Supplementary Information

Investigation of Methacrylic Acid at High Pressure Using Neutron Diffraction.

William G. Marshall,[b] Andrew J. Urquhart[c] and Iain D.H. Oswald.[a*]

[a]Strathclyde Institute of Pharmacy and Biomedical Sciences, University of Strathclyde, 161 Cathedral Street, Glasgow, UK, G4 0RE. Tel: +441415482157. Email: iain.oswald@strath.ac.uk

[b]ISIS Neutron and Muon Source, Science and Technology Facilities Council, Rutherford Appleton Laboratory, Harwell Oxford, Didcot, Oxon, UK OX11 0QX.

[c]Department of Micro- and Nanotechnology, Building 345Ø, Ørsteds Plads, Technical University of Denmark, 2800 Kgs. Lyngby, Denmark.

Experimental Section

Raman measurements

A Merrill-Bassett diamond anvil cell[1] (DAC) was equipped with 600 µm culet diamonds attached to tungsten carbide backing discs. A 300 µm hole was drilled in a preindented 250 µm thick tunsten foil to serve as the sample chamber. A piece of ruby was placed in the chamber so that the pressure could be measured *in-situ* using the Ruby fluorescence technique.[2] The same solution of methacrylic acid-d_6 in PTM from the neutron experiment was loaded into the diamond anvil cell and pressure applied. Raman measurements were taken regularly up to 8 GPa on a ThermoScientific DXR Raman microscope using a 532 nm laser and equipped with an extended range grating. The spectra were analysed using OMNIC 8.0 software. The samples used for the Raman measurements were single crystalline in nature and so there may be orientational issues associated with the spectra.

Cambridge Structural Database (CSD) search

The Cambridge Structural Database was searched for the carboxylic acid dimer with O…O distance specified between 2.5-3.2 Å. The search was conducted on CSD version 5.34 plus the February and May updates using Conquest version 1.15[3] and restricted to only organics without disorder, and errors and having an R-factor less than or equal to 7.5 %. The contact distances between O…O for each hydrogen bond and C1…C1' were extracted. The resulting data were analysed in OriginPro 9.0.

