Electronic Supplementary Material (ESI) for Materials Advances.

SUPPLEMENTARY INFORMATION

Organic acids under pressure: elastic properties, negative mechanical phenomena and pressure induced phase transitions in the lactic, maleic, succinic and citric acids

Francisco Colmenero[a*]

[a] Instituto de Estructura de la Materia (IEM-CSIC), 28006 Madrid, Spain

[*] E-mail: francisco.colmenero@iem.cfmac.csic.es

Appendix A. First-principles solid-state methods

The crystal structure and mechanical properties of the selected organic acids were modeled employing the Cambridge Serial Total Energy Program (CASTEP),[1] a component of the Materials Studio program suite.[2] The theoretical solid-state treatment employed in this work is based on Periodic Density Functional Theory using large plane wave basis sets and pseudopotential functions to describe the internal atomic electrons.[3] The computations were carried out using the Perdew-Burke-Ernzerhof (PBE) energy-density functional[4] supplemented with Grimme's empirical dispersion correction.[5] The specific pseudopotentials utilized were standard norm-conserving pseudopotentials[6] from CASTEP package. The unit-cell parameters and the associated atomic positions were fully optimized by means of the Broyden–Fletcher–Goldfarb–Shanno (BFGS) technique[7] with a convergence threshold on atomic forces of 0.01 eV/Å. The calculation parameters, the plane wave kinetic energy cutoffs, ε, and k-point meshes,[8] employed are given in Table S.1 together with the most important material data of the selected organic acids. These calculation parameters were chosen to attain well converged crystal structures, energies and mechanical properties. The X-ray powder diffraction patterns of the considered materials were determined from the computed and experimental crystal structures[9] using the software REFLEX included in Materials Studio package of programs.[2]

The elasticity tensor[10] elements required to calculate the mechanical properties of the materials under consideration and to study the mechanical stability of their crystal structures were determined using the finite deformation method.[11] The computation of the elasticity tensors of these materials was very expensive due to the fact that the required finite structure deformations lead to unsymmetrical crystal structures. The last feature imposes that all the required calculations must be carried out without exploitation of the crystal symmetry. Despite of this difficulty, the deformed crystal structures were optimized with the same convergence parameters as the equilibrium structure.

For each material, the unit-cell volumes in the vicinity of the equilibrium structure were calculated by optimizing the crystal structure under eighteen different external isotropic pressures with values in the range −1.0 to 11.0 GPa. The computed lattice volumes and associated hydrostatic pressures were then adjusted to a 4th order Birch-Murnaghan equation of state[12] (BM-EOS) in order to extract the derivatives of the bulk modulus with respect to pressure. Angel's EOSFIT 5.2 code[13-14] was employed for fitting the pressure-volume data to the selected equation of state. The structural optimizations under pressure were also performed using the BFGS method.

The computation of the matrix elements of the elastic tensor and all crystal structure optimizations performed in this work were carried out with stringent convergence tolerances in the variation of the total energy, maximum atomic force, maximum atomic displacement and maximum stress of 0.5×10^{-5} eV/atom, 0.01 eV/Å, 0.5×10^{-3} Å and 0.02 GPa, respectively. These convergence parameters correspond to the standard "hyperfine" optimization in CASTEP. The spatial representations of the elastic properties as a function of the orientation of the applied strain were performed with the ElAM software.[15]

Appendix B. Mechanical stability conditions for crystals with orthorhombic space symmetry

For crystalline materials having orthorhombic space symmetry, a closed set of necessary and sufficient mechanical stability conditions is known. These conditions are:[16]

$$C_{ii} > 0 \ (i = 1, 4, 5, 6) \qquad (B.1)$$

$$C_{11}C_{22} - C_{12}^2 > 0 \qquad (B.2)$$

$$C_{11}C_{22}C_{33} + 2\,C_{12}C_{13}C_{23} - C_{11}C_{23}^2 - C_{22}C_{13}^2 - C_{33}C_{12}^2 > 0 \qquad (B.3)$$

where C_{ij} are elements of the matrix representation of the elasticity tensor.

Table S.1. Material data and calculation parameters.

Material	Structural formula	Crystal system	Space group	ε(eV)	k-mesh
L-(+)-Lactic acid	$C_3H_6O_3$	Orthorhombic	$P2_12_1\,2_1\,(no.\,19)$	950	5 × 3 × 3
Maleic acid	$C_4H_4O_4$	Monoclinic	$P\,2_1/c\,(\,no.\,14)$	950	4 × 3 × 4
Succinic acid	$C_4H_6O_4$	Monoclinic	$P\,2_1/c\,(\,no.\,14)$	950	4 × 3 × 2
Citric acid	$C_6H_8O_7$	Monoclinic	$P\,2_1/c\,(\,no.\,14)$	950	2 × 5 × 3
Citric acid monohydrate	$C_6H_8O_7.H_2O$	Orthorhombic	$P2_12_1\,2_1\,(no.\,19)$	950	5 × 3 × 2

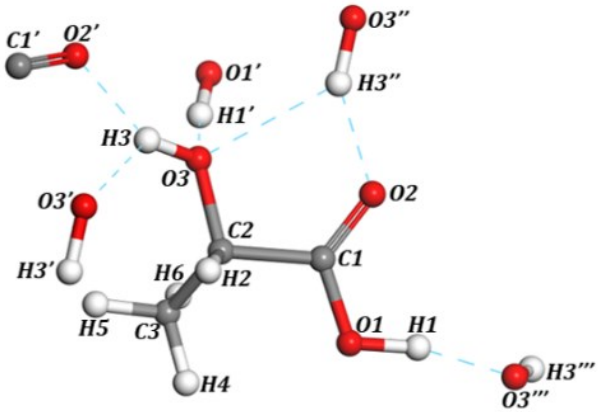

Fig. S.1. Atom labelling convention employed for the crystal structure of L-(+)-lactic acid.

Table S.2. Interatomic distances in L-(+)-lactic acid (in Å).

