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Supplementary Information.

Structural Assessment of Anhydrous Sulfates with High Field ^{33}S Solid State NMR and First Principles Calculations.

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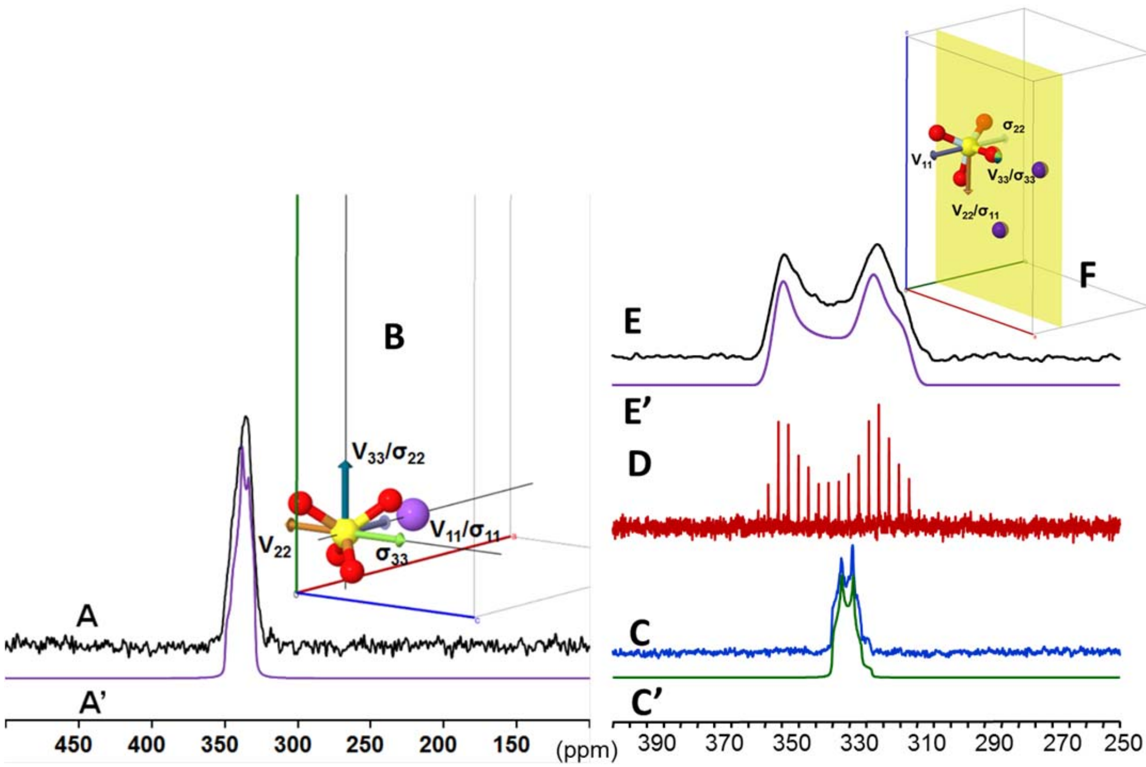

Figure S1 A – stationary ^{33}S Hahn Echo spectrum of Na_2SO_4 at 21.1T with corresponding simulation accounting for both the EFG and CSA (A'). B - representative portion of the Na_2SO_4 unit cell demonstrating the calculated orientations for the principal components of the EFG and CSA tensors. The black lines are proper C_2 rotation axes present through sulfur. C – experimental 5 kHz MAS Bloch Decay ^{33}S spectrum of K_2SO_4 at 21.1T, C' – corresponding simulation. D – stationary QCPMG spectrum of K_2SO_4 at 21.1T, E - stationary ^{33}S Hahn Echo spectrum of K_2SO_4 at 21.1T with corresponding simulation accounting for both the EFG and CSA (E'). F - Representative portion of the K_2SO_4 unit cell showing the calculated orientations for the principal components of the EFG and CSA tensors. Sulfur, oxygen, and alkali metal are shown in yellow, red, and purple respectively. The mirror plane present through sulfur is shown in yellow.

