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Insight into the Hydrogen Bonding of Uranyl Hydroxide Layers and Capsules using ^{1}H MAS NMR Spectroscopy

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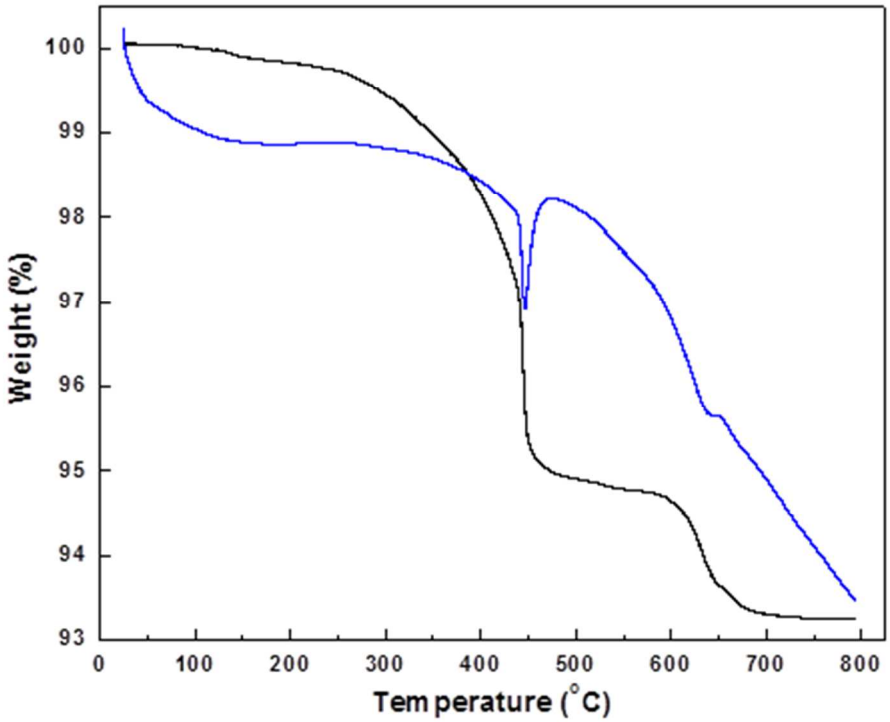

Figure S1: TGA/DSC result of α-$UO_2(OH)_2$. Only a small weight loss is observed up to ~150 ^{o}C consistent with small concentration of surface adsorbed waters, while the higher temperature weight loss is consistent with the loss of water to form the UO_3 phase. The black line is the weight loss, and the blue line is the first derivative of the weight loss.