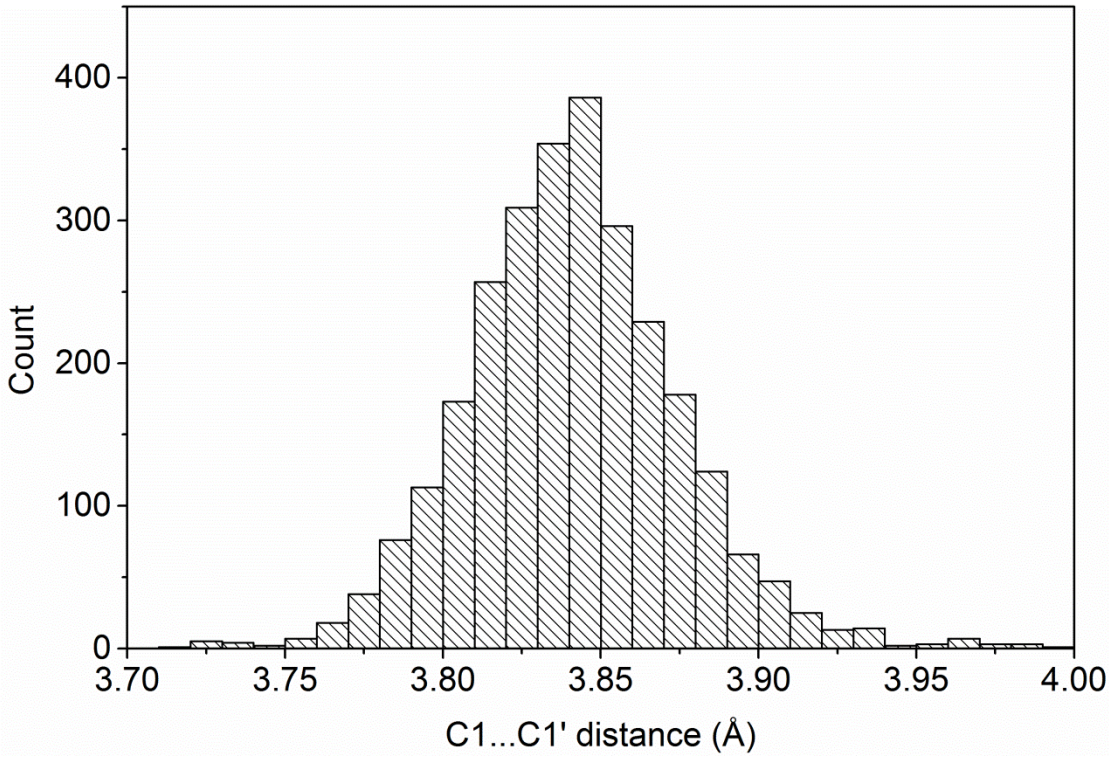

Figure ES1: A histogram of carboxylic acid distances in the CSD where the distance measured is between the two carbonyl carbon atoms across the dimer. At 5.12 GPa the structure of methacrylic acid Phase III gives a value of 3.734 Å close to the minimum observed value in the CSD.

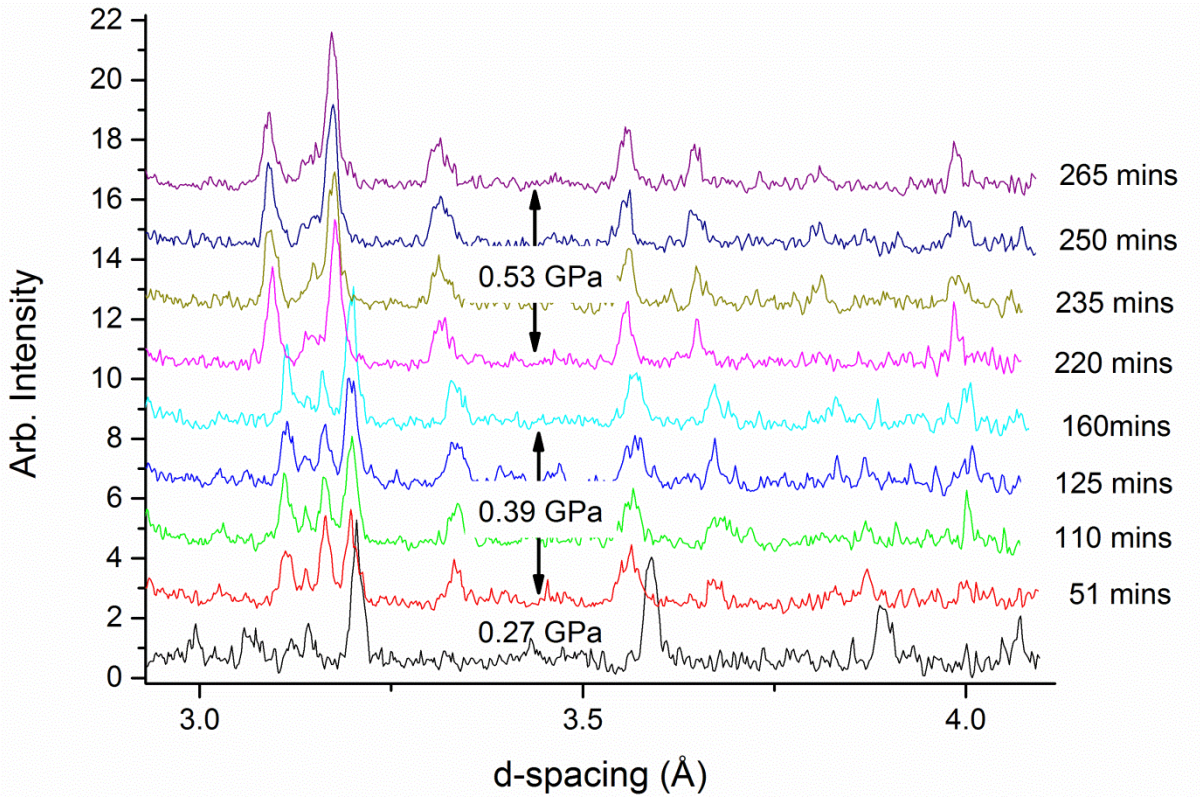

Figure ES2: Powder patterns of the Phase I-II transition in methacrylic acid-d_6 at various pressures indicating the length of time from when Phase II first appeared. The transition was still not complete with little sign of doing so before pressure was increased.