Distance	Exp.[17]	Calc.
C-C		
C1-C2	1.519(1)	1.527
C2-C3	1.521(2)	1.531
C-O		
C1-O2	1.208(1)	1.228
C1-O1	1.320(1)	1.323
C2-O3	1.425(1)	1.425
C-H		
C2-H2	0.96(2)	1.101
C3-H4	1.02(2)	1.098
C3-H5	0.96(2)	1.097
C3-H6	0.98(2)	1.098
O-H		
O1-H1	0.79(2)	1.029
O3-H3	0.82(2)	0.994
Hydrogen bonds (Oi-Hj···Ok)		
O1···O3’’’	2.63	2.564
H1···O3’’’	1.85	1.552
O3···O2’	2.63	2.649
H3···O2’	2.00	1.745
O3···O3’	3.15	3.126
H3···O3’	2.46	2.385

Table S.3. Interatomic angles in L-(+)-lactic acid (in degrees).

Angle	Exp.[17]	Calc.
C-C-C		
C1-C2-C3	112.60(9)	113.59
O-C-O		
O1-C1-O2	123.9(1)	123.84
O-C-C		
O1-C1-C2	111.87(9)	112.38
O2-C1-C2	124.24(9)	123.75
O3-C2-C1	106.44(9)	107.01
O3-C2-C3	111.7(1)	112.28
C-O-H		
C1-O1-H1	112(1)	111.64
C2-O3-H3	110(1)	112.75
O3-C2-H2	110(1)	109.50
H-C-C		
H2-C2-C1	107(1)	105.74
H2-C2-C3	109(1)	108.47
H4-C3-C2	107(1)	109.79
H5-C3-C2	108(1)	108.44
H6-C3-C2	110(1)	110.94
H-C-H		
H4-C3-H5	109(1)	109.05
H5-C3-H6	109(2)	108.97
H6-C3-H4	114(1)	109.62
Hydrogen bonds (Oi-Hj···Ok)		
O1-H1···O3''	168	166.59
O3-H3···O2'	145	149.36
O3-H3···O3'	143	130.75

Table S.4. Unit-cell volume and lattice parameters of lactic acid under the effect of different external isotropic pressures.

P (GPa)	Vol. ($Å^3$)	a (Å)	b (Å)	c (Å)
-0.7420	461.4547	5.6977	8.4851	9.5450
-0.4887	438.6226	5.5578	8.3828	9.4145
-0.2519	426.7498	5.5072	8.2821	9.3562
0.0000	421.7510	5.4858	8.2410	9.3290
0.2445	416.7488	5.4580	8.2105	9.2998
0.5074	407.5064	5.4147	8.1267	9.2608
0.7476	401.4066	5.3848	8.1158	9.1851
1.0073	396.7155	5.3711	8.0874	9.1329
1.0258	397.2337	5.3508	8.1018	9.1633
1.0333	366.6874	5.3590	8.6451	7.9148
1.0562	366.6713	5.3590	8.6450	7.9146
1.1798	365.0062	5.3525	8.6359	7.8965
1.3190	361.4192	5.3300	8.6235	7.8633
1.4736	359.2115	5.3236	8.6109	7.8361
1.5301	358.9779	5.3220	8.6093	7.8347
1.5612	356.6913	5.2978	8.6421	7.7908
1.5790	356.7437	5.2973	8.6427	7.7921
1.6668	356.4926	5.2971	8.6408	7.7886
1.8364	353.8676	5.2838	8.6350	7.7560
1.9988	351.4619	5.2540	8.6224	7.7582
2.4980	345.1458	5.2048	8.6009	7.7101

Table S.5. Interatomic distances (in Å) in Phase II of lactic acid under the external isotropic pressures P = 1.5301 and P = 1.5612 GPa. The third column (Δ) gives the variation of the corresponding distances.

Distance	P = 1.5301 GPa	P = 1.5612 GPa	Δ(P = 1.5612 – P = 1.5301)
		C-C	
C1-C2	1.527	1.526	-0.001
C2-C3	1.521	1.520	-0.001
		C-O	
C1-O2	1.231	1.232	0.001
C1-O1	1.317	1.318	0.001
C2-O3	1.425	1.426	0.001
		C-H	
C2-H2	1.101	1.101	0.000
C3-H4	1.094	1.094	0.000
C3-H5	1.093	1.094	0.001
C3-H6	1.095	1.095	0.000
		O-H	
O1-H1	1.039	1.039	0.000
O3-H3	0.993	0.993	0.000
		Hydrogen bonds (Oi-Hj···Ok)	
O1···O3’’’	2.540	2.542	0.002
H1···O3’’’	1.502	1.504	0.002
O3···O2’	2.568	2.570	0.002
H3···O2’	1.655	1.659	0.004

Table S.6. Interatomic angles (in degrees) in Phase II of lactic acid under the isotropic pressures P = 1.5301 and P = 1.5612 GPa. The third column (Δ) gives the variation of the corresponding angles.

Angle	P = 1.5301 GPa	P = 1.5612 GPa	Δ(P = 1.5612 – P = 1.5301)
		C-C-C	
C1-C2-C3	113.50	113.64	0.140
		O-C-O	
O1-C1-O2	122.78	122.78	0.000
		O-C-C	
O1-C1-C2	114.46	114.58	0.120
O2-C1-C2	122.74	122.62	-0.120
O3-C2-C1	108.75	108.72	-0.030
O3-C2-C3	109.83	109.65	-0.180
		C-O-H	
C1-O1-H1	108.89	108.92	0.030
C2-O3-H3	114.77	114.67	-0.100
O3-C2-H2	110.01	110.00	-0.010
		H-C-C	
H2-C2-C1	105.76	105.63	-0.130
H2-C2-C3	108.91	109.10	0.190
H4-C3-C2	110.22	110.41	0.190
H5-C3-C2	108.67	108.82	0.150
H6-C3-C2	110.21	110.03	-0.180
		H-C-H	
H4-C3-H5	108.98	108.95	-0.030
H5-C3-H6	109.31	109.26	-0.050
H6-C3-H4	109.42	109.35	-0.070
		Hydrogen bonds (Oi-Hj⋯Ok)	
O1-H1⋯O3’’’	177.60	177.41	-0.190
O3-H3⋯O2’	150.77	150.56	-0.210

Table S.7. Unit-cell volume and lattice parameters of lactic acid under the effect of different external stresses applied in the direction of the minimum Poisson's ratio.