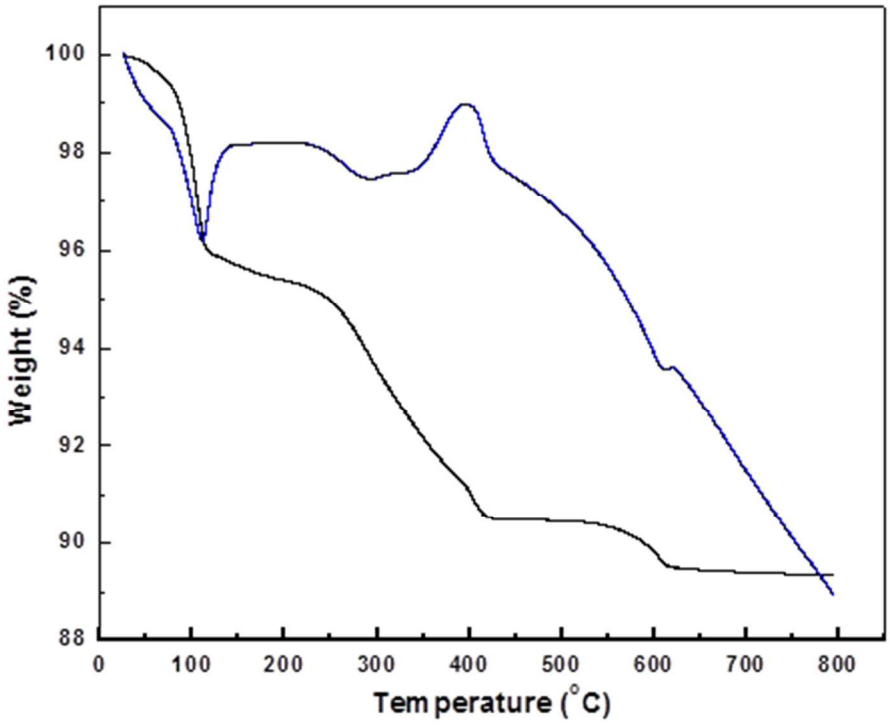

Figure S2: TGA/DSC result for metaschoepite, $(UO_2)_4O(OH)_6 \cdot 5H_2O$ reveals a more complex behavior with the inter-layer waters being lost between 110 to 240 ^oC , with the final conversion to UO_3 occurring above 300 ^oC. The black line is the weight loss, and the blue line is the first derivative of the weight loss.

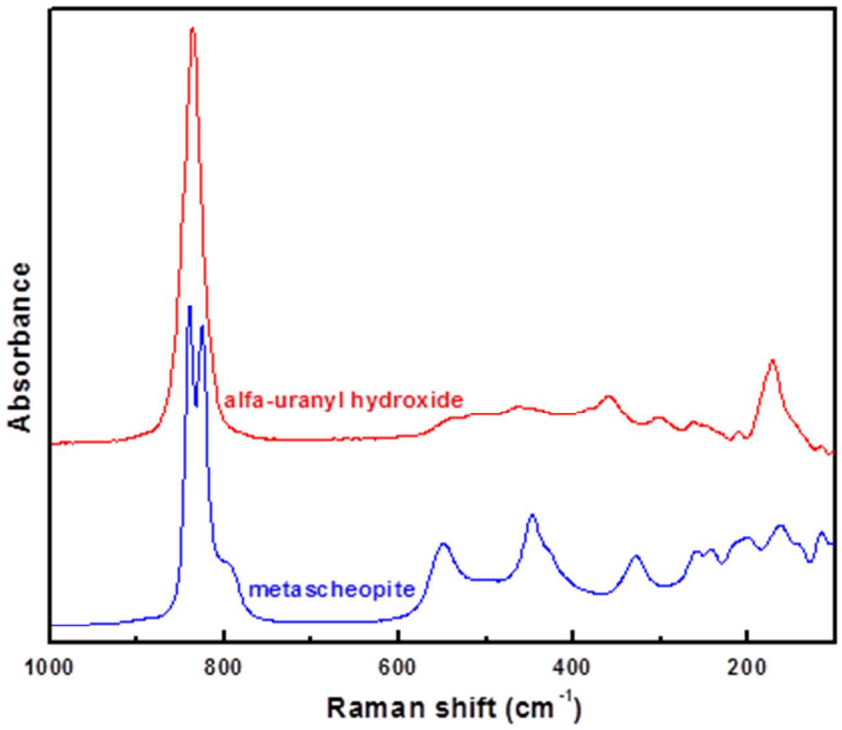

Figure S3: Raman of α-$UO_2(OH)_2$ and metaschoepite, $(UO_2)_4O(OH)_6 \cdot 5H_2O$, showing the dominant U=O absorbance at ~ 800 cm^{-1}.