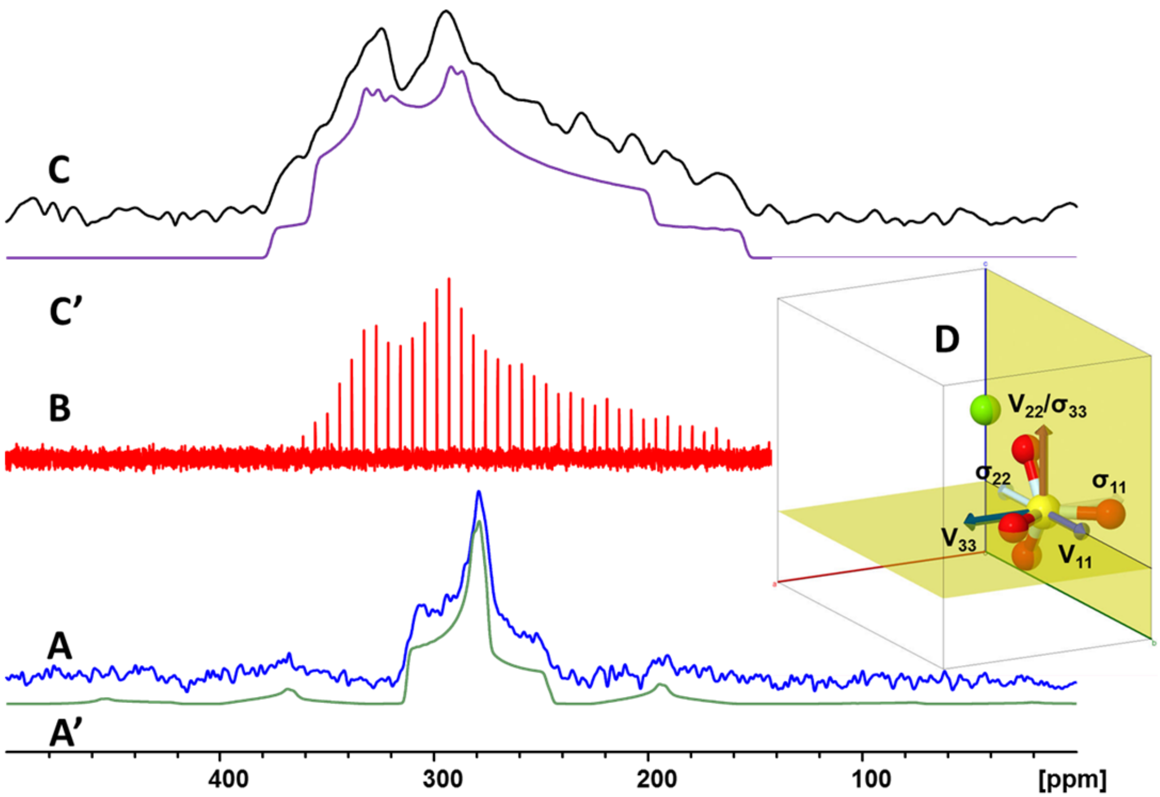

Figure S2 ^{33}S SS-NMR spectra of α-$MgSO_4$ at 21.1T. A - experimental 5 kHz MAS Bloch Decay, A'- simulation of the MAS spectrum. B – stationary QCPMG spectrum. C – experimental stationary Hahn Echo spectrum, C' - simulation of the stationary spectrum accounting for both the EFG and CSA interactions. D - representative portion of the unit cell showing the calculated orientations for the principal components of the EFG and CSA tensors. Sulfur, oxygen, and alkali earth metal are shown in yellow, red, and green respectively. The two mirror planes present through sulfur are shown in yellow. The black line at the intersection of the planes is the proper C2 rotation axis through sulfur.