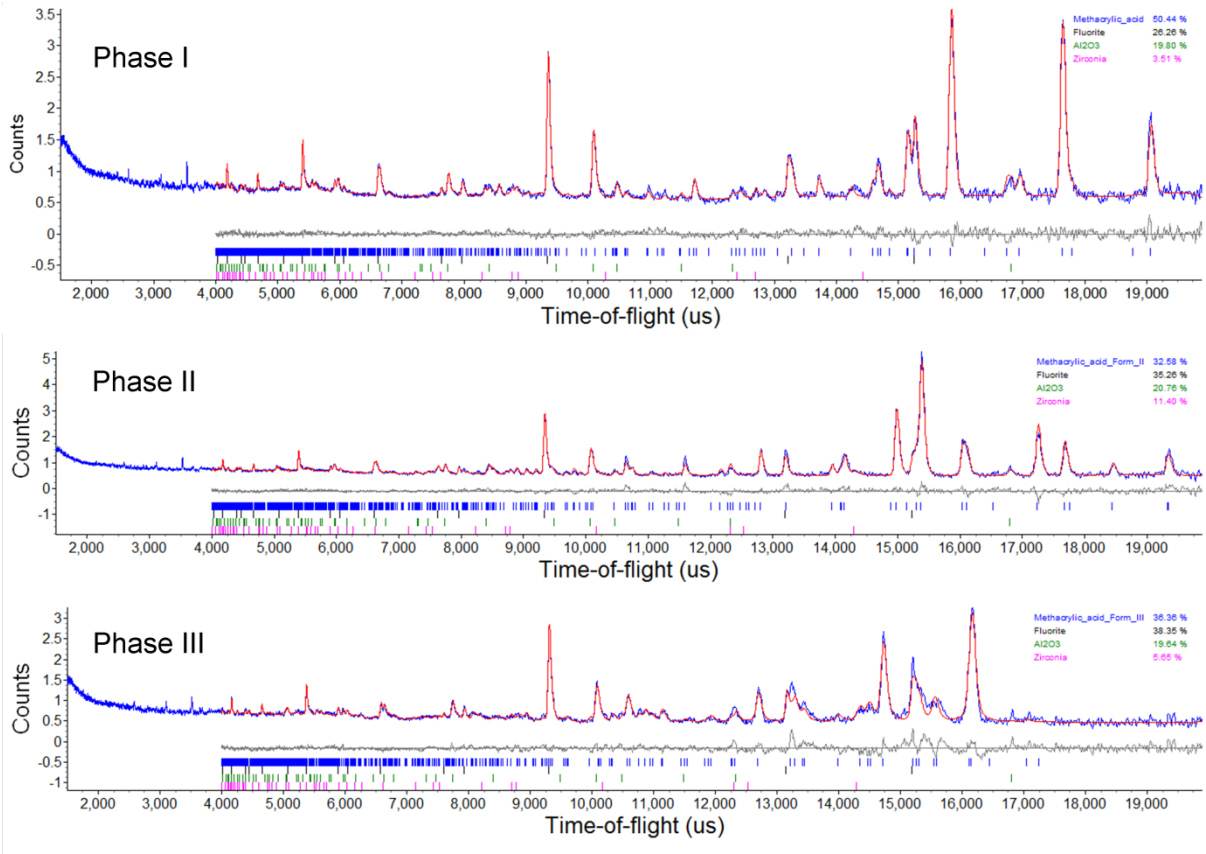

Figure ES3: The Rietveld refinements for the three phases of methacrylic acid: Phase I at 0.12 GPa; Phase II at 0.83 GPa; and Phase III at 1.4GPa.