P (GPa)	Vol. (Å^3)	a (Å)	b (Å)	c (Å)
-0.2350	430.0824	5.5772	8.3769	9.2056
0.0000	421.7499	5.4858	8.2410	9.3290
0.2350	413.8439	5.3824	8.1255	9.4626
0.4700	408.9742	5.3191	8.0074	9.6021
0.7050	403.8430	5.2516	7.8402	9.8083
0.9400	400.0177	5.2009	7.7302	9.9497
1.4100	392.6972	5.0728	7.5612	10.2381
1.8800	385.3704	4.9307	7.3546	10.6270

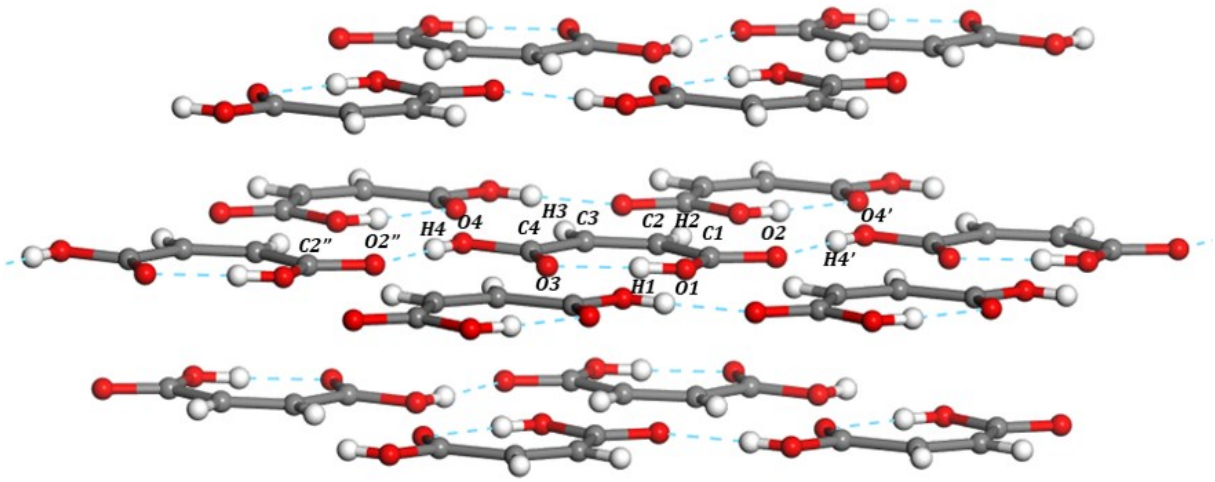

Fig. S.2. Atom labelling convention employed for the crystal structure of maleic acid.

Table S.8. Interatomic distances in maleic acid (in Å).

Distance	Exp.[18]	Calc.
	C-C	
C1-C2	1.482(3)	1.490
C2-C3	1.323(3)	1.349
C3-C4	1.470(3)	1.482
	C-O	
C1-O2	1.213(2)	1.243
C1-O1	1.307(2)	1.313
C4-O3	1.223(2)	1.248
C4-O4	1.304(2)	1.313
	C-H	
C2-H2	0.930(3)	1.091
C3-H3	0.93(2)	1.092
	O-H	
O1-H1	0.82(2)	1.049
O4-H4	0.82(3)	1.030
Hydrogen bonds (Oi-Hj···Ok)		
O1···O3	2.50	2.471
H1···O3	1.68	1.427
O4···O2''	2.65	2.573
H4···O2''	1.83	1.545

Table S.9. Interatomic angles in maleic acid (in degrees).

Angle	Exp.[18]	Calc.
C-C-C		
C1-C2-C3	132.1(2)	130.90
C2-C3-C4	128.3(2)	128.13
O-C-O		
O1-C1-O2	118.6(2)	118.70
O3-C4-O4	122.4(2)	122.40
O-C-C		
O1-C1-C2	121.1(2)	121.44
O2-C1-C2	120.3(2)	119.86
O3-C4-C3	124.9(2)	124.55
O4-C4-C3	112.6(2)	113.05
C-O-H		
C1-O1-H1	109.5	111.35
C4-O4-H4	109.5	110.33
H-C-C		
H2-C2-C1	114.0	112.62
H2-C2-C3	114.0	116.48
H3-C3-C2	115.8	117.32
H3-C3-C4	115.8	114.55
Hydrogen bonds (Oi-Hj···Ok)		
O1-H1···O3	174.7	172.74
O4-H4···O2''	178.2	174.72

Table S.10. Unit-cell volume and lattice parameters of maleic acid under the effect of different external isotropic pressures.

P (GPa)	Vol. ($Å^3$)	a (Å)	b (Å)	c (Å)	β (deg)
-0.8006	527.3746	7.4544	10.3861	8.1015	122.78
-0.7623	526.7096	7.4521	10.3802	8.0969	122.76
-0.5012	484.2005	7.0886	10.2796	7.6215	119.32
-0.2481	466.4498	6.9438	10.1885	7.4757	118.12
-0.0105	455.6945	6.8630	10.1248	7.3947	117.52
0.2549	446.9222	6.7911	10.0824	7.3259	117.00
0.5112	438.5673	6.7262	10.0346	7.2621	116.52
0.7298	431.7627	6.6721	9.9962	7.2086	116.10
0.8683	427.8133	6.6470	9.9718	7.1588	115.63
0.9376	426.4431	6.6343	9.9644	7.1516	115.58
0.9982	424.4145	6.6245	9.9495	7.1292	115.42
1.0942	422.6135	6.6070	9.9400	7.1182	115.31
1.1586	420.1964	6.6803	9.9378	6.9826	114.98
1.2535	418.2001	6.6767	9.9249	6.9545	114.84
1.3969	415.0499	6.6659	9.9044	6.9162	114.64
1.5017	413.2745	6.6613	9.8939	6.8913	114.50
1.6745	410.2431	6.6612	9.8768	6.8399	114.27
1.7650	408.8448	6.6894	9.8659	6.7862	114.10
1.8152	407.6153	6.6783	9.8560	6.7835	114.09
1.8939	406.2203	6.6552	9.8504	6.7813	113.97
2.0734	403.3437	6.6394	9.8124	6.7719	113.90
2.3035	400.0982	6.6282	9.8096	6.7124	113.55
2.3787	398.8401	6.6274	9.8024	6.6928	113.46
2.5093	397.3673	6.6248	9.7953	6.6710	113.37
2.5783	396.0132	6.6267	9.7855	6.6484	113.28
2.6640	394.7948	6.6558	9.7712	6.6066	113.24
2.8378	392.4459	6.6568	9.7519	6.5734	113.12
3.0097	390.4511	6.6560	9.7384	6.5454	113.03

Table S.11. Unit-cell volume and lattice parameters of maleic acid under the effect of different external stresses applied in the direction of the minimum Poisson's ratio.

