SAND2015-3029C

Solid-State Dynamics and Hydrogen Bonding in Uranyl Clusters using Multi-Nuclear MAS NMR Spectroscopy

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Photograph by Sarah K. McIntyre

INTRODUCTION

Understanding fundamental uranyl-polyoxometalate (POM) chemistry in solution and the solid-state is the first step to developing new actinide materials and separation processes that are vital to every step of the nuclear fuel cycle. Many solid-state geometries of uranyl-POMs have been described, but we are only beginning to understand their chemical behavior which thus far includes the role of templates in their self-assembly, and the dynamics of encapsulated species in solution. Multi-nuclear (^1H, ^{23}Na and ^7Li) MAS NMR and 2D ^1H-^{23}Na and ^1H-^7Li HETCOR MAS NMR correlation experiments have been used to investigate the solid state exchange dynamics and location of the exchangeable cations in these uranyl clusters. While it has been recognized that capsule-like molybdate and uranyl POMs exchange encapsulated species when dissolved in water, analogous exchange in the solid-state has not been documented, or even considered. Here we observe the extremely high rate of transport of Li+ and aqua species across the uranyl shell in the solid-state, that is impacted by both temperature and pore-blocking by larger species. These results highlight the untapped potential of emergent f-element materials and vesicle-like POMs.

In many of these uranyl cluster materials the structural location of the proton species is lacking or disordered in many cases. In this study we have utilized variable temperature moderate-speed (30 kHz) ^1H MAS NMR and 2D ^1H-^1H DQ and NOESY NMR correlation experiments to probe the structure and dynamics of water and μ-OH ligand in the uranyl clusters and a series of model layered uranyl hydroxides. A correlation between the U-O-H•••(H_2O) hydrogen bond length and the observed ^1H NMR chemical was developed based on CASTEP GIPAW NMR chemical shift calculations of the periodic uranyl hydroxide model systems. These correlations allowed the assignment of the different ^1H environments and improved understanding of the hydrogen bonding that is occurring in these uranyl materials.

MATERIALS AND NMR SPECTROSCOPY

- The U_{24} capsules with different alkali cations were prepared as detailed previously.[1-3]
- All solid state NMR spectra were obtained on a Bruker Avance III using a 4 mm MAS NMR probe at 233.2 MHz (^7Li) and 158.7 MHz (^{23}Na). The 2D ^1H-^{23}Na and ^1H-^7Li CP and HETCOR experiments were performed using standard CP-based sequences. Additional, ^7Li ^{23}Na and ^1H MAS NMR (600.1 MHz) were obtained using a 2.5 mm probe with spinning frequencies between 25 and 33 kHz, with the 2D SQ-DQ correlation experiments utilizing the BABA excitation/reconversion sequence. Sample temperatures were corrected for for frictional heating.
- Depleted uranium (U) was utilized for all samples. To reduce the risk of contamination and exposure, all samples were packed in radiological controlled labs and monitored for residual radiation. In addition, all 4 mm samples were packed in Kel-F HRMAS inserts to provide additional containment protection.

[1] M. Nyman, M. A. Rodriguez, T. M. Alam, *Eur. J. Inorg. Chem* . (2011), 2197-2205.
[2] M. Nyman, T. M. Alam, *J. Am. Chem. Soc.* (2012), **134**, 20131-20138.
[3] T. M. Alam, Z. Liao, L. N. Zacharov, M. Nyman, *Chem. Eur. J.* (2013) **20**, 8302-8307.

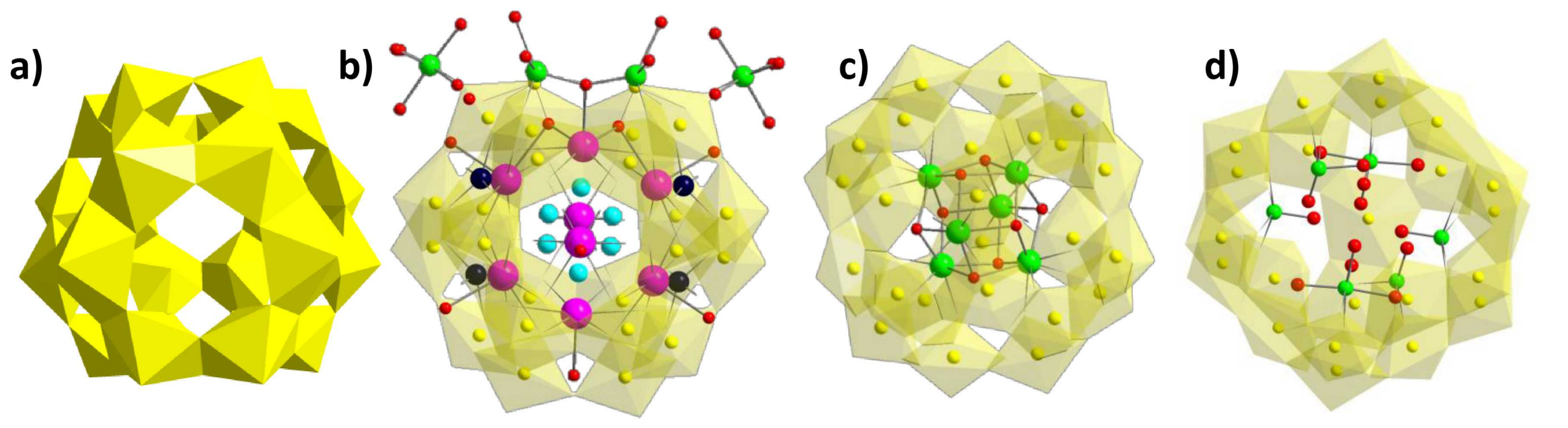
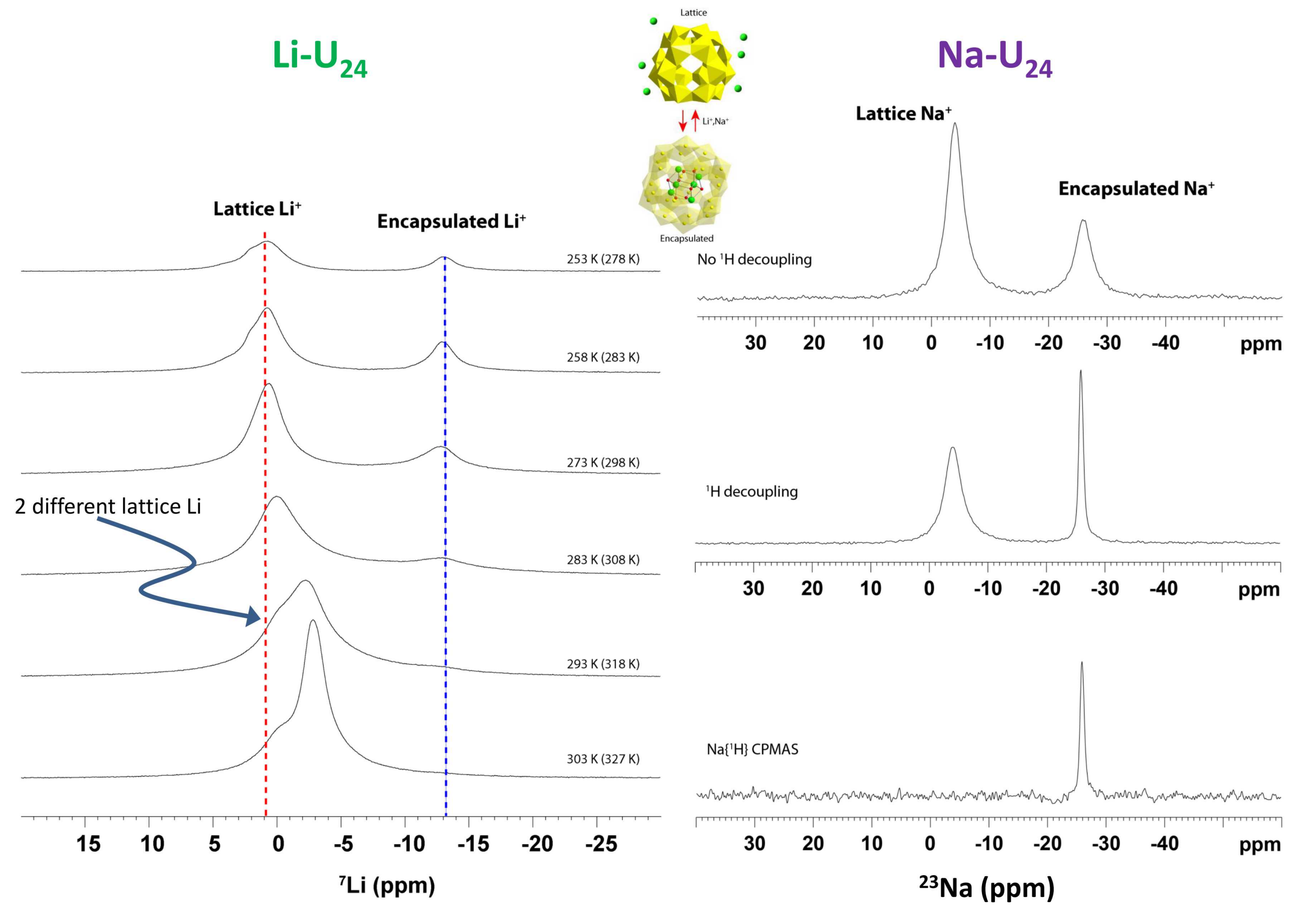


