3	2	1	2	A	7096.4221	-0.0052
3	0	3	2	1	2	E	7096.6807	0.0053	3	0	3	2	1	2	E	7096.6807	0.0086
2	1	2	1	0	1	E	7147.1684	-0.0010	2	1	2	1	0	1	E	7147.1684	-0.0022
2	1	2	1	0	1	A	7147.5695	-0.0072	2	1	2	1	0	1	A	7147.5695	-0.0015
3	1	3	2	1	2	A	7951.2362	-0.0082	3	1	3	2	1	2	A	7951.2362	-0.0082
3	1	3	2	1	2	E	7951.2362	0.0014	3	1	3	2	1	2	E	7951.2362	0.0044
3	2	2	3	1	3	E	8055.5030	0.0030	3	2	2	3	1	3	E	8055.5779	0.0026
3	2	2	3	1	3	A	8057.2079	0.0180	3	2	2	3	1	3	A	8057.2239	-0.0206
3	0	3	2	0	2	E	8441.0548	0.0037	3	0	3	2	0	2	E	8441.0548	0.0024
3	0	3	2	0	2	A	8441.1454	-0.0018	3	0	3	2	0	2	A	8441.1454	-0.0054
3	2	2	2	2	1	A	8879.3144	-0.0079	3	2	2	2	2	1	A	8879.3275	0.0002
3	2	2	2	2	1	E	8881.7144	0.0053	3	2	2	2	2	1	E	8881.6989	0.0161
3	1	3	2	0	2	E	9295.6272	0.0167	3	1	3	2	0	2	E	9295.6076	-0.0045
3	1	3	2	0	2	A	9295.9819	0.0082	3	1	3	2	0	2	A	9295.9622	-0.0057
4	2	3	4	1	4	E	9307.3108	0.0022	4	2	3	4	1	4	E	9307.3966	0.0023
4	2	3	4	1	4	A	9308.6183	-0.0054	4	2	3	4	1	4	A	9308.7011	0.0029
3	2	1	2	2	0	E	9315.0265	-0.0001	3	2	1	2	2	0	E	9315.0500	0.0029
3	2	1	2	2	0	A	9317.4843	-0.0131	3	2	1	2	2	0	A	9317.5037	-0.0003
4	0	4	3	1	3	A	10025.9509	0.0020	4	0	4	3	1	3	A	10025.9509	-0.0113
4	0	4	3	1	3	E	10026.0907	0.0059	4	0	4	3	1	3	E	10026.0907	0.0025
4	0	4	3	0	3	E	10880.6474	0.0031	4	0	4	3	0	3	E	10880.6474	-0.0005
4	0	4	3	0	3	A	10880.7725	-0.0029	4	0	4	3	0	3	A	10880.7725	-0.0070
4	1	4	3	0	3	E	11350.4252	0.0097	4	1	4	3	0	3	E	11350.4119	-0.0020
4	1	4	3	0	3	A	11350.7254	-0.0011	4	1	4	3	0	3	A	11350.7141	-0.0040
2	2	1	1	1	0	A	11900.3030	-0.0090	2	2	1	1	1	0	A	11900.3650	0.0033
5	0	5	4	1	4	A	12752.1617	0.0026	5	0	5	4	1	4	A	12752.1617	-0.0086
5	0	5	4	1	4	E	12752.2033	0.0048	5	0	5	4	1	4	E	12752.2033	0.0003
5	1	5	4	1	4	E	12983.7041	0.0040	5	1	5	4	1	4	E	12983.7041	0.0080
5	1	5	4	1	4	A	12983.7563	-0.0107	5	1	5	4	1	4	A	12983.7563	-0.0089
5	0	5	4	0	4	E	13221.9726	0.0028	5	0	5	4	0	4	E	13221.9726	0.0036
5	0	5	4	0	4	A	13222.1066	-0.0037	5	0	5	4	0	4	A	13222.1066	-0.0025
5	1	5	4	0	4	E	13453.4724	0.0011	5	1	5	4	0	4	E	13453.4724	0.0104
5	1	5	4	0	4	A	13453.7093	-0.0089	5	1	5	4	0	4	A	13453.7093	0.0054
3	2	2	2	1	1	E	14284.1384	0.0029	3	2	2	2	1	1	E	14284.2379	0.0225
3	2	2	2	1	1	A	14285.8726	-0.0139	3	2	2	2	1	1	A	14285.9307	-0.0106

[a] (Measured transition frequency) – (Fit transition frequency).

Completion of Ref. 23.

M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian 09, Revision D.01, Gaussian, Inc., Wallingford, CT, **2013**.