P (GPa)	Vol. ($Å^3$)	a (Å)	b (Å)	c (Å)	β (deg)
-0.0945	461.4110	7.5491	10.1111	6.8517	118.08
-0.0684	458.6098	7.1289	10.1246	7.1605	117.46
-0.0297	455.9233	6.8663	10.1257	7.3949	117.53
-0.0106	455.6945	6.8630	10.1248	7.3947	117.52
0.0154	455.3501	6.8556	10.1283	7.3944	117.52
0.0290	455.3291	6.8556	10.1283	7.3942	117.52
0.0349	453.8096	6.8084	10.1388	7.4094	117.47
0.0426	454.0558	6.7788	10.1456	7.4453	117.53
0.0454	456.3706	6.6062	10.1462	7.7549	118.60
0.0542	457.4931	6.4929	10.1451	7.9841	119.55
0.0799	457.3797	6.4218	10.1573	8.1117	120.18
0.0932	457.2671	6.4205	10.1573	8.1114	120.18

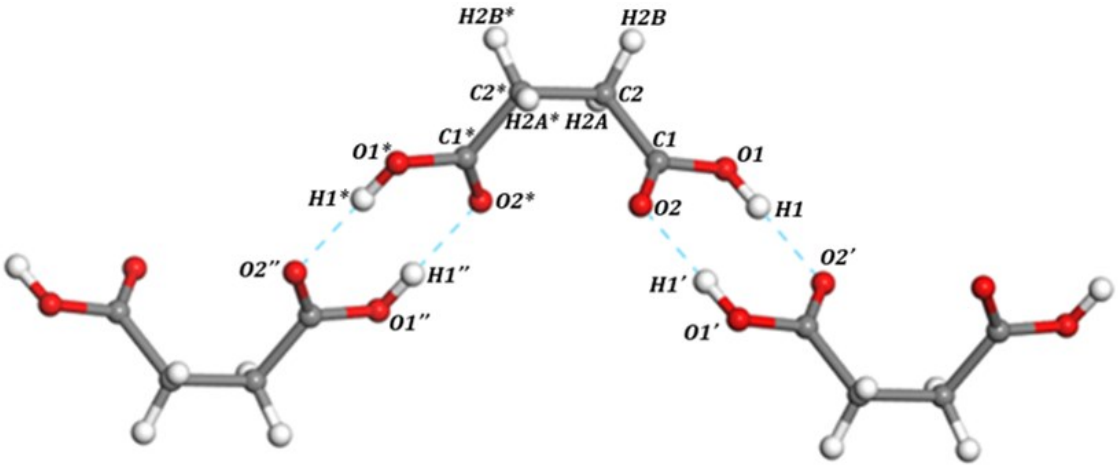

Fig. S.3. Atom labelling convention employed for the crystal structure of succinic acid.

Table S.12. Interatomic distances in succinic acid (in Å).

Distance	Exp.[19]	Calc.
	C-C	
C1-C2	1.497(2)	1.507
C2-C2*	1.519(3)	1.522
	C-O	
C1-O2	1.224(2)	1.241
C1-O1	1.317(2)	1.319
	C-H	
C2-H2A	0.99(2)	1.099
C2-H2B	0.99(2)	1.101
	O-H	
O1-H1	0.90(2)	1.026
Hydrogen bonds (Oi-Hj···Ok)		
O1···O2’	2.24	2.256
H1···O2’	1.77	1.570

Table S.13. Interatomic angles in succinic acid (in degrees).

Angle	Exp.[19]	Calc.
C-C-C		
C1-C2-C2*	113.17(12)	113.56
O-C-O		
O1-C1-O2	123.18(15)	123.54
O-C-C		
O1-C1-C2	112.74(13)	113.22
O2-C1-C2	124.08(14)	123.24
C-O-H		
C1-O1-H1	111.50(12)	111.25
H-C-C		
H2A-C2-C1	108.9	107.65
H2A-C2-C2*	108.9	111.97
H2B-C2-C1	108.9	106.34
H2B-C2-C2*	108.9	110.69
H-C-H		
H2A-C2-H2B	107.8	106.20
Hydrogen bonds (Oi-Hj···Ok)		
O1-H1···O2’	177.6	175.74

Table S.14. Unit-cell volume and lattice parameters of succinic acid under the effect of different external isotropic pressures.

P (GPa)	Vol. ($Å^3$)	a (Å)	b (Å)	c (Å)	β (deg)
-0.7576	515.9252	5.8566	8.3037	10.6134	91.68
-0.4929	497.4526	5.7654	8.2039	10.5179	90.67
-0.2557	484.9889	5.6949	8.1507	10.4484	89.97
-0.0102	477.4754	5.6594	8.1169	10.3944	89.62
0.2432	471.4804	5.6383	8.0785	10.3516	89.35
0.3628	466.2306	5.6076	8.0523	10.3269	88.98
0.5118	461.4479	5.6001	8.0101	10.2894	88.77
0.6364	457.9564	5.6005	7.9777	10.2530	88.60
0.7521	454.7242	5.6058	7.9373	10.2233	88.47
0.8564	452.2302	5.6058	7.9133	10.1987	88.36
0.9204	450.8201	5.5953	7.9110	10.1893	88.28
1.0568	447.8577	5.5897	7.8871	10.1640	88.14
1.1351	446.0917	5.5869	7.8721	10.1490	88.01
1.1788	445.7026	5.5780	7.8778	10.1489	88.02
1.2536	444.0519	5.5719	7.8684	10.1350	87.93
1.3324	442.4902	5.5747	7.8512	10.1171	87.83
1.3632	441.5836	5.5762	7.8412	10.1067	87.81
1.5212	439.4051	5.5572	7.8408	10.0927	87.67
1.6250	437.2665	5.5537	7.8260	10.0696	87.58
1.7506	435.1598	5.5493	7.8093	10.0514	87.45
1.8759	433.2097	5.5388	7.8009	10.0371	87.34
1.9941	431.1431	5.5400	7.7776	10.0180	87.21
2.0838	429.9725	5.5411	7.7667	10.0033	87.15
2.1448	429.2847	5.5304	7.7733	9.9986	87.11
2.1820	428.5386	5.5323	7.7618	9.9928	87.08
2.2432	427.3665	5.5337	7.7525	9.9752	87.04
2.5002	423.9550	5.5193	7.7321	9.9494	86.84
2.7385	420.6623	5.5105	7.7101	9.9181	86.64

Table S.15. Unit-cell volume and lattice parameters of succinic acid under the effect of different external stresses applied in the direction of the minimum Poisson's ratio.