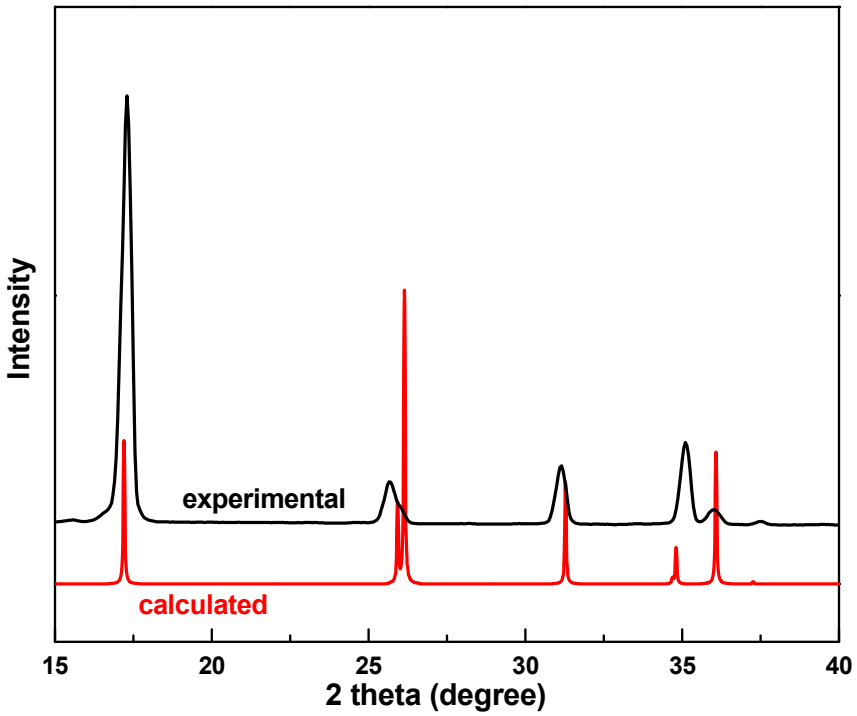

Figure S4: Experimental and simulated XRD patterns of α-$UO_2(OH)_2$.

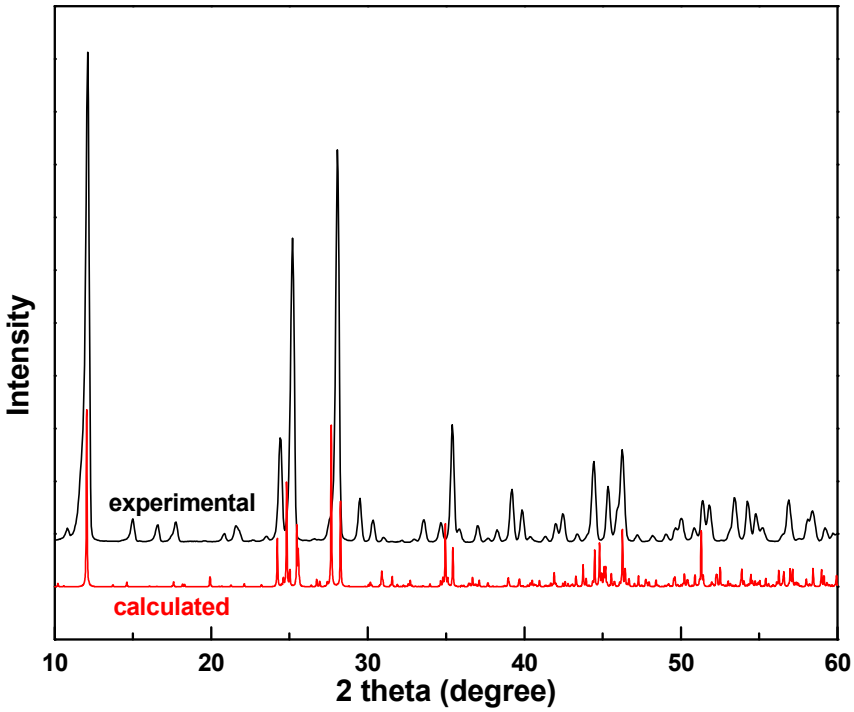

Figure S5: Experimental and simulated XRD patterns of metaschoepite, $(UO_2)_4O(OH)_6 \cdot 5H_2O$.