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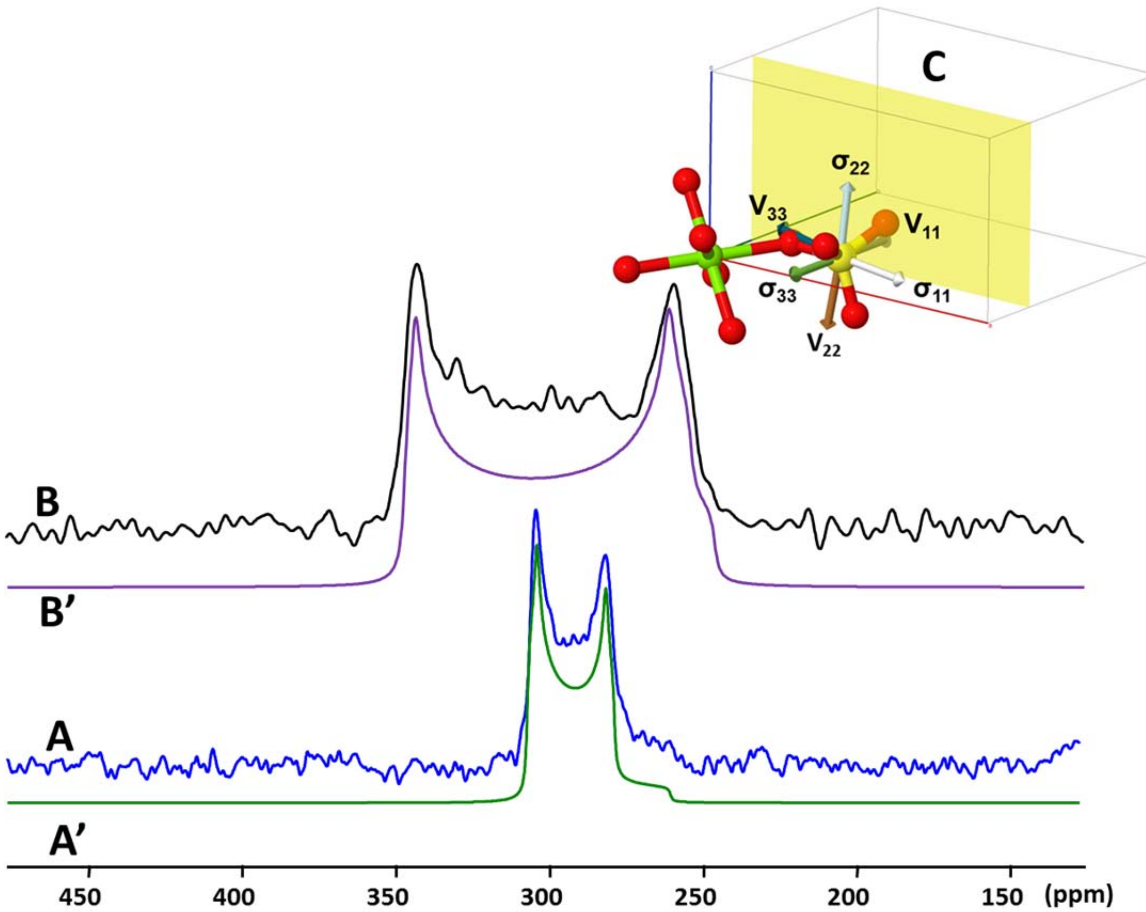

Figure S3 ^{33}S SS-NMR spectra (experimental and simulated) of β-$MgSO_4$. A,A' - 5 kHz DFS MAS Bloch Decay. B, B' - Static Hahn Echo. C - representative portion of the unit cell showing the calculated orientations for the principal components of the EFG and CSA tensors. Sulfur, oxygen, and alkali earth metal are shown in yellow, red, and green respectively. The mirror plane present through sulfur is shown in yellow.