P (GPa)	**Vol. ($Å^3$)**	a **(Å)**	b **(Å)**	c **(Å)**	β **(deg)**
-0.5007	505.0031	5.4983	8.4091	10.9282	91.89
-0.2444	486.7118	5.6525	8.1830	10.5226	90.21
-0.0101	477.4754	5.6594	8.1169	10.3944	89.62
0.2415	466.2120	5.7335	7.9838	10.1883	88.52
0.4985	459.6942	5.8325	7.8946	9.9895	88.02
0.5647	457.9056	5.8508	7.8746	9.9457	87.86
0.6113	456.6210	5.8656	7.8588	9.9134	87.76
0.6903	455.2336	5.8992	7.8322	9.8611	87.63
0.7456	453.9666	5.9234	7.8125	9.8191	87.52
0.8097	452.8322	5.9508	7.7922	9.7756	87.41
0.8680	451.5115	5.9660	7.7760	9.7433	87.31
0.9374	450.4890	5.9835	7.7606	9.7125	87.25
0.9905	449.7059	6.0005	7.7467	9.6861	87.19
1.0783	447.5038	6.0355	7.7175	9.6203	87.04
1.1283	447.3805	6.0354	7.7165	9.6190	87.04
1.1755	447.1988	6.0353	7.7151	9.6170	87.04
1.2435	445.1574	6.0371	7.6996	9.5903	86.95
1.3208	444.9526	6.0368	7.6978	9.5886	86.95
1.4036	449.4863	6.3589	7.5659	9.3484	87.99
1.5051	469.7676	8.1412	6.5638	8.9497	100.80
1.6285	466.2057	13.7380	4.7524	8.2590	120.16
1.7567	462.0475	14.2903	4.7968	8.2721	125.43
1.9055	459.5100	14.3349	4.7818	8.2412	125.57
1.9864	458.9763	14.5162	4.8043	8.1340	125.99
2.5014	449.4902	14.5495	4.7559	8.0756	126.45
2.9980	442.9805	14.7432	4.7263	8.0087	127.46

Table S.16. Interatomic distances (in Å) in succinic acid under the external stresses with P = 1.404 and P = 1.757 GPa applied in the direction of the minimum Poisson's ratio. The third column (Δ) gives the variation of the corresponding distances.

Distance	P = 1.404 GPa	P = 1.757 GPa	Δ(P = 1.757 – P = 1.404)
		C-C	
C1-C2	1.501	1.503	0.002
C2-C2*	1.519	1.523	0.004
		C-O	
C1-O2	1.241	1.239	-0.002
C1-O1	1.315	1.317	0.002
		C-H	
C2-H2A	1.098	1.100	0.002
C2-H2B	1.099	1.095	-0.004
	O-H		
O1-H1	1.030	1.026	-0.004
		Hydrogen bonds (Oi-Hj···Ok)	
O1···O2'	2.256	2.250	-0.006
H1···O2'	1.539	1.556	0.017

Table S.17. Interatomic angles (in deg.) in succinic acid under the external stresses with P=1.404 and P=1.757 GPa applied in the direction of the minimum Poisson's ratio. The third column (Δ) gives the variation of the corresponding distances.

Angle	P = 1.5301 GPa	P = 1.5612 GPa	Δ(P = 1.5612 – P = 1.5301)
		C-C-C	
C1-C2-C2*	113.54	113.04	-0.500
		O-C-O	
O1-C1-O2	123.93	123.29	-0.640
		O-C-C	
O1-C1-C2	113.21	114.76	1.550
O2-C1-C2	122.86	121.95	-0.910
		C-O-H	
C1-O1-H1	111.41	110.06	-1.350
		H-C-C	
H2A-C2-C1	107.03	107.06	0.030
H2A-C2-C2*	112.04	111.74	-0.300
H2B-C2-C1	106.82	108.45	1.630
H2B-C2-C2*	111.06	110.41	-0.650
		H-C-H	
H2A-C2-H2B	105.90	105.81	-0.090
		Hydrogen bonds (Oi-Hj···Ok)	
O1-H1···O2'	175.95	172.95	-3.000

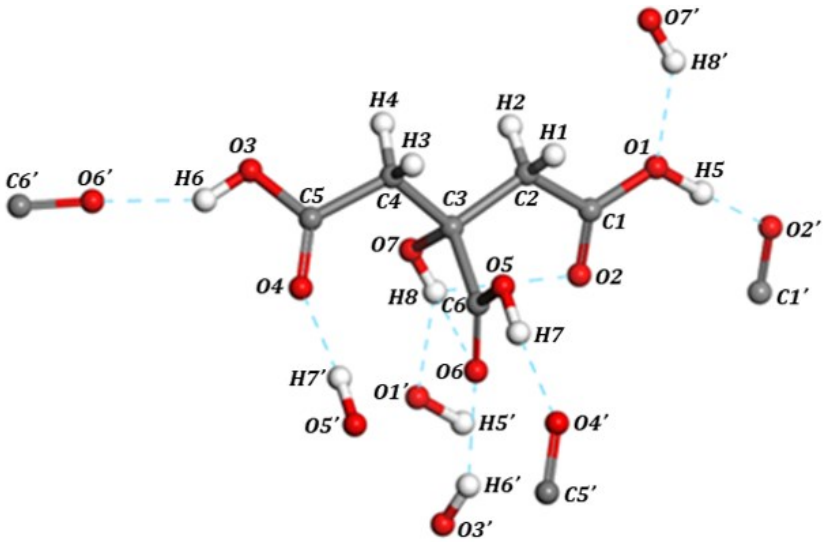

Fig. S.4. Atom labelling convention employed for the crystal structure of citric acid.

Table S.18. Interatomic distances in citric acid (in Å).