Figure 1: Views of: a) U_{24}, $[UO_2(O_2)(OH)]_{24}^{24-}$ without any encapsulated species. b) LiK-U_{24} showing K^+ under the hexagonal faces (pink), Li^+ just inside four of the square faces (navy) bonded to the peroxide ligands, encapsulated OH^- (turquoise), and two coordination positions of Li^+ cations (light green) just outside of the hexagonal faces. Red spheres are water molecules. c) Na-U_{24} with Na^+ (green) under the six square faces bonded to $U=O_{yl}$, and water molecules under the hexagonal faces. d) Li-U_{24} with Li^+ (green) under two of the six square faces bonded to $U=O_{yl}$, and four additional encapsulated Li^+-cations (green) and their associated water molecules (red). Front uranyl polyhedra removed for ease of viewing in all three views of encapsulated species.

^{23}Na and ^7Li MAS NMR Reveal Encapsulated Alkali Species!!



- Both ^{23}Na and ^7Li reveal an encapsulated species with increased chemical shielding.
- Different CP and ^1H decoupling behavior reveal "rigid" proton species in **Na-U_{24}** capsule.
- The VT behavior of the ^7Li (**Li-U_{24}**) reveal exchange between encapsulated and lattice.

Exchange of Encapsulated Alkali *and* Water Species!!

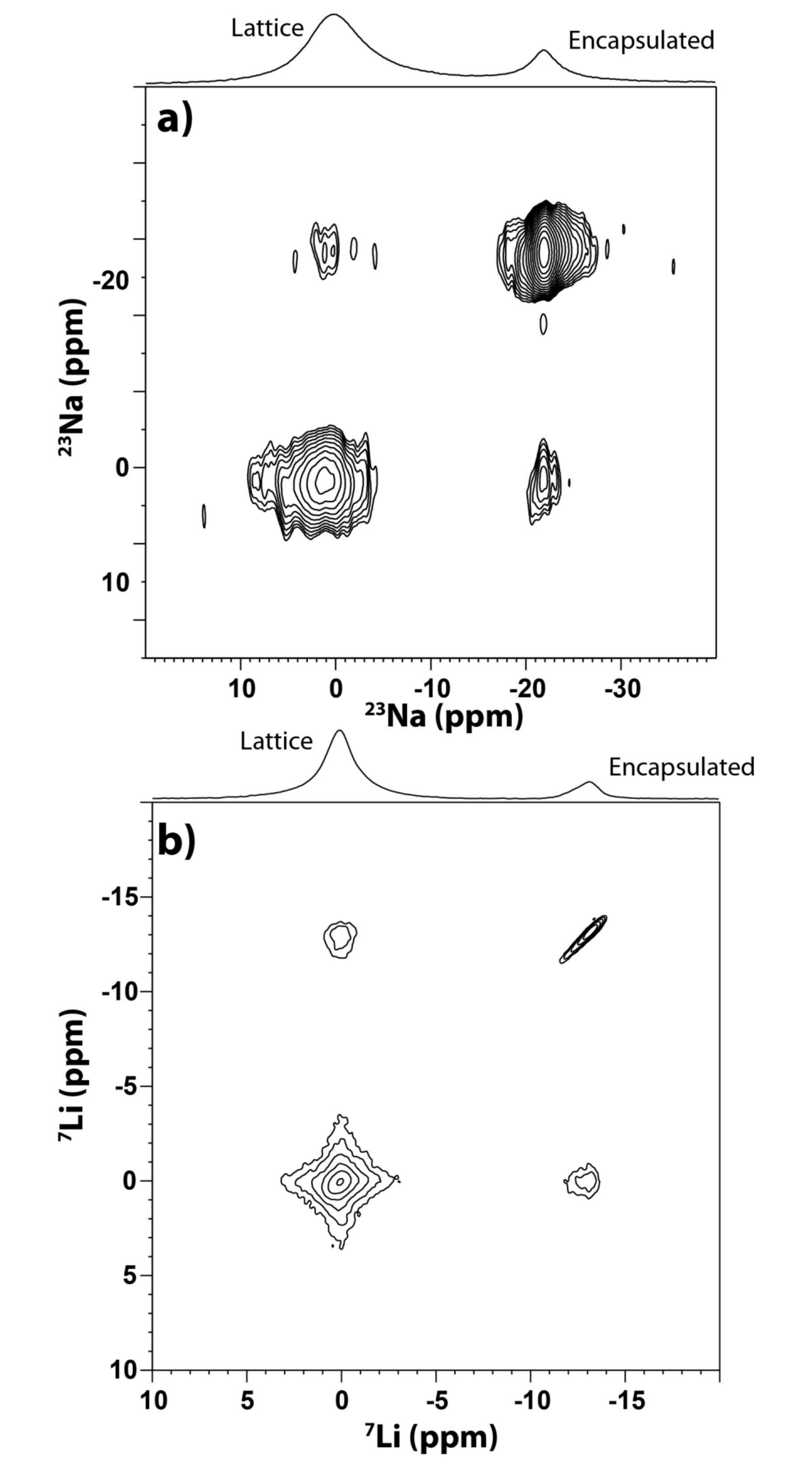


Figure 2: 2D MAS NMR exchange spectra: a) ^{23}Na-^{23}Na (τ_{mix} = 6 ms) for Na-U_{24} (308 K) and b) ^7Li-^7Li (τmix = 10 ms) for LiK-U_{24} (318 K). Cation exchange between the lattice and encapsulated sites is clearly is occurring on the ms time scale.