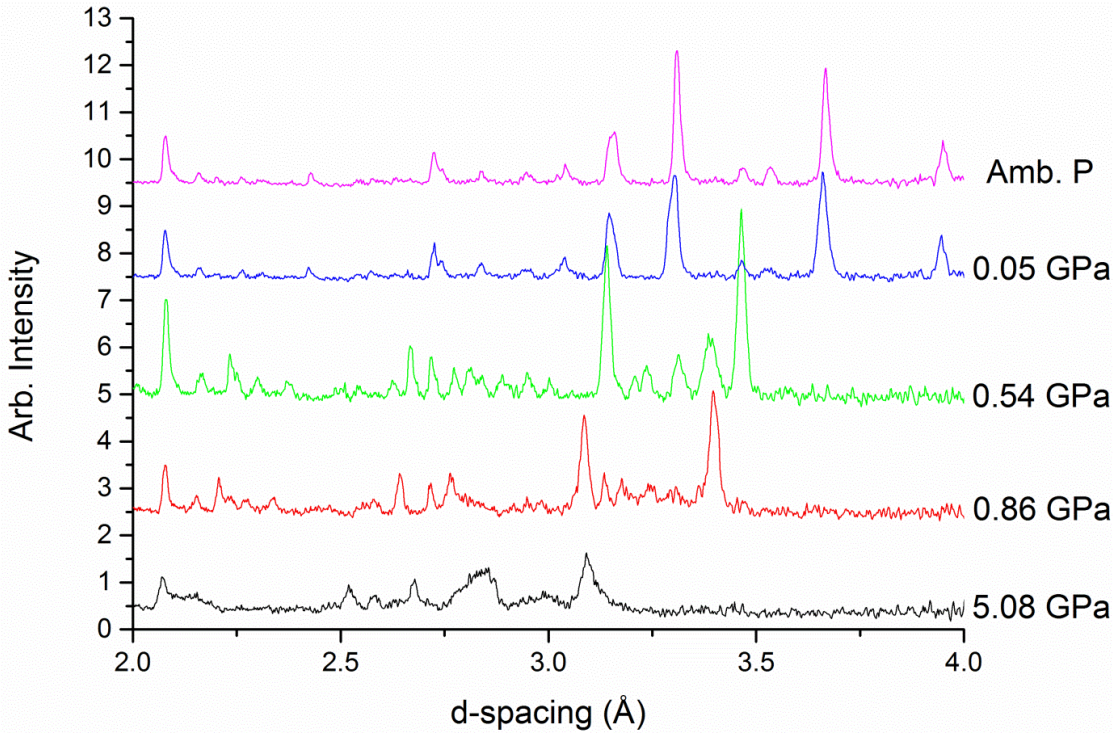

Figure ES4: The evolution of the Phase III diffraction pattern on decompression. The pattern becomes particularly well-resolved between the two main peaks at 3.0 and 3.4 Å. At 0.05 GPa the pattern has transformed back to Phase I.

Table ES1: Energies of intermolecular interactions as highlighted by Pixel calculations for Phases I, II and III. The energies are all in kJ/mol.

Pressure (GPa)	Centroid distance (Å)	Coloumbic (kJ mol^{-1})	Polarisation (kJ mol^{-1})	Dispersion (kJ mol^{-1})	Repulsion (kJ mol^{-1})	Total Energy (kJ mol^{-1})
Phase I						
Interaction 1 Symmetry operator: 2-x, 2-y, 1-z						
0.12	5.22	-155.8	-78.6	-23.2	197.1	-60.5
0.27	5.225	-154.1	-77.2	-23.1	193.9	-60.4
0.39	5.22	-155.4	-78.4	-22.7	197	-59.5
Interaction 2 Symmetry operator: 1-x, y- 1/2, 1/2-z						
0.12	6.572	-4.7	-1.9	-6.6	4.6	-8.5
0.27	6.535	-5	-2.1	-7	5.2	-8.7
0.39	6.493	-5.1	-2.2	-7.3	5.7	-9
Interaction 3 Symmetry operator: x-1, y, z						
0.12	3.882	-1	-1.6	-15.7	10.2	-8.2
0.27	3.83	-2	-2.1	-17.3	13.1	-8.3
0.39	3.793	-2.4	-2.2	-18.2	14.9	-7.9
Interaction 4 Symmetry operator: 1-x, 2-y, 1-z						
0.12	5.617	-3.5	-0.6	-2.3	0.1	-6.3
0.27	5.623	-3.6	-0.6	-2.4	0.2	-6.4
0.39	5.61	-3.8	-0.6	-2.4	0.2	-6.7
Interaction 5 Symmetry operator: 2-x, y-1/2, 1/2-z						
0.12	6.319	-0.3	-0.6	-3.5	0.5	-3.9
0.27	6.225	-0.4	-0.7	-4.3	0.8	-4.5