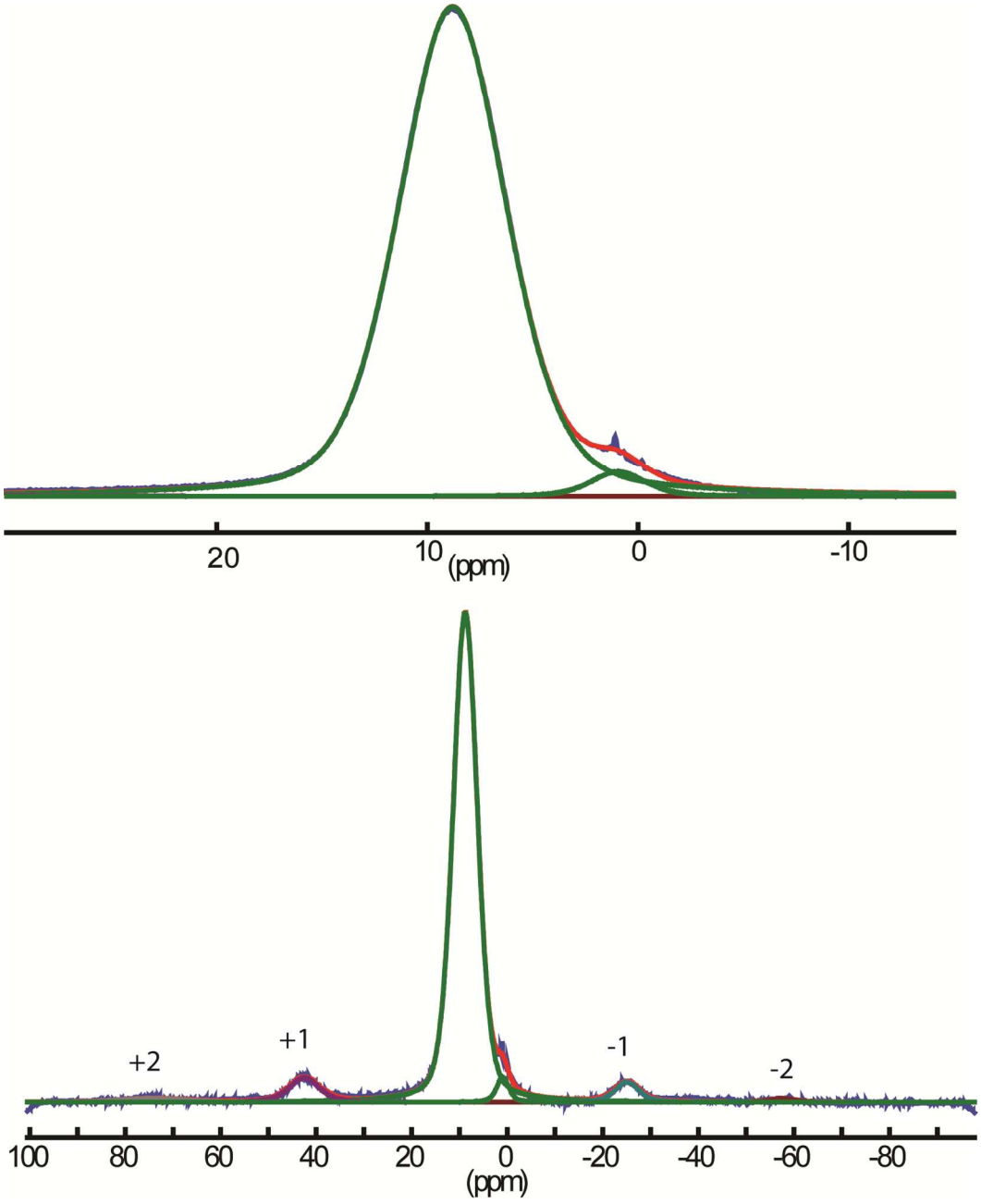

Figure S6: Solid state ^{1}H MAS NMR spectrum and spectral deconvolution for α-$UO_2(OH)_2$ showing the isotropic chemical shift region expansion (top) along with the full spinning sideband manifold. Chemical shifts and line widths are summarized in Table S1.