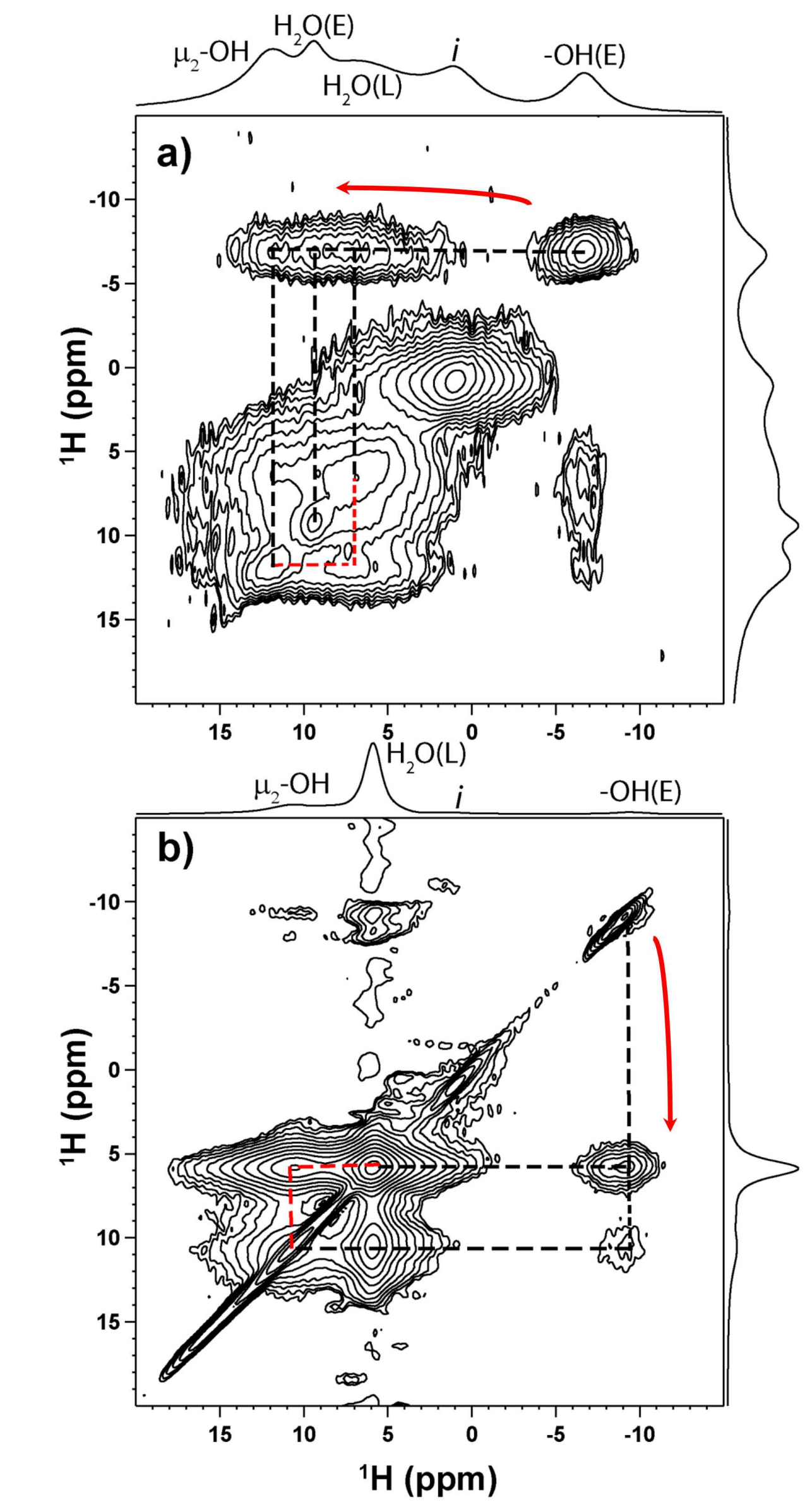
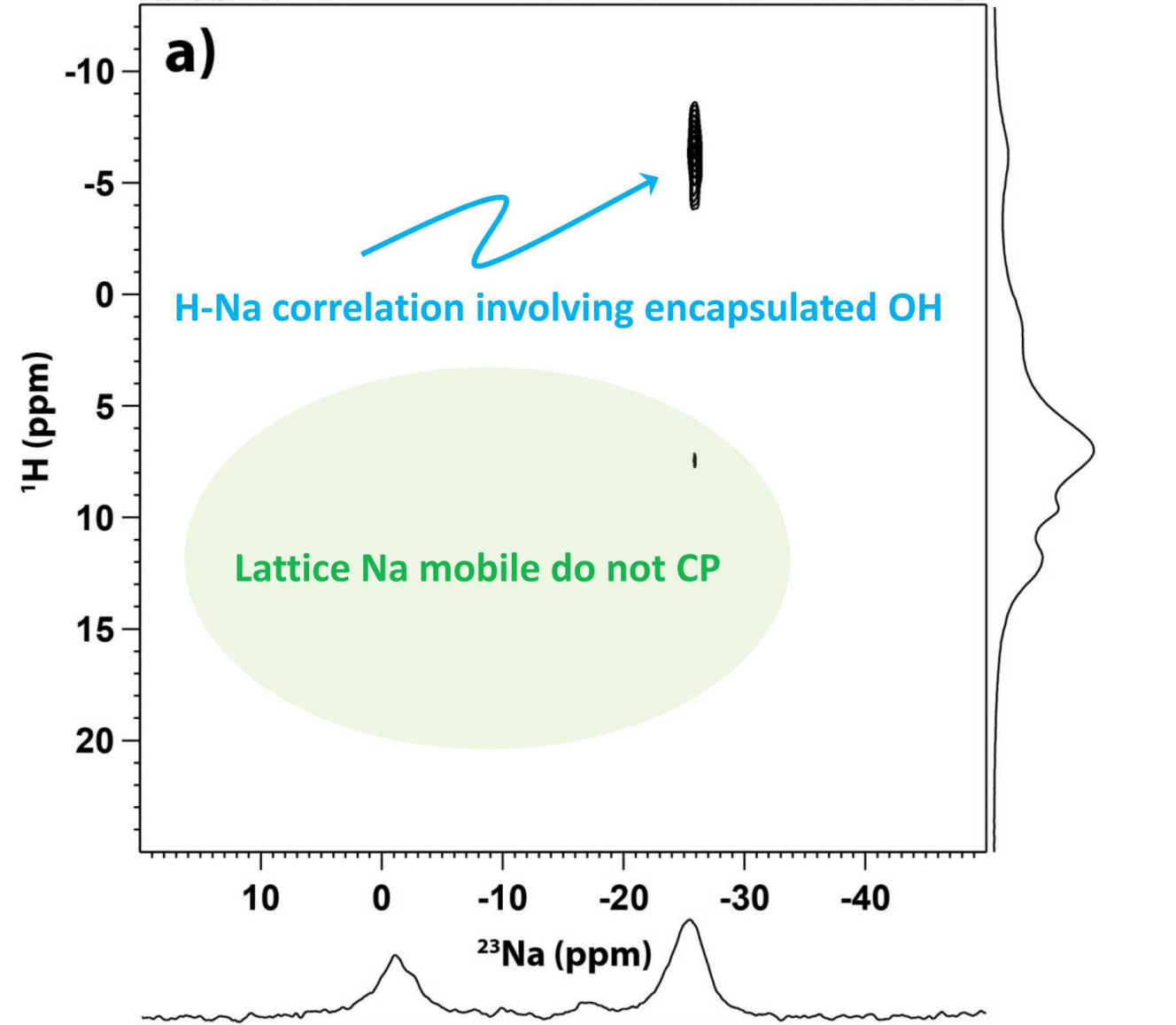
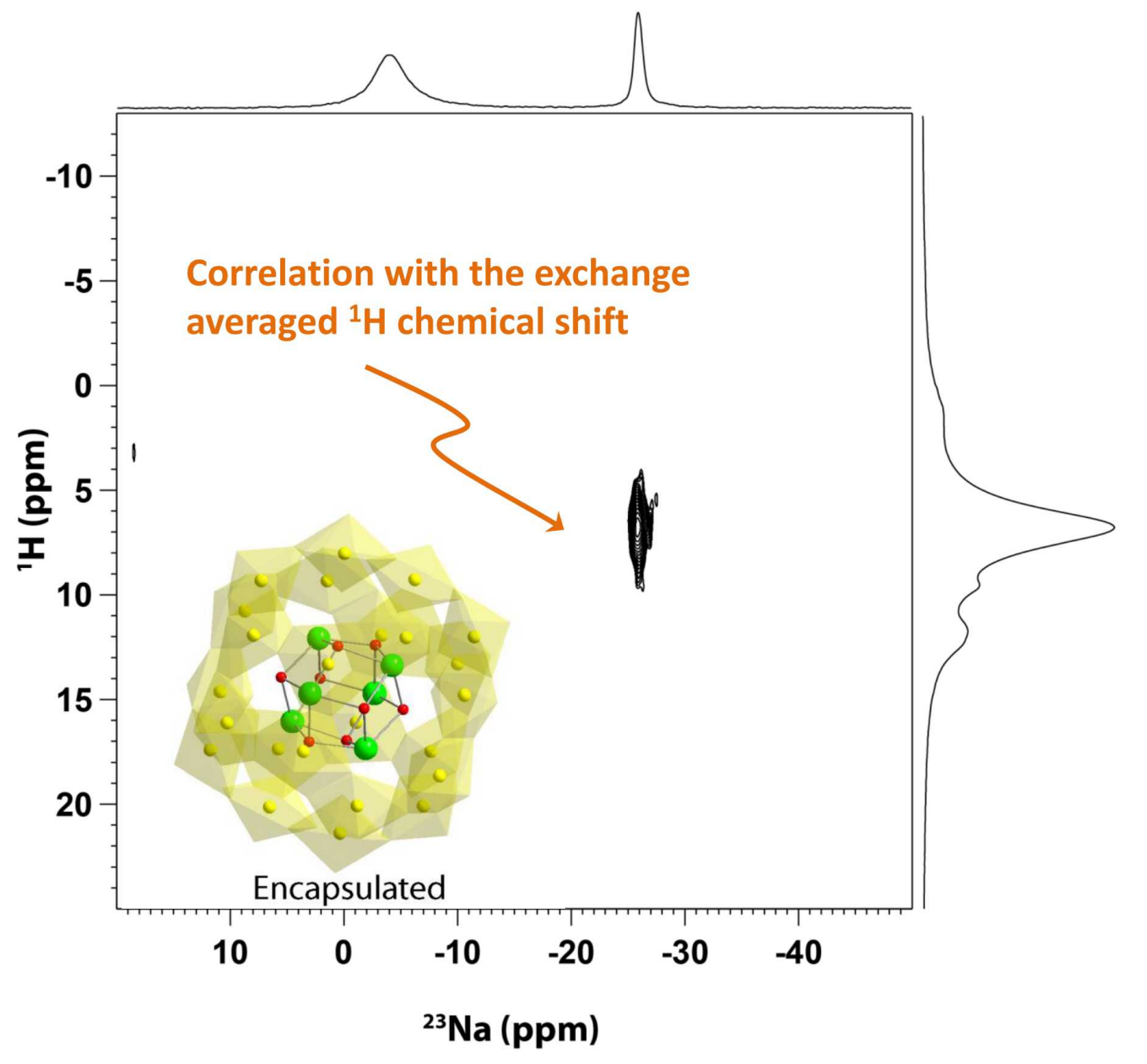


