Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Ultra-High Resolution ^{17}O Solid-State NMR Spectroscopy of Biomolecules: A Comprehensive Spectral Analysis of Monosodium L-Glutamate·Monohydrate

Supplementary Materials

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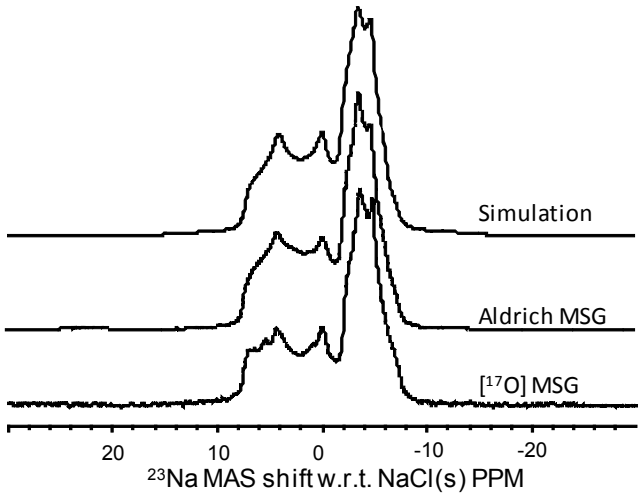

Figure S1. ^{23}Na MAS spectra of MSG. All spectra were acquired on a Bruker Avance II^{+} 600 with a Bruker 4-mm MAS probe, spinning at a 12500 Hz frequency. The Aldrich MSG sample was purchase from Sigma-Aldrich without purification. [^{17}O] MSG is the same sample used for the ^{17}O NMR study. The following ^{17}O NMR parameters were used to simulate the MAS spectrum,

Experimental results (MAS simulation):
Na1 χ_q = 2.42(2) MHz, η_q = 0.39(4), δ_{iso} = 8.00(5) ppm
Na2 χ_q = 1.47(2) MHz, η_q = 0.49(4), δ_{iso} = –1.84 (5) ppm

DFT results (from a fully optimised mode)
Na1 χ_q = –2.53 MHz, η_q = 0.30, δ_{iso} = 9.75 ppm
Na2 χ_q = 1.85 MHz, η_q = 0.42(4), δ_{iso} = –2.00 ppm.