Distance	Exp.[20]	Calc.
C-C		
C1-C2	1.497	1.509
C2-C3	1.544	1.550
C3-C4	1.532	1.544
C3-C6	1.535	1.547
C4-C5	1.508	1.513
C-O		
C1-O2	1.239	1.239
C1-O1	1.298	1.318
C3-O7	1.407	1.411
C6-O6	1.202	1.223
C6-O5	1.316	1.321
C5-O4	1.210	1.233
C5-O3	1.310	1.324
C-H		
C2-H1	0.994	1.098
C2-H2	0.931	1.102
C4-H3	0.986	1.099
C4-H4	0.980	1.097
O-H		
O1-H5	1.070	1.036
O7-H8	0.840	0.979
O5-H7	0.922	1.008
O3-H6	0.892	0.999
Hydrogen bonds (Oi-Hj···Ok)		
O1···O2’	2.234	2.253
H5···O2’	1.549	1.517
O7···O2	2.867	2.907
H8···O2	2.415	2.418
O7···O1’	2.867	2.809
H8···O1’	2.145	1.939
O7···O6	2.700	2.717
H8···O6	2.294	2.302
O5···O4’	2.745	2.641
H7···O4’	1.825	1.639
O3···O6’	2.676	2.601
H6···O6’	1.906	1.672

Table S.19. Interatomic angles in citric acid (in degrees).

Angle	Exp.[20]	Calc.
C-C-C		
C1-C2-C3	116.19	116.13
C2-C3-C4	107.86	107.22
C2-C3-C6	110.79	109.63
C3-C4-C5	112.03	112.13
O-C-O		
O1-C1-O2	123.41	123.56
O6-C6-O5	124.46	124.93
O3-C5-O4	122.91	122.51
O-C-C		
O1-C1-C2	114.11	113.01
O2-C1-C2	122.48	123.43
O5-C6-C3	112.48	113.29
O6-C6-C3	123.06	121.76
O7-C3-C2	112.06	111.95
O7-C3-C4	106.38	106.80
O7-C3-C6	109.91	110.34
O3-C5-C4	111.40	111.74
O4-C5-C4	125.69	125.76
C-O-H		
C1-O1-H5	114.39	111.91
C6-O5-H7	111.00	110.10
C3-O7-H8	105.78	109.08
C5-O3-H6	106.89	113.01
H-C-C		
H1-C2-C1	108.90	108.81
H1-C2-C3	111.21	111.10
H2-C2-C1	104.65	106.25
H2-C2-C3	109.06	107.93
H3-C4-C3	111.90	110.07
H3-C4-C5	106.86	109.15
H4-C4-C3	109.38	109.09
H4-C4-C5	108.52	108.66
H-C-H		
H1-C2-H2	106.18	106.04
H3-C4-H4	108.01	107.63
Hydrogen bonds (Oi-Hj···Ok)		
O1-H5···O2’	176.97	175.57
O7-H8···O2	114.55	110.33
O7-H8···O1’	142.02	146.79
O7-H8···O6	110.04	104.46
O5-H7···O4’	175.47	172.54
O3-H6···O6’	143.51	152.80

Table S.20. Unit-cell volume and lattice parameters of citric acid under the effect of different external isotropic pressures.

P (GPa)	**Vol. (Å^3)**	a **(Å)**	b **(Å)**	c **(Å)**	β **(deg)**
-0.9994	854.3956	13.2217	5.7494	11.8940	109.10
-0.7464	806.8623	13.0243	5.6781	11.6549	110.59
-0.6078	780.5403	12.8242	5.6438	11.5740	111.29
-0.4998	771.0575	12.8174	5.6174	11.5107	111.51
-0.3710	759.1084	12.8376	5.5785	11.4251	111.91
-0.2456	747.8182	12.8254	5.5469	11.3479	112.13
-0.1387	747.0323	12.8209	5.5450	11.3438	112.13
-0.0047	746.1776	12.8179	5.5423	11.3389	112.13
0.1382	745.0446	12.8094	5.5404	11.3334	112.13
0.2518	740.0845	12.7819	5.5281	11.3147	112.23
0.3627	737.8923	12.7736	5.5224	11.3022	112.25
0.4914	720.1391	12.5559	5.4903	11.2994	112.55
0.6242	714.5465	12.5167	5.4789	11.2751	112.46
0.7523	710.8851	12.5015	5.4730	11.2472	112.52
1.0021	701.2255	12.4265	5.4579	11.2008	112.62
1.4961	687.0800	12.3545	5.4241	11.1259	112.85
2.0057	675.1925	12.2857	5.3961	11.0732	113.11
2.5248	664.7628	12.2257	5.3653	11.0431	113.41

Table S.21. Unit-cell volume and lattice parameters of citric acid under the effect of different external stresses applied in the direction of the minimum Poisson's ratio.

P (GPa)	**Vol. (Å^3)**	a **(Å)**	b **(Å)**	c **(Å)**	β **(deg)**
-0.2671	763.8238	12.2063	5.7190	11.7948	111.92
-0.1333	754.9968	12.4962	5.6201	11.5933	111.98
-0.0029	746.0548	12.8142	5.5431	11.3391	112.14
0.0888	739.1102	12.9195	5.4930	11.2419	112.11
0.1163	740.2504	12.9548	5.4904	11.2230	111.98
0.1613	750.2413	13.7599	5.4320	10.8533	112.36
0.1675	750.2131	13.7601	5.4319	10.8530	112.36
0.2307	744.7074	13.8248	5.4063	10.7833	112.48
0.4026	735.9923	14.1897	5.3484	10.4925	112.44
0.5364	732.3052	14.3272	5.3138	10.3821	112.11
0.6600	729.2900	14.5853	5.2734	10.2265	112.00
0.7931	727.4684	14.7980	5.2449	10.1044	111.94

Table S.22. Interatomic distances (in Å) in citric acid under the external stresses with P=0.1163 and P=0.1613 GPa applied in the direction of the minimum Poisson's ratio. The third column (Δ) gives the variation of the corresponding distances.