Figure 3: 2D ^1H MAS NMR NOESY spectra for the a) Na-U_{24} cluster (293 K, τ_{mix} = 1ms) and b) KLi-U_{24} (323 K, τ_{mix} = 10 ms). Magnetization exchange between all different proton environments suggesting water exchange bgetween lattice and encapsulated environments.





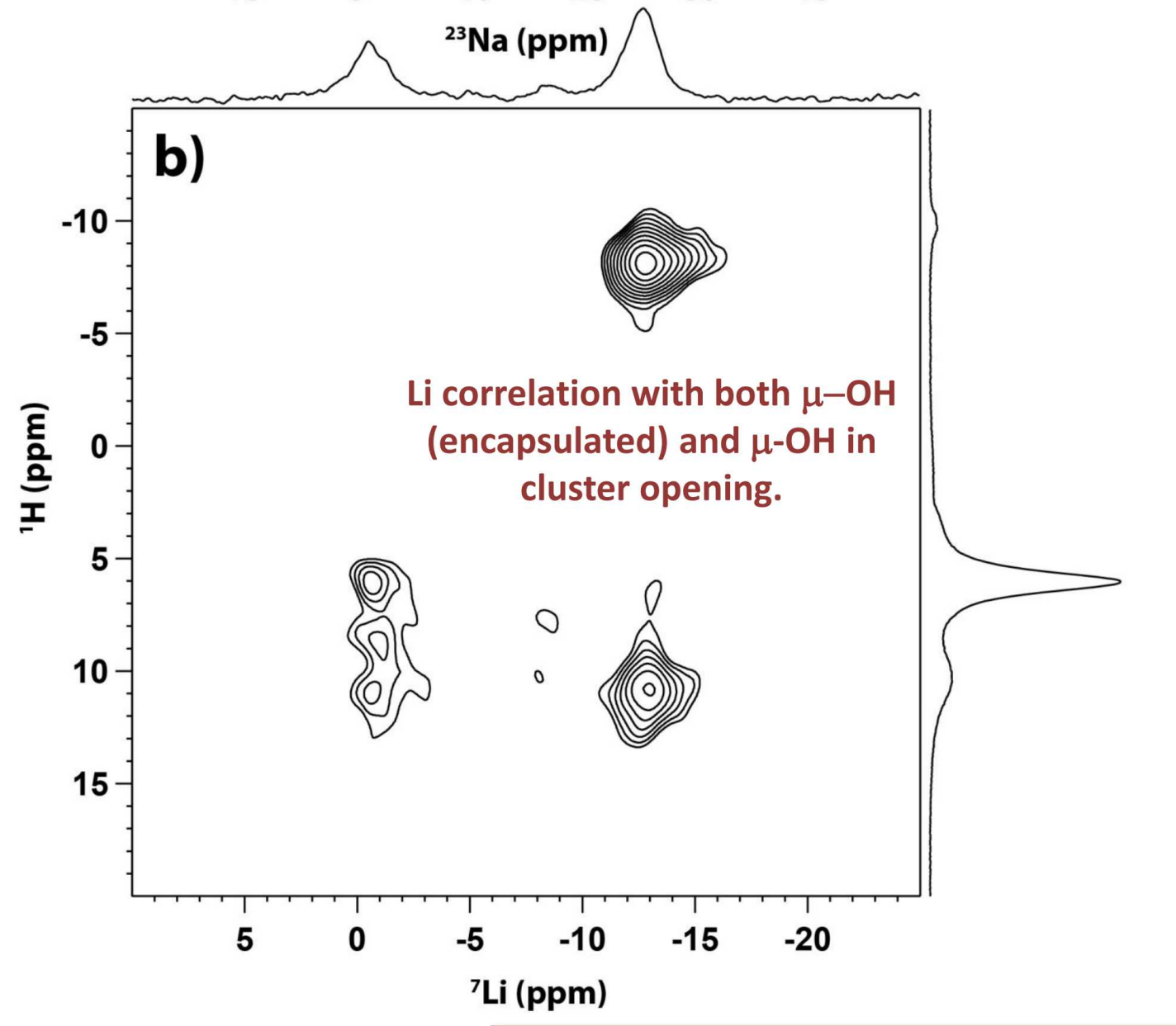
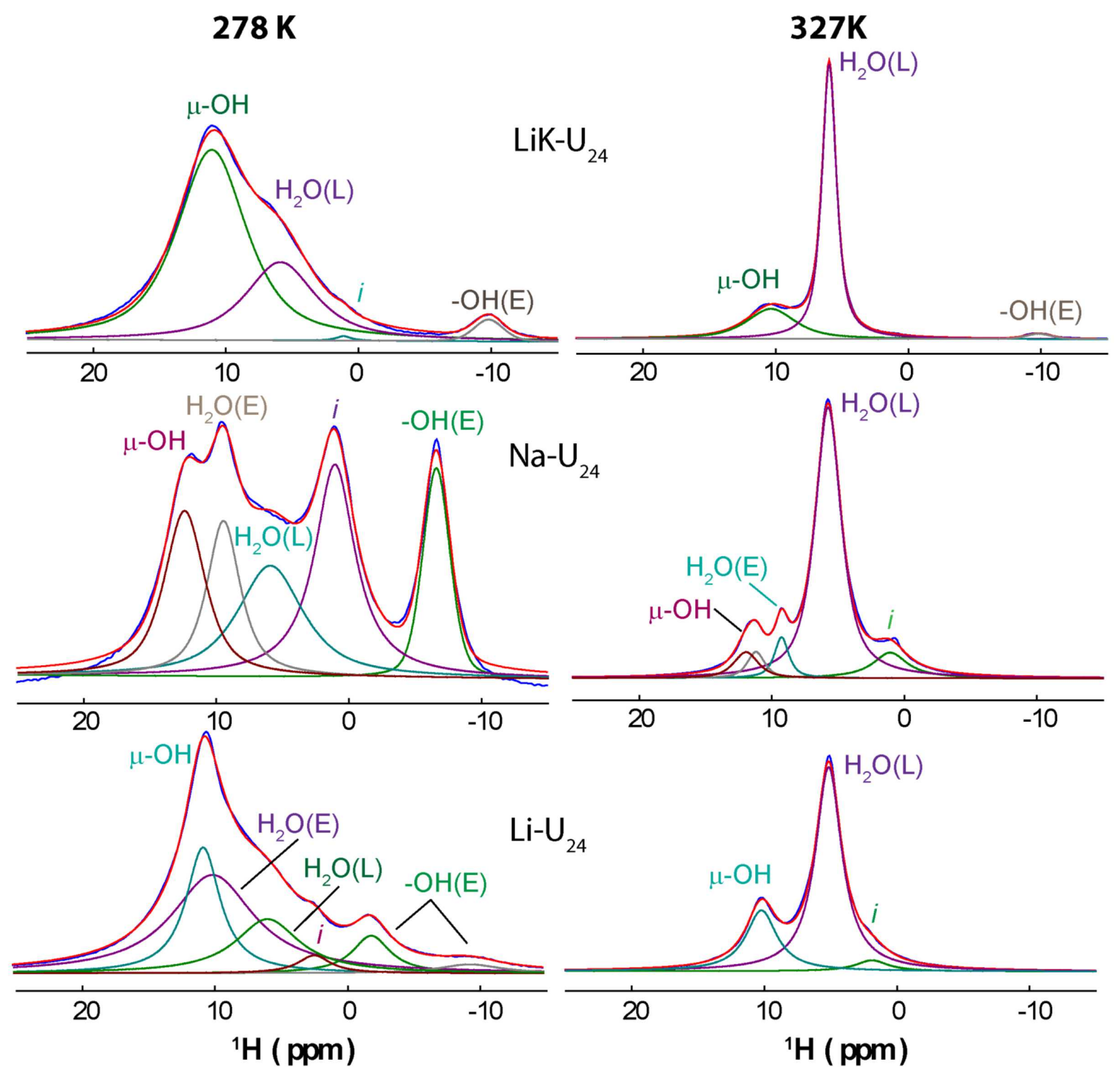