0.39	6.155	-0.5	-0.8	-4.9	1.2	-5
Phase II						
Interaction 1 Symmetry operator: 2-x, 1-y, 2-z						
0.39	5.197	-159.2	-88	-23.9	211.2	-59.9
0.53	5.192	-160.8	-88.5	-24.1	214	-59.5
0.66	5.182	-163.8	-90.3	-24.3	221.1	-57.3
0.84	5.179	-164.9	-90.6	-24.2	223.1	-56.6
1.21	5.161	-172	-93.5	-24.8	235.4	-54.9
1.31	5.16	-172.8	-93.8	-24.8	236.1	-55.3
Interaction 2 Symmetry operator: 1-x, 1-y, 1-z						
0.39	5.564	-4.5	-1.6	-9.4	7	-8.5
0.53	5.555	-5	-1.8	-9.8	7.9	-8.7
0.66	5.543	-4.6	-1.7	-9.5	7	-8.7
0.84	5.485	-4.7	-1.8	-10.2	7.8	-8.9
1.21	5.433	-5.1	-2	-11.2	9.5	-8.8
1.31	5.433	-5.2	-2.1	-11.3	9.7	-8.9
Interaction 3 Symmetry operator: 1+x, y, z						
0.39	3.937	-1.6	-1.7	-16.8	12	-8.1
0.53	3.905	-1.6	-1.8	-17.1	12.6	-7.8
0.66	3.874	-2.1	-1.9	-18.1	14.7	-7.4
0.84	3.843	-3	-2.5	-19.4	17.2	-7.7
1.21	3.788	-4.5	-3.3	-21.4	21.7	-7.5
1.31	3.776	-4.7	-3.5	-21.7	22.7	-7.3
Interaction 4 Symmetry operator:						
0.39	5.342	-3.5	-0.7	-3.1	0.3	-7.1
0.53	5.302	-3.6	-0.7	-3.2	0.3	-7.3
0.66	5.269	-3.8	-0.8	-3.4	0.3	-7.6
0.84	5.255	-4.1	-0.8	-3.5	0.4	-8
1.21	5.273	-4.4	-0.9	-3.5	0.5	-8.3
1.31	5.256	-4.5	-0.9	-3.6	0.5	-8.5
Interaction 5 Symmetry operator: x-1, 1/2-y, z-1/2						
0.39	6.382	-2.8	-1.7	-8.5	6.8	-6.2
0.53	6.347	-2.8	-1.9	-9.2	7.9	-6.1
0.66	6.314	-3.1	-2.1	-9.6	8.8	-6
0.84	6.293	-3.7	-2.3	-9.9	9.7	-6.2
1.21	6.23	-4.4	-2.7	-10.8	11.8	-6.1
1.31	6.224	-4.4	-2.7	-11	12.1	-6
Interaction 6 Symmetry operator: x, 1/2-y, z-1/2						
0.39	5.715	-1.2	-0.8	-9.6	5.8	-5.7
0.53	5.678	-1.5	-1	-10.3	7	-5.7
0.66	5.643	-1.7	-1.1	-10.7	7.8	-5.7
0.84	5.621	-1.9	-1.2	-11.3	8.6	-5.8
1.21	5.554	-2.6	-1.5	-12.3	10.9	-5.6
1.31	5.543	-2.8	-1.6	-12.6	11.5	-5.5
Phase III						
Interaction 1 Symmetry operator: -x, 1-y, -z						
1.296	5.199	-158.5	-85.6	-23.9	207.8	-60.2
1.426	5.201	-124.7	-61.1	-23.6	157.2	-52.1
1.657	5.216	-124.4	-60.8	-23.7	153.2	-55.8
2.03	5.189	-124.1	-59.5	-24	157.4	-50.1