Distance	P=0.1163 GPa	P=0.1613 GPa	Δ(P=0.1613 - P=0.1163)
		C-C	
C1-C2	1.508	1.503	-0.005
C2-C3	1.549	1.545	-0.004
C3-C4	1.543	1.554	0.011
C3-C6	1.547	1.550	0.003
C4-C5	1.513	1.512	-0.001
		C-O	
C1-O2	1.239	1.241	0.002
C1-O1	1.317	1.316	-0.001
C3-O7	1.410	1.408	-0.002
C6-O6	1.223	1.225	0.002
C6-O5	1.321	1.318	-0.003
C5-O4	1.233	1.234	0.001
C5-O3	1.324	1.325	0.001
		C-H	
C2-H1	1.098	1.098	0.000
C2-H2	1.102	1.100	-0.002
C4-H3	1.098	1.097	-0.001
C4-H4	1.097	1.097	0.000
		O-H	
O1-H5	1.037	1.045	0.008
O7-H8	0.980	0.981	0.001
O5-H7	1.008	1.015	0.007
O3-H6	0.999	0.998	-0.001
		Hydrogen bonds (Oi-Hj···Ok)	
O1···O2'	2.253	2.255	0.002
H5···O2'	1.508	1.482	-0.026
O7···O2	2.901	2.983 (broken)	0.082
H8···O2	2.408	2.527 (broken)	0.119
O7···O1'	2.794	2.753	-0.041
H8···O1'	1.914	1.844	-0.070
O7···O6	2.717	2.732	0.015
H8···O6	2.301	2.352	0.051
O5···O4'	2.646	2.599	-0.047
H7···O4'	1.644	1.596	-0.048
O3···O6'	2.605	2.639	0.034
H6···O6'	1.677	1.722	0.045

Table S.23. Interatomic angles (in degrees) in citric acid under the external stresses with P=0.1163 and P=0.1613 GPa applied in the direction of the minimum Poisson's ratio. The third column (Δ) gives the variation of the corresponding distances.

Angle	P=0.1163 GPa	P=0.1613 GPa	Δ(P=0.1613 - P=0.1163)
C-C-C			
C1-C2-C3	115.95	115.44	-0.510
C2-C3-C4	107.15	106.21	-0.940
C2-C3-C6	111.12	109.30	-1.820
C3-C4-C5	112.36	113.20	0.840
O-C-O			
O1-C1-O2	123.61	123.74	0.130
O6-C6-O5	124.92	125.46	0.540
O3-C5-O4	122.64	122.63	-0.010
O-C-C			
O1-C1-C2	113.06	113.38	0.320
O2-C1-C2	123.33	122.88	-0.450
O5-C6-C3	113.22	111.93	-1.290
O6-C6-C3	121.84	122.61	0.770
O7-C3-C2	111.88	111.91	0.030
O7-C3-C4	106.83	107.45	0.620
O7-C3-C6	110.37	111.10	0.730
O3-C5-C4	111.60	111.89	0.290
O4-C5-C4	125.76	125.47	-0.290
C-O-H			
C1-O1-H5	112.13	113.30	1.170
C6-O5-H7	109.96	111.59	1.630
C3-O7-H8	108.94	109.44	0.500
C5-O3-H6	113.33	113.81	0.480
H-C-C			
H1-C2-C1	108.62	107.55	-1.070
H1-C2-C3	111.26	111.07	-0.190
H2-C2-C1	106.42	107.31	0.890
H2-C2-C3	107.92	108.41	0.490
H3-C4-C3	110.10	109.40	-0.700
H3-C4-C5	109.21	109.07	-0.140
H4-C4-C3	108.96	108.62	-0.340
H4-C4-C5	108.47	108.31	-0.160
H-C-H			
H1-C2-H2	106.12	106.65	0.530
H3-C4-H4	107.62	108.12	0.500
Hydrogen bonds (Oi-Hj···Ok)			
O1-H5···O2'	175.91	175.33	-0.580
O7-H8···O2	110.59	108.28 (broken)	-2.310
O7-H8···O1'	148.14	152.73	4.590
O7-H8···O6	104.55	102.10	-2.450
O5-H7···O4'	172.64	168.69	-3.950
O3-H6···O6'	151.23	150.91	-0.320

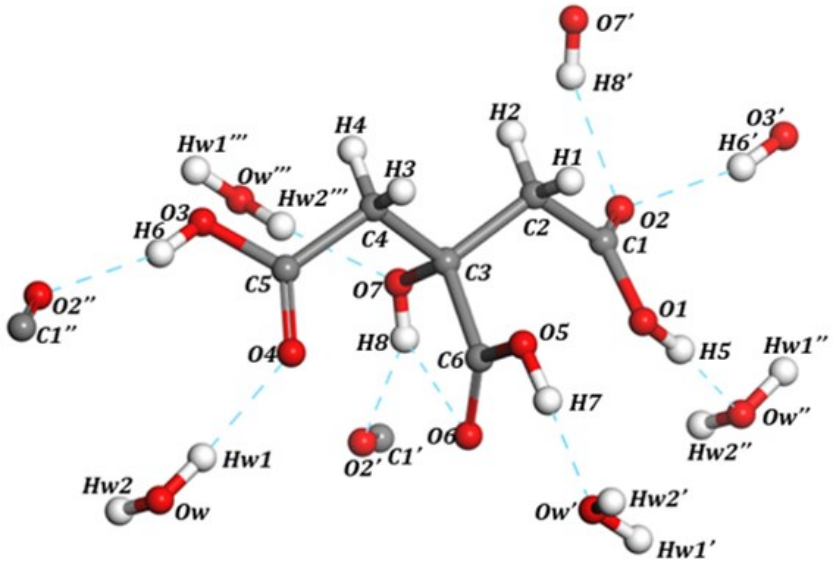

Fig. S.5. Atom labelling convention employed for the crystal structure of citric acid monohydrate.

Table S.24. Interatomic distances in citric acid monohydrate (in Å).

Distance	Exp.[21]	Calc.
C-C		
C1-C2	1.506	1.511
C2-C3	1.546	1.556
C3-C4	1.532	1.538
C3-C6	1.539	1.549
C4-C6	1.507	1.512
C-O		
C1-O2	1.221	1.242
C1-O1	1.316	1.314
C3-O7	1.421	1.426
C6-O6	1.210	1.216
C6-O5	1.325	1.331
C5-O4	1.214	1.229
C5-O3	1.326	1.331
C-H		
C2-H1	0.978	1.099
C2-H2	0.974	1.096
C4-H3	0.927	1.098
C4-H4	0.960	1.096
O-H		
O1-H5	0.864	1.037
O7-H8	0.785	0.990
O5-H7	0.891	1.014
O3-H6	0.828	1.001
Water		
Ow-Hw1	0.863	0.996
Ow-Hw2	0.858	0.999
Hydrogen bonds (Oi-Hj···Ok)		
O1···Ow''	2.612	2.552
H5···Ow''	1.754	1.516
O7···O6	2.651	2.686
H8···O6	2.166	2.150
O7···O2'	2.746	2.686
H8···O2'	2.095	1.821
O5···Ow'	2.675	2.634
H7···Ow'	1.788	1.623
O3···O2'	2.736	2.669
H6···O2'	1.931	1.699
Ow···O4	2.738	2.681
Hw1···O4	1.893	1.711
Ow''···O7	2.739	2.661
Hw2''···O7	1.913	1.691

Table S.25. Interatomic angles in citric acid monohydrate (in degrees).