Figure 3: 2D MAS NMR HETCOR spectra: a) ^1H-^{23}Na HETCOR for Na-U_{24} and b) ^1H-^7Li HETCOR for LiK-U_{24} at 298 K. c) 2D ^1H-^{23}Na MAS HETCOR NMR of Na-U_{24} at 330 K. Note the encapsulated Na now correlates with the lattice water, $H_2O(L)$, reflecting the dynamic chemical shift averaging between the encapsulated water, $H_2O(E)$ and the lattice water, $H_2O(L)$ at this temperature. No correlations are observed with the μ_2-OH environments at the hexagonal face.

^1H MAS NMR Dynamic and Complicated!!



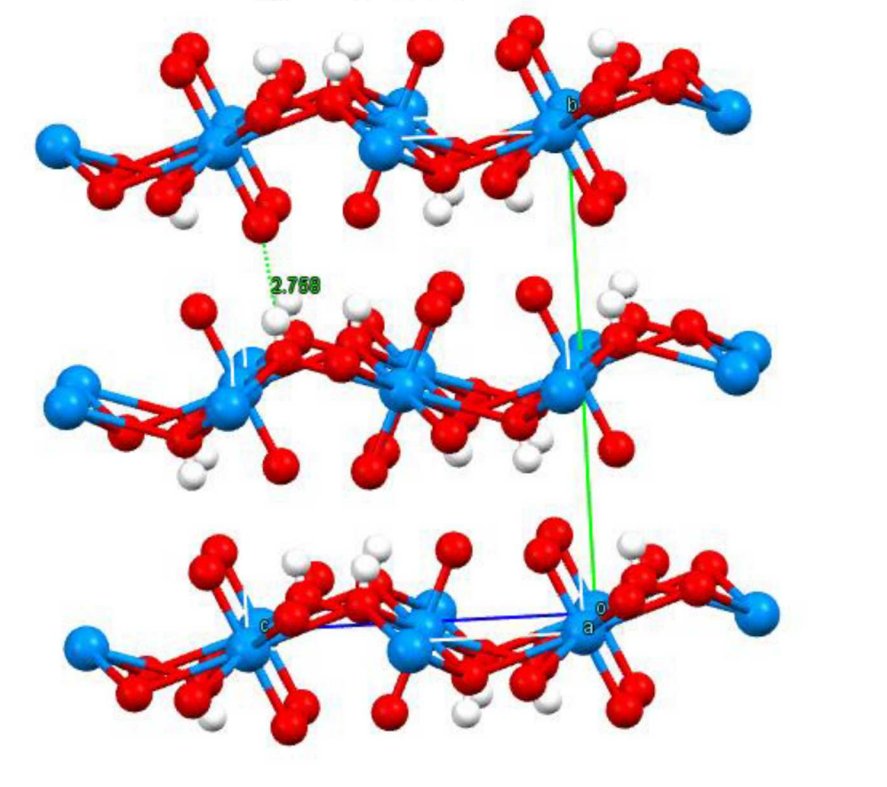
- ^1H NMR reveals extrensive chemical shift exchange averaging.
- Assignments difficult and sometime ambiguous.
- Need to develop tools to help assign different hydrogen bonded environments in uranyl species.
- Limited examples of assigned ^1H NMR for uranyl species.

WHAT CAN BE DONE?

Try and develop correlations between hydrogen bond strength and ^1H MAS NMR chemical shifts using model compounds → →