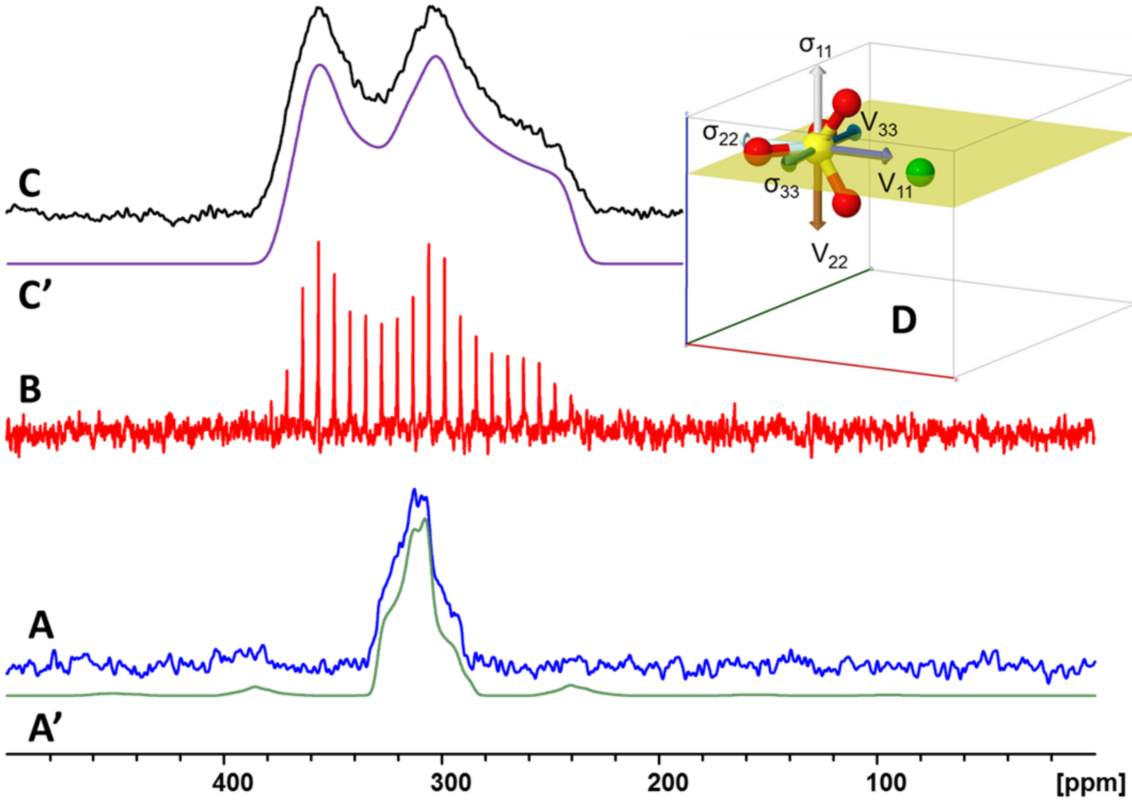

Figure S4 ^{33}S SS-NMR spectra (experimental and simulated) of $BaSO_4$. A,A' 5 kHz DFS MAS Bloch Decay at 21.1 T. B - stationary QCPMG taken at 21.1 T. C, C' Static Hahn Echo taken at 21.1 T. D- representative portion of the unit cell showing the calculated orientations for the principal components of the EFG and CSA tensors. Sulfur, oxygen, and barium are shown in yellow, red, and green respectively. The mirror plane present through sulfur is shown in yellow.

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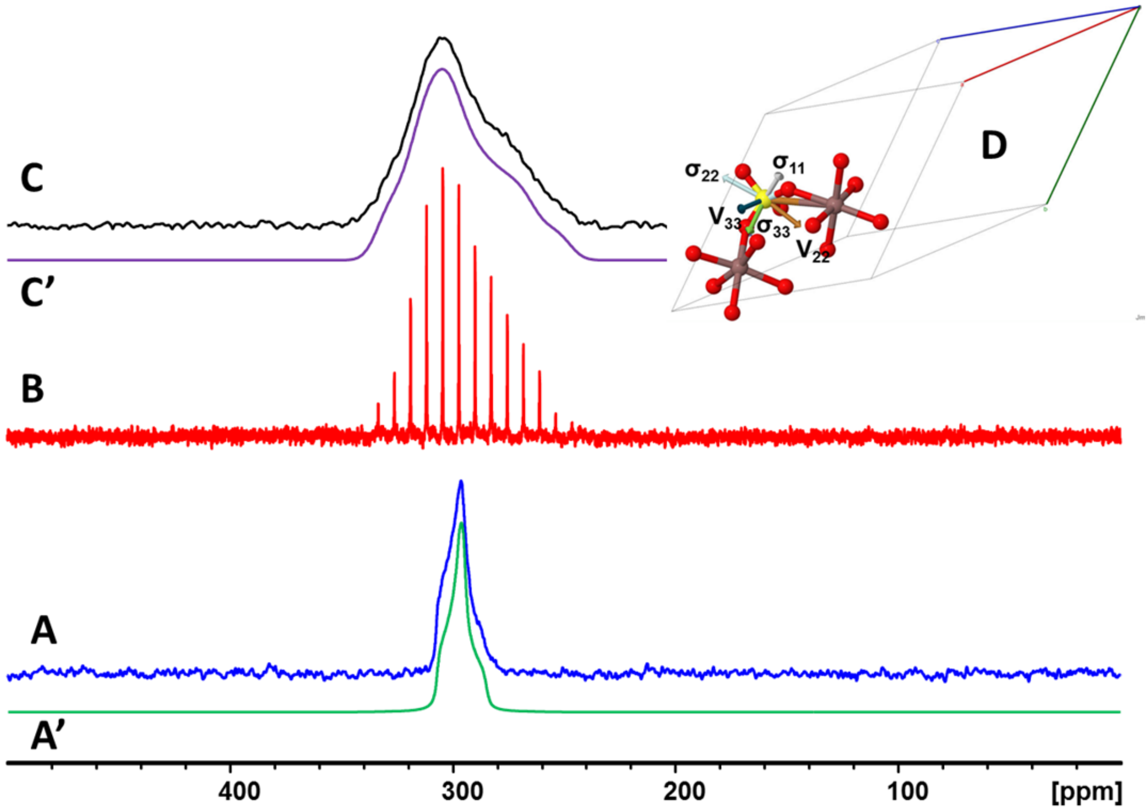