Angle	Exp.[21]	Calc.
C-C-C		
C1-C2-C3	111.38	111.31
C2-C3-C4	109.28	109.11
C2-C3-C6	110.89	110.48
C3-C4-C5	111.38	112.21
O-C-O		
O1-C1-O2	123.05	122.88
O6-C6-O5	125.57	125.76
O3-C5-O4	123.88	124.04
O-C-C		
O1-C1-C2	112.72	113.59
O2-C1-C2	124.21	123.51
O5-C6-C3	112.28	112.00
O6-C6-C3	122.13	122.20
O7-C3-C2	108.52	108.43
O7-C3-C4	107.71	107.79
O7-C3-C6	108.38	109.20
O3-C5-C4	112.77	113.02
O4-C5-C4	123.35	122.93
C-O-H		
C1-O1-H5	112.43	110.86
C6-O5-H7	110.23	109.46
C3-O7-H8	108.98	111.42
C5-O3-H6	106.83	110.26
H-C-C		
H1-C2-C1	108.72	108.72
H1-C2-C3	109.87	109.39
H2-C2-C1	108.57	109.80
H2-C2-C3	109.38	108.61
H3-C4-C3	111.23	109.88
H3-C4-C5	106.25	107.24
H4-C4-C3	107.99	109.09
H4-C4-C5	108.52	111.11
H-C-H		
H1-C2-H2	108.88	108.97
H3-C4-H4	111.46	107.17
Water		
Hw1-Ow-Hw2	109.11	110.63
Hydrogen bonds (Oi-Hj···Ok)		
O1-H5···Ow''	172.28	177.26
O7-H8···O6	120.42	112.25
O7-H8···O2'	140.34	144.05
O5-H7···Ow	174.36	174.69
O3-H6···O2'	163.70	161.89
Ow-Hw1···O4	165.51	163.57
Ow-Hw2···O7	161.08	162.72

Table S.26. Unit-cell volume and lattice parameters of citric acid monohydrate under the effect of different external isotropic pressures.

P (GPa)	Vol. (Å^3)	a (Å)	b (Å)	c (Å)
-1.0028	948.1654	6.5209	9.4655	15.36
-0.7503	919.8640	6.4205	9.3977	15.25
-0.4748	895.2417	6.3196	9.3543	15.14
-0.2579	873.4873	6.2162	9.3170	15.08
-0.0311	861.9491	6.1856	9.2915	15.00
0.2526	850.6765	6.1496	9.2697	14.92
0.5014	839.8365	6.1069	9.2550	14.86
0.7519	825.6687	6.0460	9.2196	14.81
1.4905	800.2005	5.9533	9.1583	14.68
2.5016	773.0651	5.8529	9.0927	14.53
2.9987	761.7295	5.8092	9.0616	14.47
3.9927	741.3846	5.7291	8.9976	14.38
4.9986	724.3803	5.6610	8.9628	14.28
6.9946	693.9933	5.5265	8.8709	14.16
9.0041	667.3047	5.3923	8.7720	14.11
10.9983	643.8442	5.2550	8.6857	14.11

REFERENCES

1. S. J. Clark, M. D. Segall, C. J. Pickard, P. J. Hasnip, M. I. J. Probert, K. Refson, M. C. Payne, *Z. Kristallogr.*, 2005, **220**, 567–570.
2. Materials Studio, http://3dsbiovia.com/products/collaborative-science/biovia-materials-studio/ (accessed 10 January 2020).
3. M. C. Payne, M. P. Teter, D. C. Ailan, A. Arias, J. D. Joannopoulos, *Rev. Mod. Phys.*, 1992, **64**, 1045–1097.
4. J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **7**, 3865–3868.
5. S. Grimme, *J. Comput. Chem.*, 2006, **27**, 1787–1799.
6. N. Troullier, J. L. Martins, *Phys. Rev. B.*, 1991, **43**, 1993–2006.
7. B. G. Pfrommer, M. Cote, S. G. Louie, M. L. Cohen, *J. Comput. Phys*., 1997, **131**, 233–240.
8. H. J. Monkhorst, J. D. Pack, *Phys. Rev. B*, 1976, **13**, 5188–5192.
9. R. T. Downs, K. L. Bartelmehs, G. V. Gibbs, M. B. Boisen, *Am. Mineral.*, 1993, **78**, 1104–1107.
10. J. F. Nye, *Physical Properties of Crystals*, Clarendon, Oxford, 1976.
11. R. Yu, J. Zhu, H. Q. Ye, *Comput. Phys. Commun*., 2010, **181**, 671−675.
12. F. Birch, *Phys. Rev.*, 1947, **71**, 809−824.
13. R. J. Angel, *Rev. Mineral. Geochem.*, 2000, **41**, 35−60.
14. EOSFIT 5.2 software, http://programming.ccp14.ac.uk/ccp/webmirrors/ross-angel/crystal/software.html (accessed 10 January 2020).
15. A. Marmier, Z. A. D. Lethbridge, R, I. Walton, C. W. Smith, S. C. Parker, K. E. Evans, *Comput. Phys. Commun.*, 2010, **181**, 2102−2115.
16. F. Mouhat, F. X. Coudert, *Phys. Rev. B*, 2014, **90**, 224104.
17. A. Schouten, J. A. Kanters, J. van Krieken, *J. Mol. Struc*., 1994, **323**, 165−168.
18. D. Rychkov, S. Arkhipov, E. Boldyreva, *Acta Crystallogr. B*, 2016, **72**, 160−163.
19. P. Lucaioli, E. Nauha, I. Gimondi, L. S. Price, R. Guo, L. Iuzzolino, I. Singh, M. Salvalaglio, S. L. Price, N. Blagden, *CrystEngComm*, 2018, **20**, 3971−3977.
20. A. Rammohan, J. A. Kaduk, *Acta Crystallogr. B*, 2018, **74**, 239−252.
21. M. D. King, E. A. Davis, T. M. Smith, T. M. Korter, *J. Phys. Chem. A*, 2011, **115**, 11039−11044.