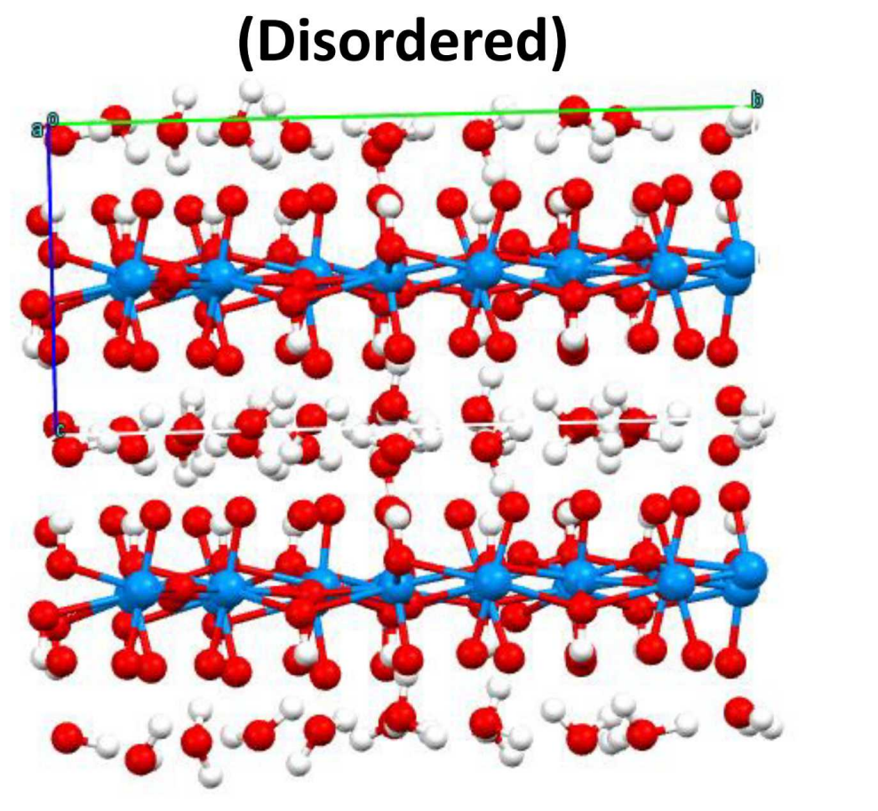
CASTEP and Hydrogen Bond Correlations

α - UOH

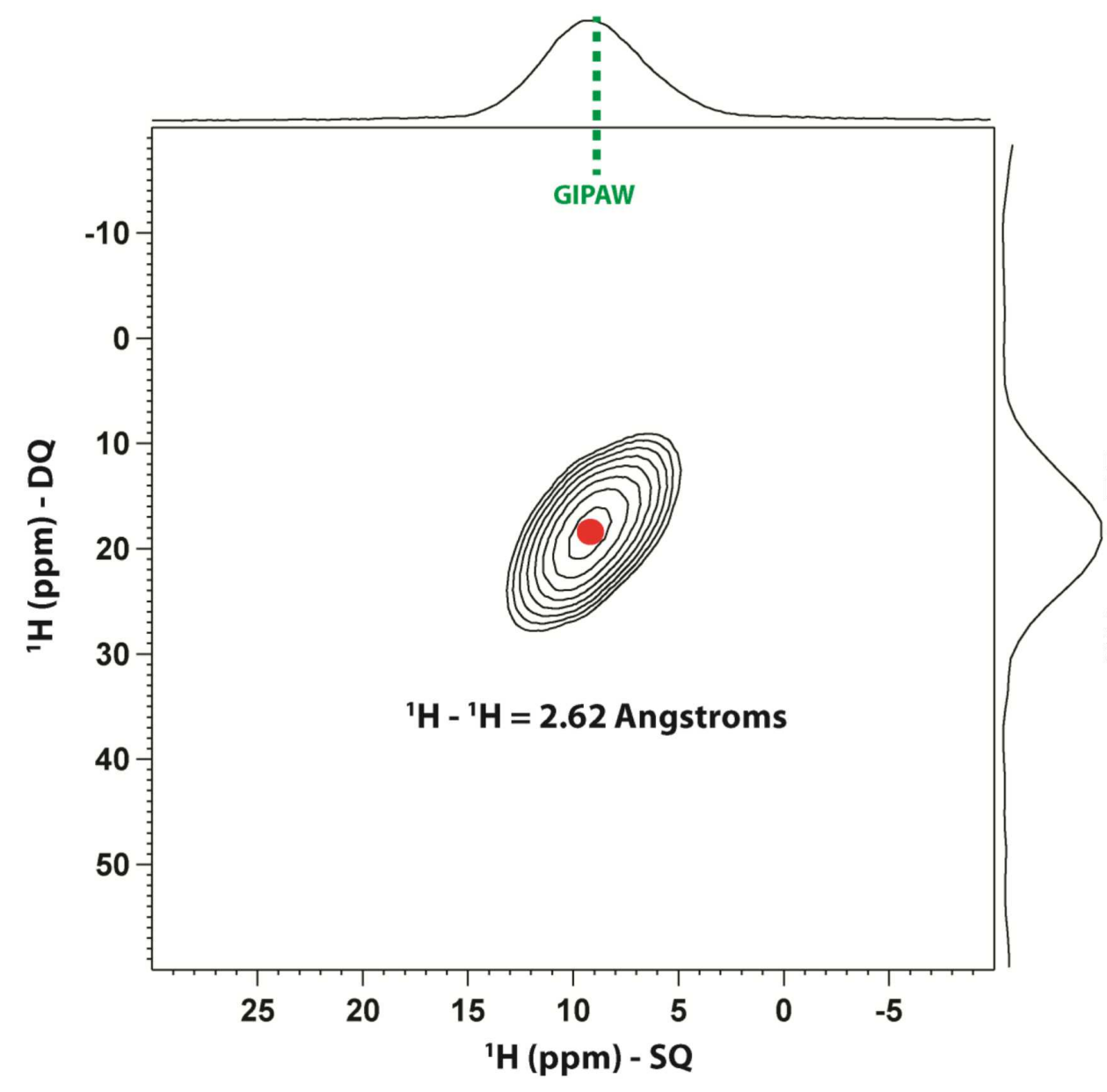


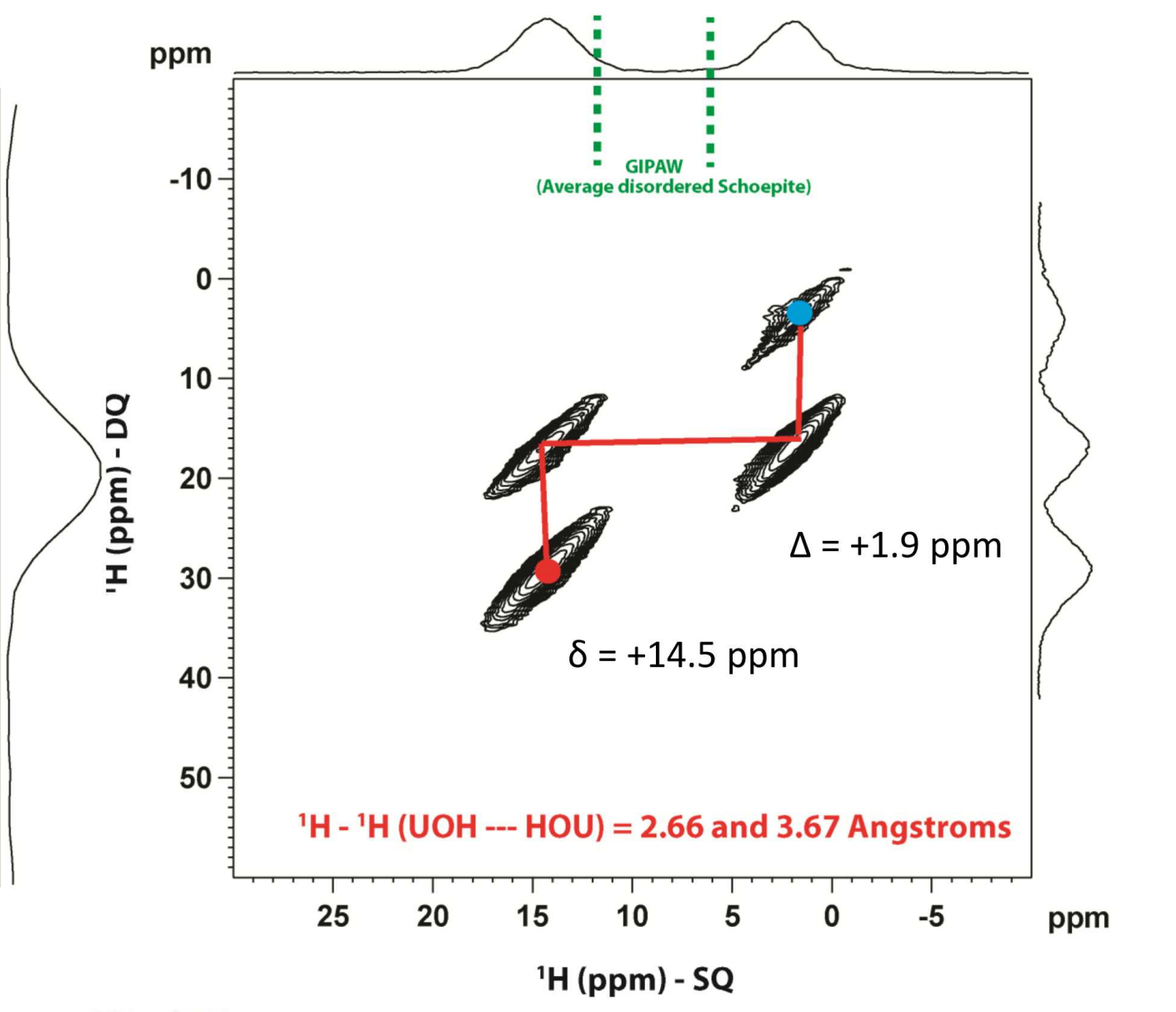
*** UO-H bond distance in crystal structure too short (0.76 Å). Reoptimized in CASTEP to 0.989 Å**