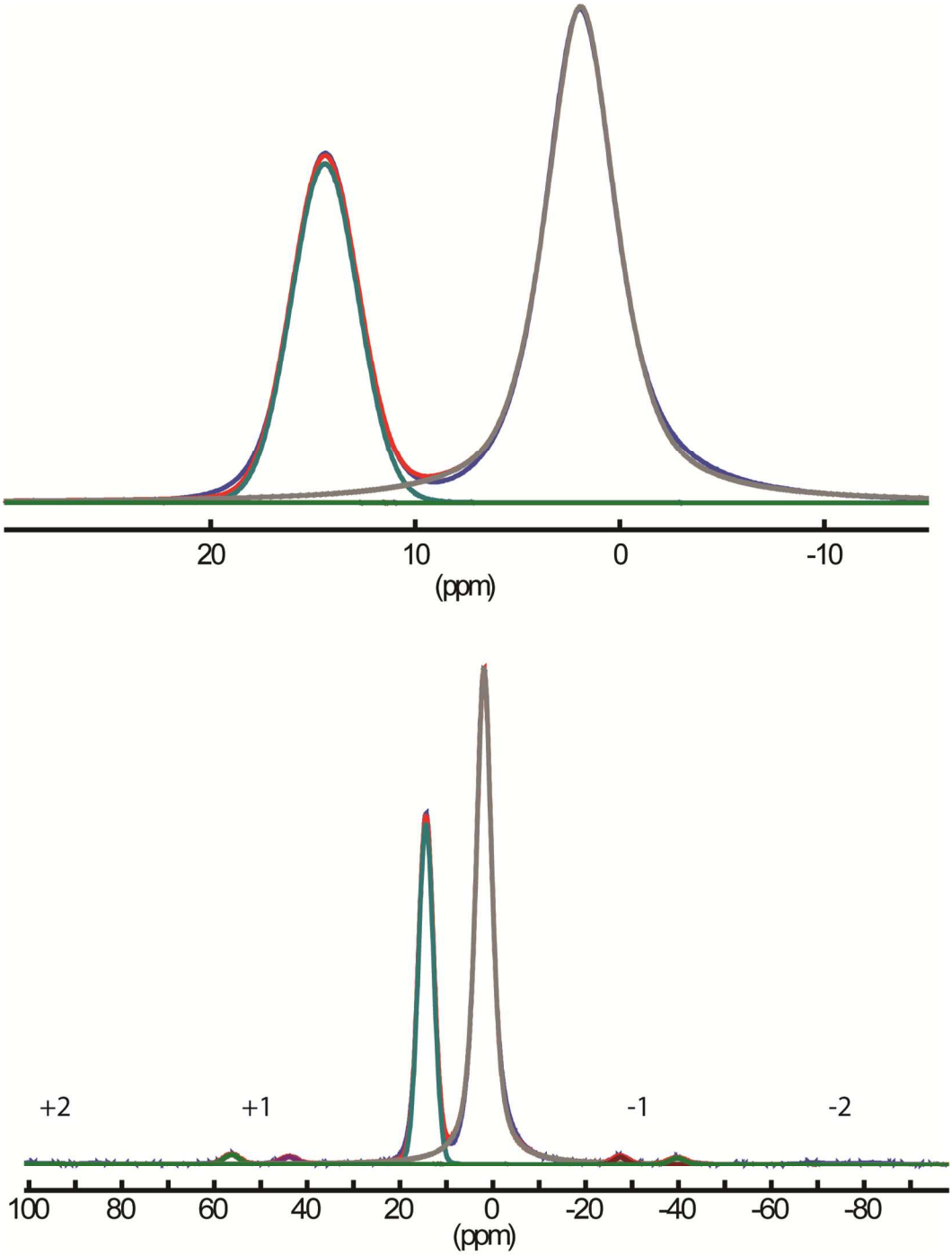

Figure S7: Solid state ^{1}H MAS NMR spectrum and spectral deconvolution for metaschoepite $(UO_2)_4O(OH)_6 \cdot 5H_2O$ showing the isotropic chemical shift region expansion (top) along with the full spinning sideband manifold. Chemical shifts and line widths are summarized in Table S1.