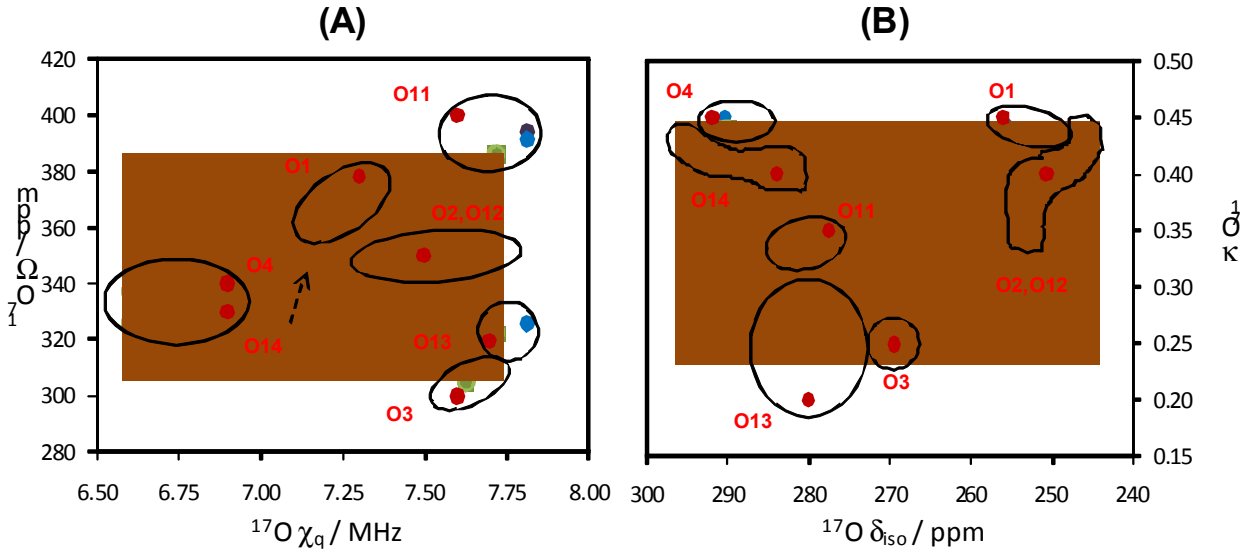

Figure S2. (A) A 2D NMR parameters comparison between Ω *vs* χ_q and (B) κ *vs* δ_{iso}. For all the plots, the experimental NMR data are represented by solid red circles; fully optimised model by solid purple; O,H-optimised by solid blue; H-optimised by transparent green; and X-ray structure by transparent brown. The DFT Ω and χ_q values are scaled by 0.76 and 0.93, respectively. Refer to Table 3 (in text) for the original un-scaled DFT values and to Table 2 (in text) for the experimental NMR data. The 2D comparison displayed here are similar to Figures 5C and 5D in text, in such that the experimental values and the DFT results are clustered together aiding the site assignments,

Table S1. ^{1}H and ^{13}C NMR results of MSG: DFT[a] and experiment.

H site	DFT ^{1}H δ_{iso} (O,H-optimised) Ppm	DFT ^{1}H δ_{iso} (X-ray) ppm	Experimental ^{1}H δ_{iso} ± 0.1 ppm
CH	6.48	6.18	6.3
CH	5.32	4.88	5.0
CH_2	2.64	2.34	2.0
CH_2	2.09	2.07	–
CH_2	1.71	1.60	–
CH_2	2.00	1.84	–
CH_2	2.10	1.80	–
CH_2	2.01	1.73	–
CH_2	1.41	0.38	–
CH_2	1.25	0.68	–
NH_3	9.43	10.58	–
NH_3	7.77	8.68	–
NH_3	8.01 (8.40)[b]	9.37 (9.54)[b]	8.5
NH_3	7.46	8.41	–
NH_3	10.21	11.04	–
NH_3	6.77 (8.15)[b]	8.30 (9.25)[b]	8.2
H_2O	5.74	1.98	5.0
H_2O	5.69	-5.69	–
H_2O	4.79	1.28	–
H_2O	5.03	-3.41	–
C site	DFT ^{13}C δ_{iso} (O,H-optimised) Ppm	DFT ^{13}C δ_{iso} (X-ray) ppm	Experimental ^{13}C δ_{iso} ± 0.2 ppm
CO	180.28	175.97	176.1
CO	181.31	178.36	176.1
CO	186.89	184.56	180.8
CO	188.43	184.79	182.5
CN	57.27	56.83	55.2
CN	55.23	55.20	54.0
CH_2	27.58	27.44	27.5
CH_2	38.37	38.38	39.2
CH_2	29.54	28.89	27.5
CH_2	36.38	31.71	35.0

(a) $\delta_{iso} = \sigma_{ref} - \sigma_{iso}$, where $\sigma_{ref}(^{1}H) = 30.70$ ppm and $\sigma_{ref}(^{13}C) = 169.80$ ppm.

(b) The parentheses indicate the average shift for NH_3.

Table S2. DFT results of the ^{17}O tensor components.