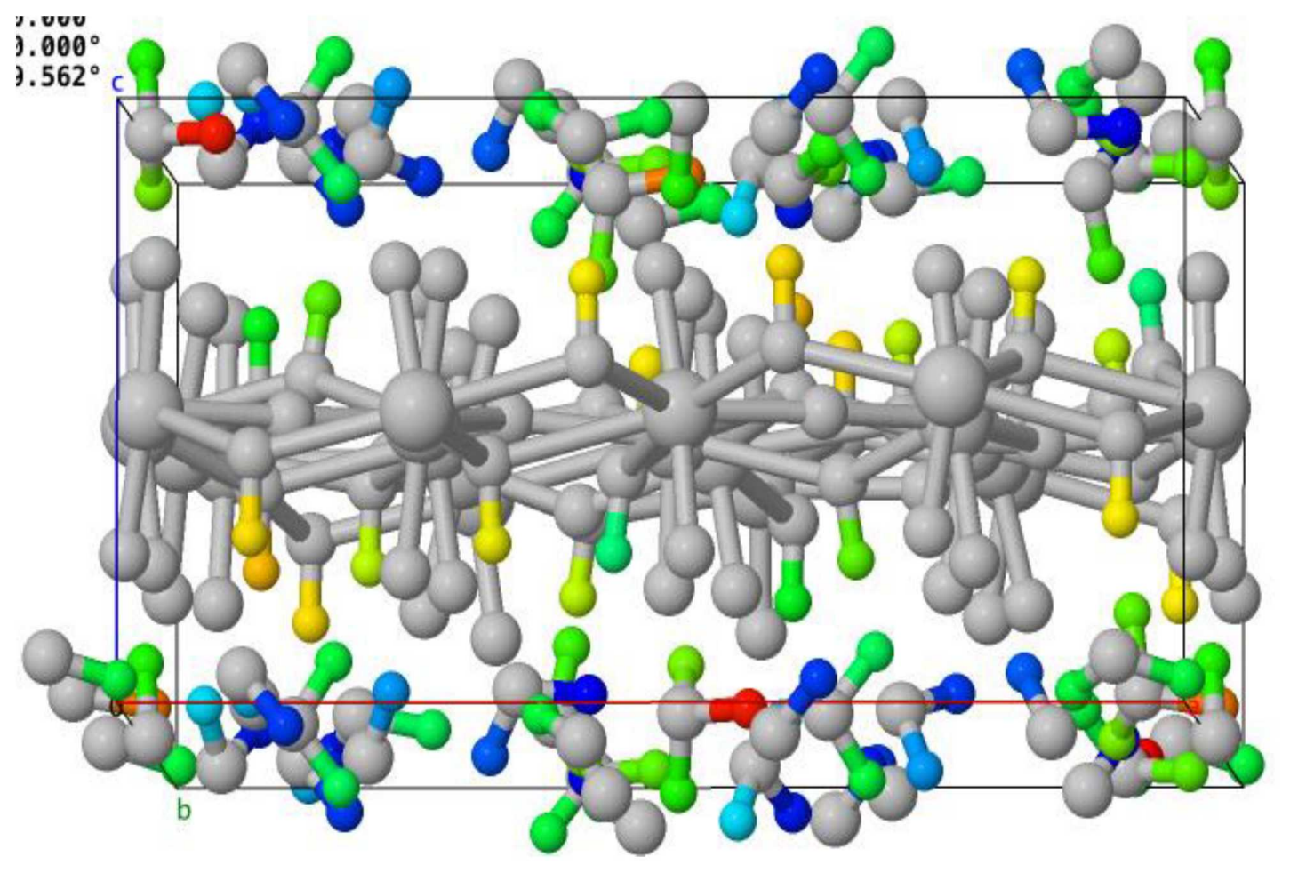
Meta Schoepite (Disordered)

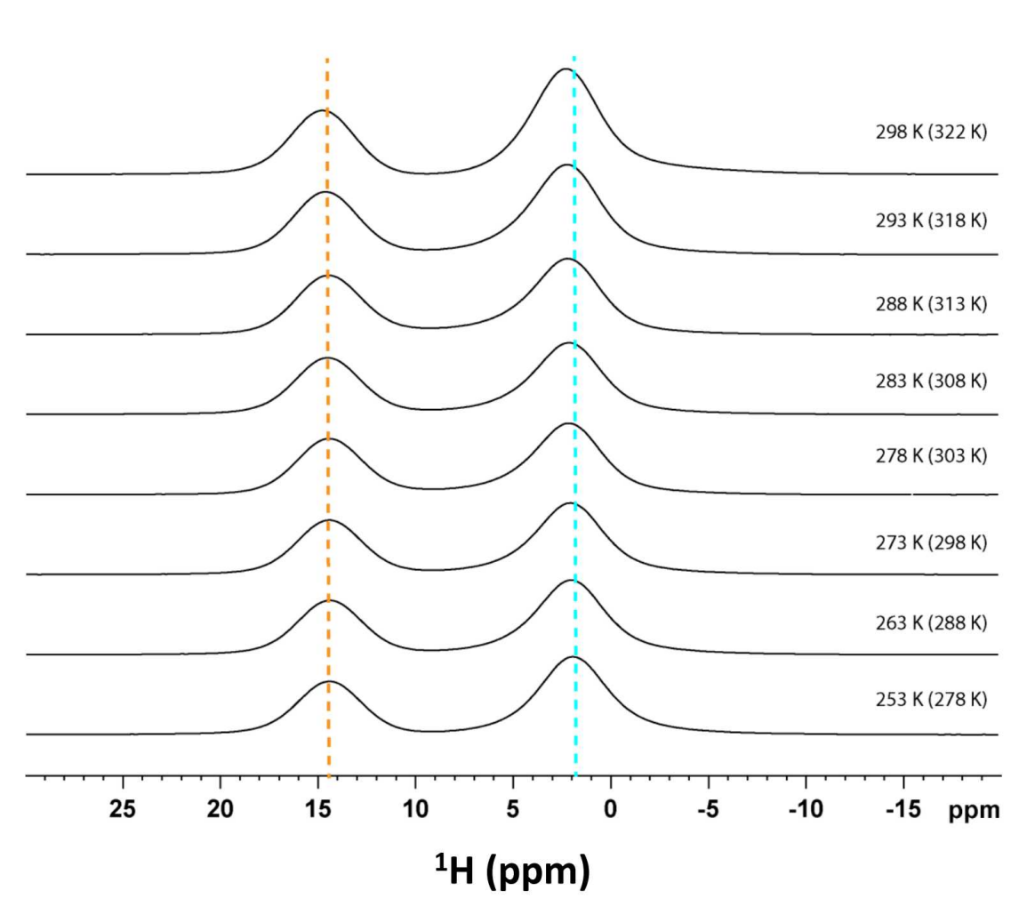


*** UO-H bond distance NOT available in crystal structure. Obtained from DFT CASTEP optimization.**
[4] S. Ostanin and P. Zeller, *J. Phys.: Condens. Matter* (2007) **19**, 246108.