Table S1: ^{1}H MAS NMR chemical shifts, line widths, relative concentration and assignment for the different uranyl materials.

Sample (treatment)	δ (ppm)	FWHM (Hz)	Fraction (%)	Assignment
α-UOH	8.8	3580	98	μ_2-OH
	0.9	2430	2	impurity
Metaschoepite	14.4	2270	35	μ_2-OH
	1.9	2463	65	H_2O
100 ^{o}C, 6 hours	14.4[a]	2304 [a]	13	μ_2-OH
	11.8	2075	30	μ_2-OH
	1.9 [a]	1570	14	
	0.9	2045	43	H_2O
200 ^{o}C, 48 hours	14.4 [a]	2304 [a]	13	μ_2-OH
	11.8	2080	31	μ_2-OH
	1.9 [a]	1600	13	H_2O
	0.8	2070	43	H_2O
300 ^{o}C, 48 hours	17.6	1820	3	μ_2-OH
	14.4 [a]	2304 [a]	15	μ_2-OH
	11.9	1977	24	μ_2-OH
	3.4	2444	11	H_2O
	0.2	2026	44	H_2O
	-3.9	1719	3	unassigned

[a] This chemical shift and/or line width of this resonance was fixed to the starting metaschoepite values during deconvolution.

FWHM = Full Width and Half Maximum

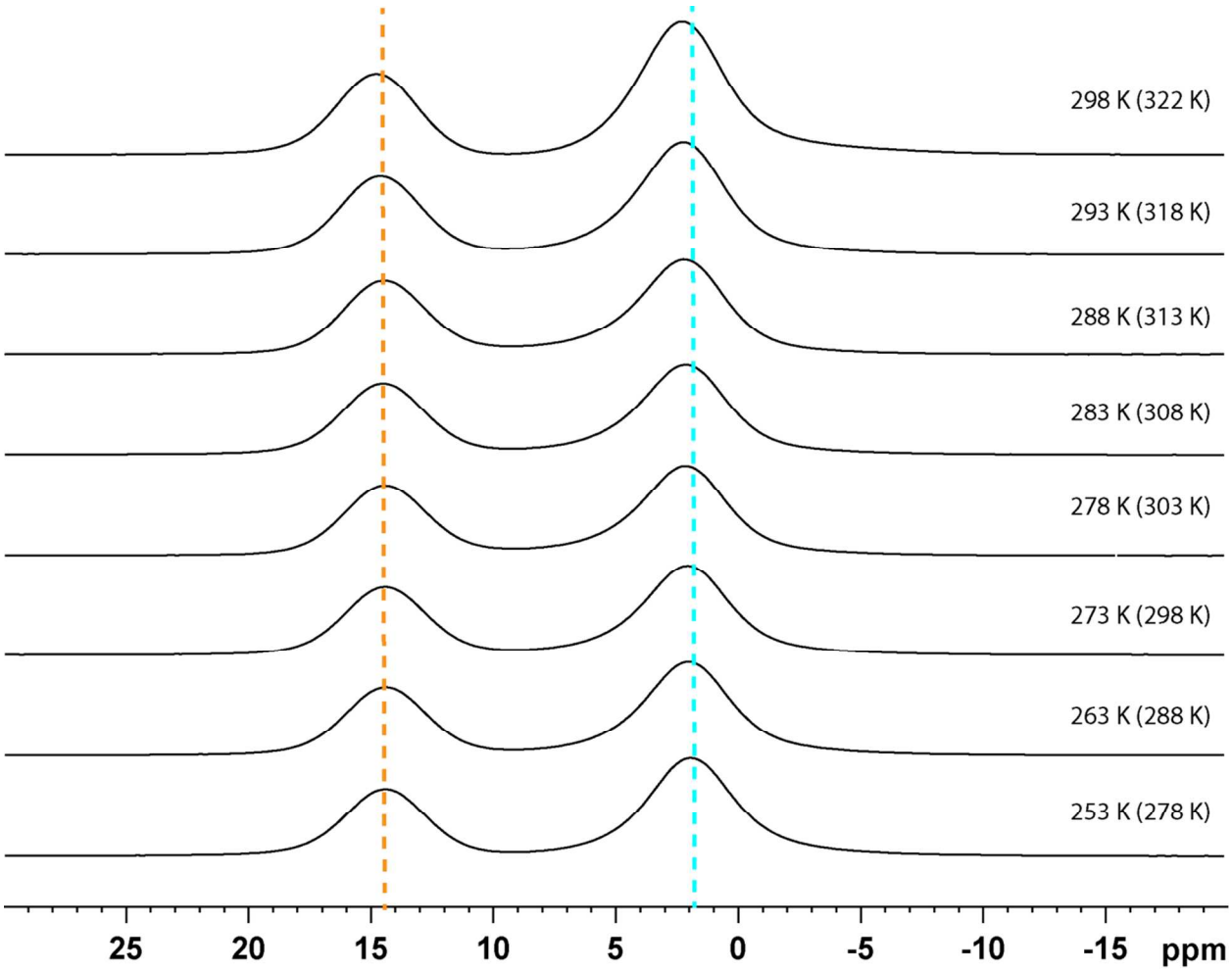