2.438	5.176	-164.7	-90.2	-24.6	221.9	-57.7
2.841	5.168	-167.2	-91.6	-24.8	227.2	-56.4
3.325	5.164	-168.7	-92.5	-25.1	230.1	-56.3
3.891	5.146	-174.4	-96.5	-25.6	242.4	-54
4.426	5.134	-178.3	-99	-25.6	250.7	-52.1
5.126	5.115	-183.5	-103.4	-26.1	265.1	-48
Interaction 2 Symmetry operator: 1-x, 1-y, -z						
1.296	5.004	-5.1	-1.1	-5	1.1	-10.1
1.426	4.978	-8.1	-1.3	-5.6	1.3	-13.7
1.657	5.004	-7.8	-1.3	-5.6	1.3	-13.4
2.03	4.963	-9.4	-1.5	-6	1.6	-15.3
2.438	4.955	-6.1	-1.3	-5.7	1.7	-11.4
2.841	4.944	-6.4	-1.4	-5.9	1.9	-11.7
3.325	4.936	-6.7	-1.5	-6.1	2.1	-12.2
3.891	4.898	-7.2	-1.6	-6.5	2.6	-12.7
4.426	4.884	-7.7	-1.7	-6.7	2.9	-13.1
5.126	4.859	-8.4	-1.9	-7.1	3.5	-13.9
Interaction 3 Symmetry operator: x-1/2,3/2 -y, z-1/2						
1.296	6.086	-5.2	-2.7	-11.1	10.4	-8.5
1.426	6.082	-5.1	-2.6	-11	10.3	-8.4
1.657	6.046	-5.8	-3	-11.7	11.9	-8.6
2.03	6.016	-6	-3.2	-12.2	13	-8.5
2.438	5.983	-6.8	-3.7	-12.9	14.7	-8.6
2.841	5.958	-7.3	-4	-13.4	16.2	-8.5
3.325	5.921	-8.1	-4.5	-14.1	18.3	-8.4
3.891	5.879	-9	-5	-14.9	20.7	-8.2
4.426	5.83	-10.3	-5.7	-16	23.8	-8.2
5.126	5.783	-11.2	-6.5	-16.9	27.2	-7.5
Interaction 4 Symmetry operator: 1-x, 1-y, 1-z						
1.296	5.346	-6.4	-2.1	-12	14.2	-6.3
1.426	5.319	-7	-2.5	-12.8	16	-6.4
1.657	5.291	-8	-2.8	-13.4	17.9	-6.2
2.03	5.268	-8.2	-3	-13.7	18.8	-6.2
2.438	5.246	-9.1	-3.3	-13.9	20.1	-6.1
2.841	5.227	-9.5	-3.5	-14.2	21.4	-5.8
3.325	5.196	-10.6	-4.1	-15	23.9	-5.6
3.891	5.159	-12.2	-4.9	-15.9	27.8	-5.1
4.426	5.123	-13.8	-5.7	-16.8	31.7	-4.6
5.126	5.062	-16.3	-6.7	-17.9	37.1	-3.7
Interaction 5 Symmetry operator: x-1, y, z						
1.296	3.67	-2.6	-3.1	-21.4	21.4	-5.6
1.426	3.651	-2.8	-3.3	-21.8	23.1	-4.8
1.657	3.629	-2.9	-3.4	-22.3	24.3	-4.2
2.03	3.59	-4.1	-4.3	-23.9	28.8	-3.5
2.438	3.553	-5.1	-5.2	-25.5	32.7	-3
2.841	3.522	-6	-6	-26.7	36.6	-2
3.325	3.488	-7.3	-6.9	-28	41.4	-0.8
3.891	3.454	-9.1	-7.8	-29.6	47.3	0.8
4.426	3.43	-10.5	-8.4	-30.7	52	2.4
5.126	3.38	-13.5	-9.5	-33.5	64.1	7.6

References

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