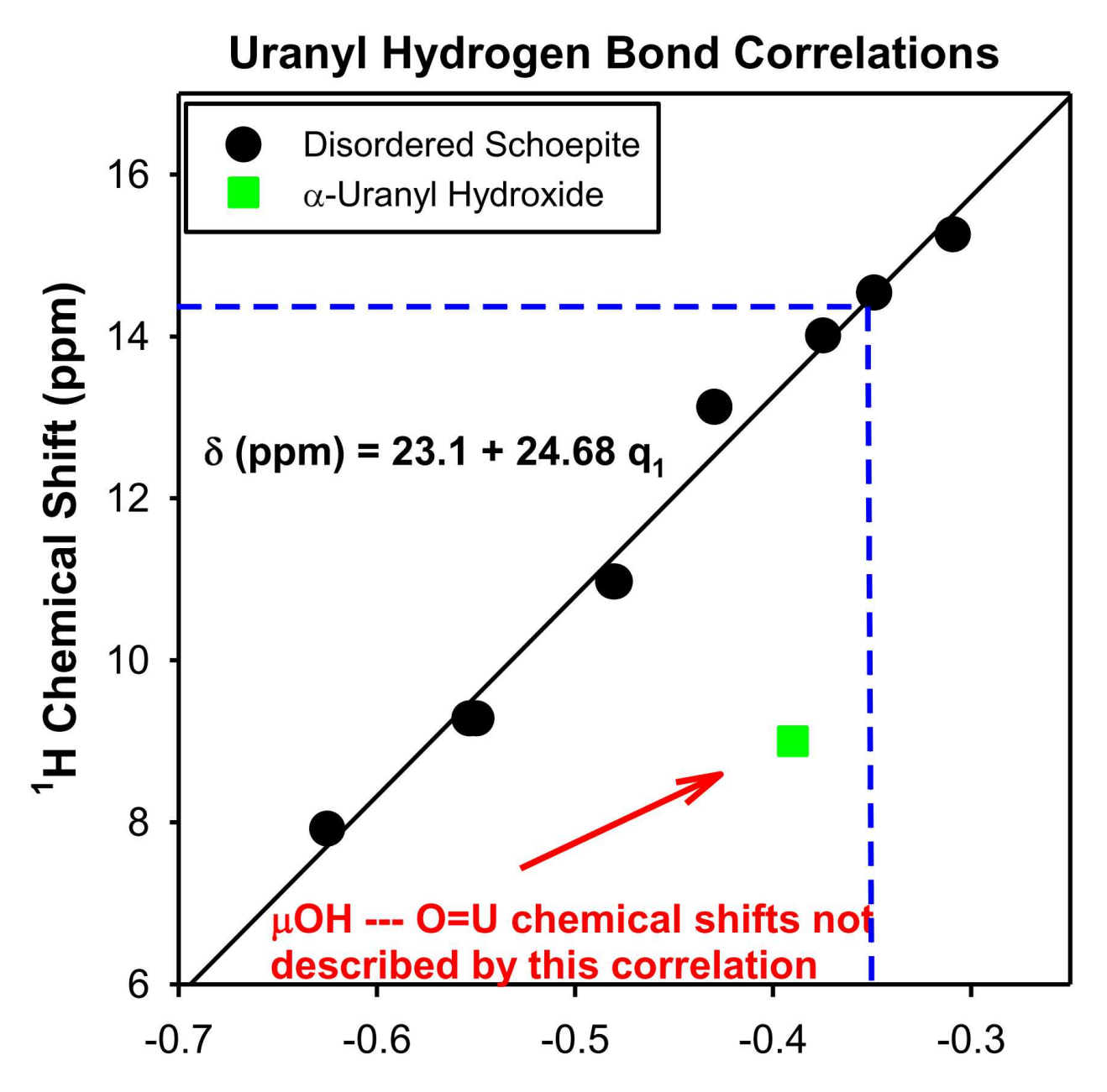


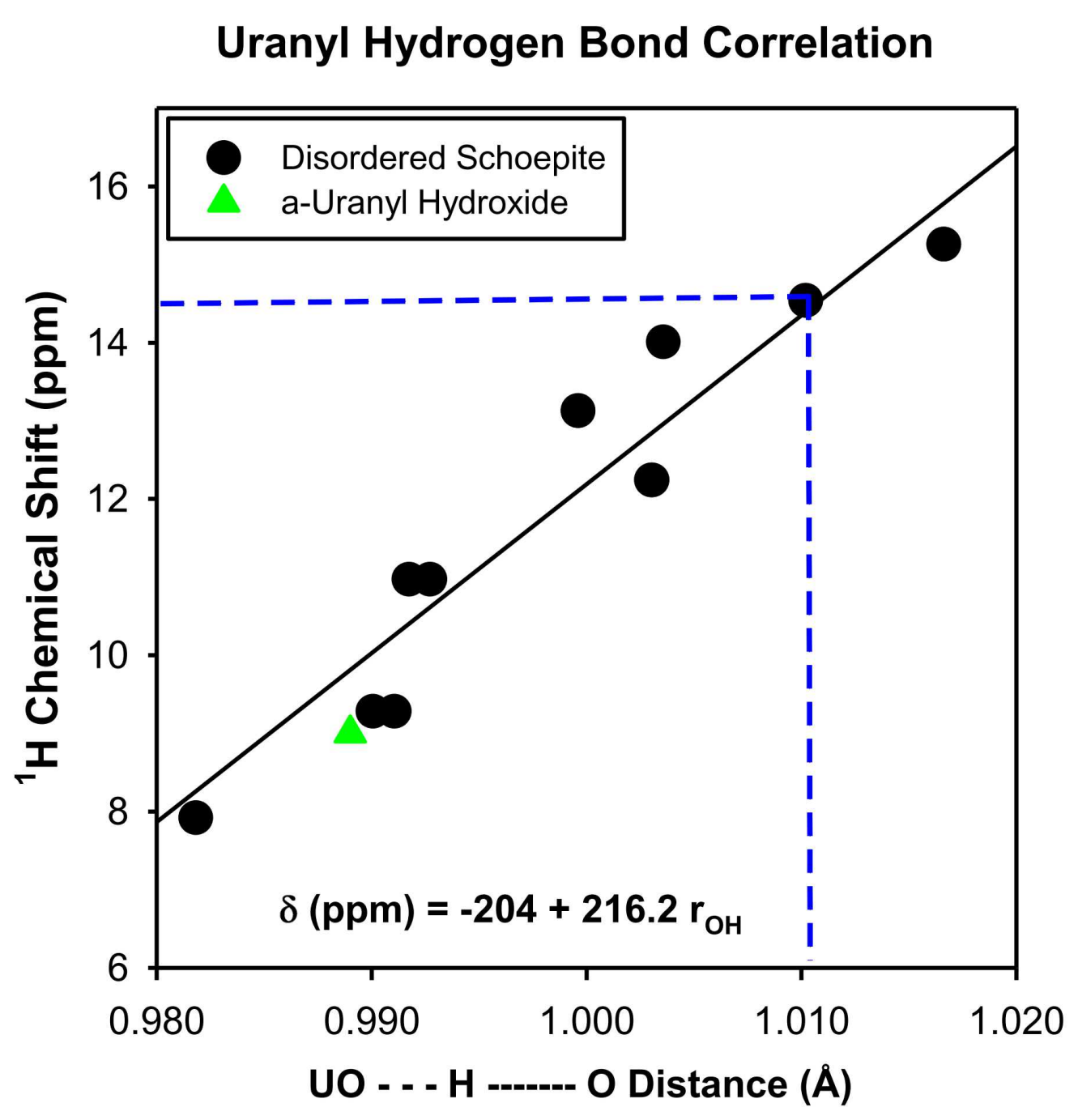




Red +17.2 ppm   blue + 2.4 ppm

- Agreement with α-UOH is excellent (single proton environment).
- Comparison to optimized Schoepite (disordered) is poor and does not reflect the disorder suggested by DFT calculations!!
- Temperaute dependence does not suggest high mobility of H_2O or OH species.
- Used this disordered structure to develop chemical shift correlations.





CONCLUSIONS

- **Multi-nuclear MAS NMR reveals cation and water exchange for U_{24} the solid state.**
- **Rate of Li dynamics depends on cluster cation speciation. KLi-U_{24} << Li-U_{24}.**
- **Rate of hydrogen exchange KLi-U_{24} << Na-U_{24} < Li-U_{24}.**
- **Correlation developed for U-OH hydrogen bond strength and ^1H chemical shift.**

Acknowledgements. This work was supported as part of the Materials Science of Actinides, an Energy Frontier Research Center funded by the Department of Energy, Office of Science Basic Energy Sciences under award number DE-SC0001089. The NMR component of the work (T. M. A.) was performed at Sandia National Laboratories, which is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin company, for the U. S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000. SAND2015-1254