Figure S8. Variable temperature solid state ^{1}H MAS NMR for metaschoepite $(UO_2)_4O(OH)_6 \cdot 5H_2O$. The set temperature and the actual sample temperature corrected for frictional heating caused by spinning (in parentheses) are shown. No significant variation in either the chemical shift of line widths were observed for this material over this temperature range.

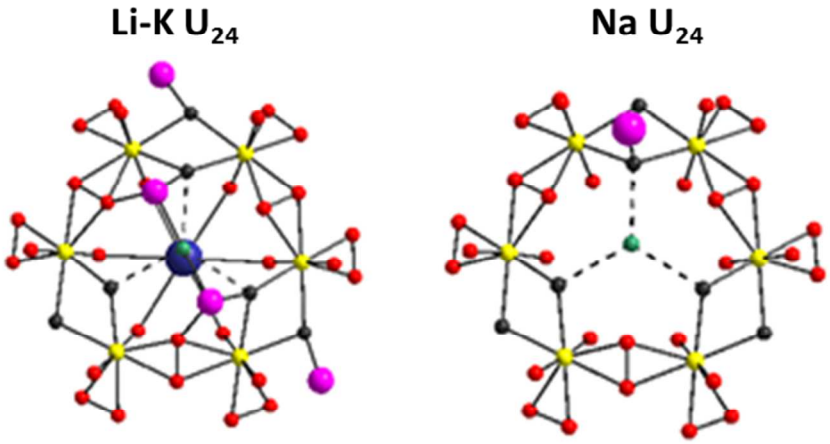

Figure S9: Comparing the bonding of the μ_2-OH ligands (gray spheres) to lattice cations and water molecules in LiK-U_{24} (left) and Na-U_{24} (right). LiK-U_{24}: blue sphere is encapsulated K^+, pink spheres are external Li^+, and the green sphere is a water molecule in the center of the hexagonal face. The dashed bonds represent possible hydrogen-bonding between this water molecule in the hexagonal face and the hydroxyl ligands. Na-U_{24}: same, except the pink sphere is Na^+.