O site	δ_{11} ppm	δ_{22} ppm	δ_{33} ppm	χ_{xx} MHz	χ_{yy} MHz	χ_{zz} MHz	∠C-O-δ_{22} °	∠C-O-χ_{yy} °
				Fully optimised				
O1	463.8	325.9	–26.9	–2.2	–5.7	7.9	143.6	178.7
O11	514.3	339.6	–4.4	–2.6	–5.8	8.4	139.3	177.6
O2	443.6	314.1	–17.9	–1.9	–6.1	8.0	147.7	178.5
O12	454.1	312.7	–7.7	–2.1	–6.2	8.3	147.1	177.3
O3	455.8	302.4	47.5	–2.0	–6.3	8.3	144.5	177.4
O13	473.7	313.7	46.9	–2.2	–6.1	8.3	143.2	177.6
O4	481.2	355.0	31.1	–1.5	–5.6	7.1	147.0	177.8
O14	475.0	341.5	31.2	–1.4	–5.7	7.1	145.5	177.2
				O,H-optimised				
O1	462.8	326.4	–23.3	–2.2	–5.7	7.9	143.0	177.8
O11	508.7	336.6	–6.0	–2.6	–5.8	8.4	137.9	177.8
O2	449.1	316.7	–16.2	–2.0	–6.1	8.0	146.1	177.7
O12	454.2	315.6	–6.0	–2.1	–6.2	8.3	146.7	176.7
O3	457.7	305.9	47.8	–2.1	–6.3	8.3	144.3	177.2
O13	475.0	317.4	46.3	–2.2	–6.1	8.4	146.8	177.7
O4	482.8	357.6	30.8	–1.6	–5.6	7.2	146.2	177.7
O14	470.8	342.7	35.0	–1.3	–5.8	7.1	147.4	177.9

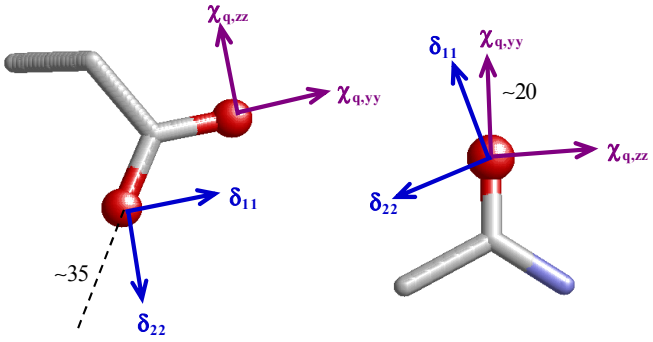

Figure S3. A diagram showing the ^{17}O CS and EFG tensor orientations in the molecular frame of carboxylate and carbonyl oxygens.

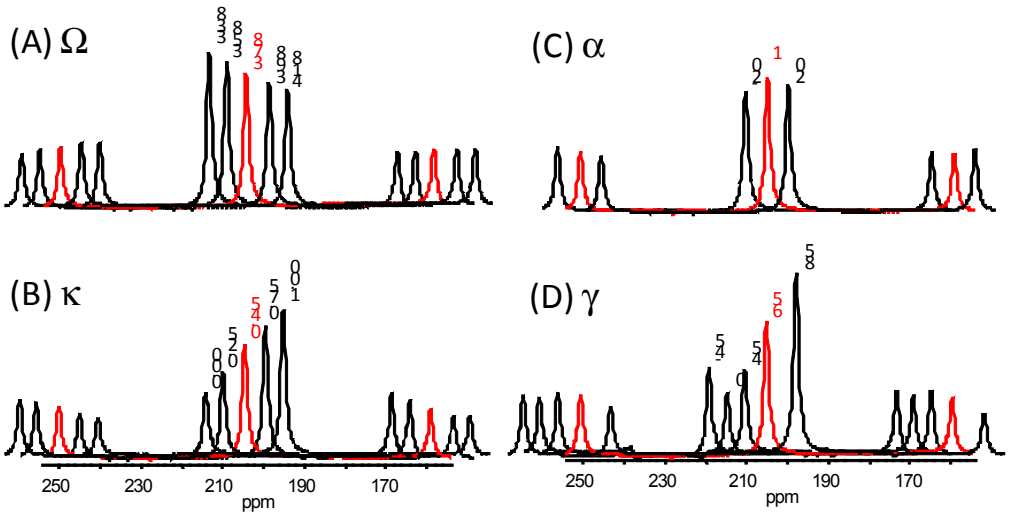

Figure S4. Simulated ^{17}O DOR spectra of P2 at 14.1 T (values can be found in Table 2 in text) by varying the following parameters: Ω, κ, α and γ. The red spectrum represents the result shown in Figure 4.