Figure S5 ^{33}S spectraof $In_2(SO_4)_3$ at 21.1T. A - experimental 5.8 kHz RAPT-MAS Bloch Decay, A' - simulation. B – stationary QCPMG spectrum. C - stationary Hahn Echo, B'-simulation of the stationary spectrum accounting for both the EFG and CSA interactions. D - Representative portion of the unit cell showing the calculated orientations for the principal components of the EFG and CSA tensors. Sulfur, oxygen, and indium are shown in yellow, red, and brown respectively.

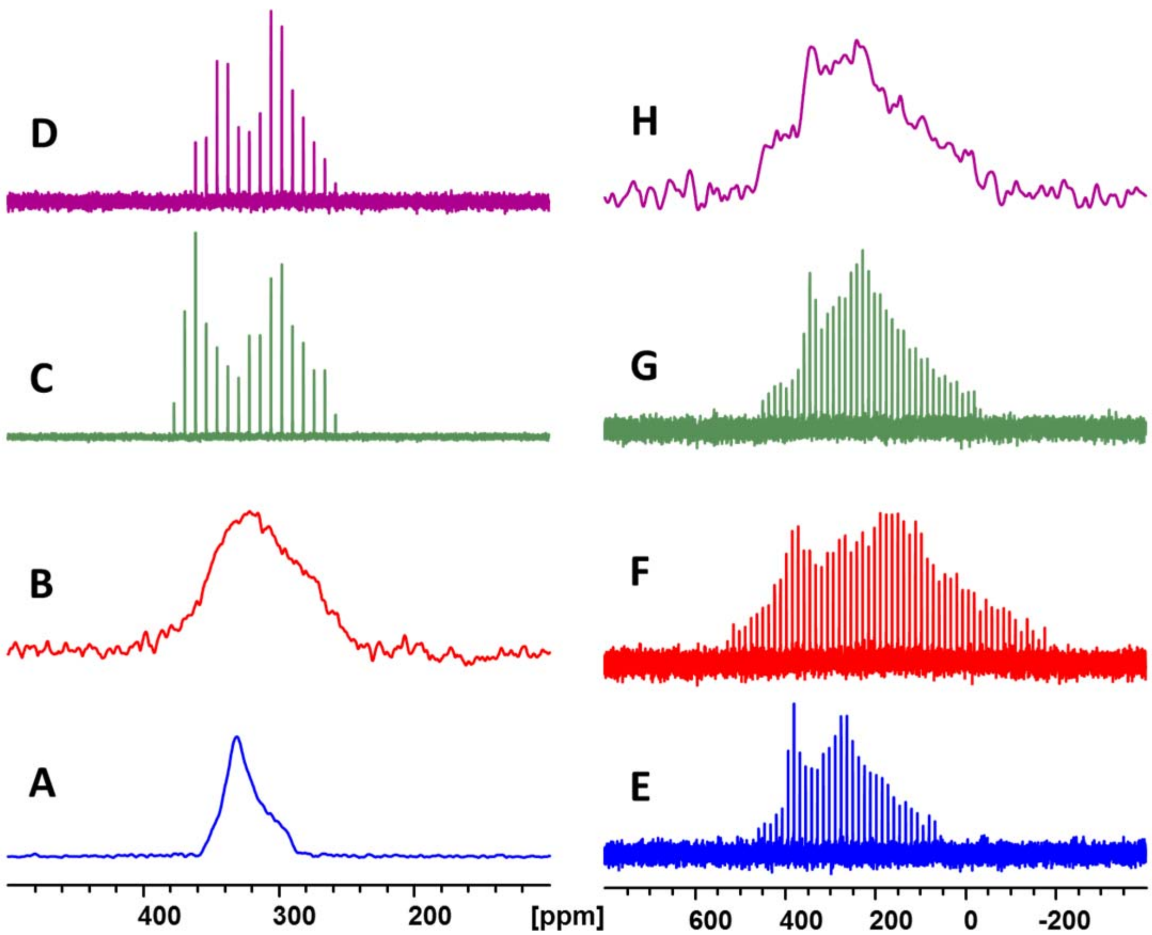

Figure 6 Representative ^{33}S stationary spectra of sulfates obtained at 11.7 T ($\nu_0(^{33}S)$ = 38.4 MHz). A - stationary Hahn Echo of $(NH_4)_2SO_4$, B - stationary Hahn Echo of Li_2SO_4, C – stationary QCPMG of K_2SO_4, D – stationary QCPMG of $CaSO_4$, E – stationary QCPMG of $BaSO_4$, F – stationary QCPMG of $Al_2(SO_4)_3$, G – stationary QCPMG of $Ga_2(SO_4)_3$, H – stationary Hahn Echo of $Ga_2(SO_4)_3$.

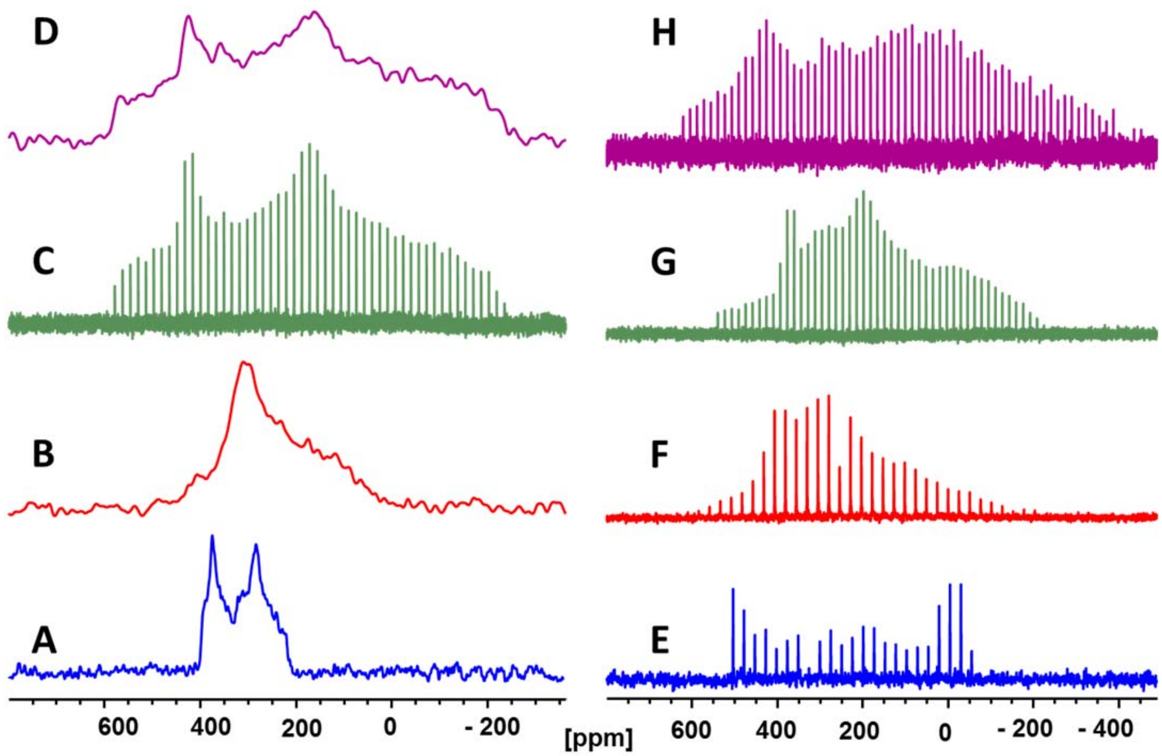

Figure 7 Representative ^{33}S stationary spectra of sulfates obtained at 9.4 T ($\nu_0(^{33}S)$ = 30.73 MHz). A - stationary Hahn Echo of K_2SO_4, B - stationary Hahn Echo of $In_2(SO_4)_3$, C – stationary QCPMG of $ZnSO_4$, D – stationary Hahn Echo of $ZnSO_4$, E – stationary QCPMG of β-$MgSO_4$, F – stationary QCPMG of $BaSO_4$, G – stationary QCPMG of $Ga_2(SO_4)_3$, H – stationary QCPMG of $Al_2(SO_4)_3$.

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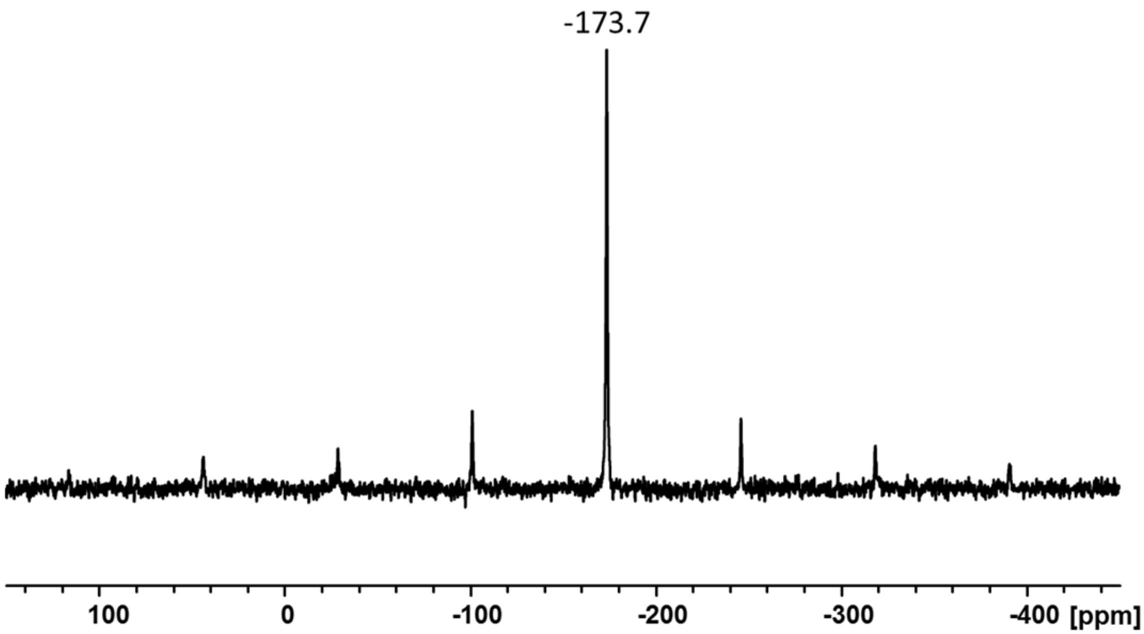

Figure S8 ^{33}S MAS NMR spectrum of K_2S obtained in a field of 21.1T at spinning rate of 5000 Hz. A total of 64 Bloch Decay scans were accumulated with relaxation delay of 100s.

Table S1 – Experimental and calculated ^{33}S NMR parameters for sulfides used in shielding correlation (Figure 8).[S1-S3]

Compound	Experimental $\delta_{iso}{}^{a}$ (ppm)	Calculated $\sigma_{iso}{}^{b}$ (ppm)
Li_2S	-343.9	803.57
Na_2S	-339.5	780.46
K_2S	-173.7	575.46
CS_2	0	448.43
CaS	-29.1	354.84
SrS	43.5	328.97
ZnS (Cubic)	-236.5	660.00
ZnS (Hexagonal)	-228	625.33
CdS	-284	727.26
PbS	-292.4	788.50

[a] All experimental δ_{iso} are from Refs.S1-S3, except for K_2S, which was measured in this work (ESM, Figure S8). [b]All calculations were performed in this work using previously reported structures.[S4]

References

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