Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supplemental Material

Computing the ^{7}Li NMR Chemical Shielding of Hydrated Li^{+} Using Cluster Calculations and Time-Averaged Configurations from *Ab Initio* Molecular Dynamic Simulations

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Table S1: Predicted ^{7}Li NMR chemical shielding (σ) as a function of theory level and basis set.

Theory/Basis Set	**Li^{+} σ (ppm)**	**$Li^{+}(H_2O)_4$ σ (ppm)**	**$Li^{+}(H_2O)_4$ $\Delta\sigma^{Li}$ (ppm)**
HF/3-21G*	94.6	92.3	+2.3
HF/6-31G(d)	95.4	93.0	+2.4
HF/6-311(d)	95.4	93.2	+2.2
HF/6-311(2d,2p)	95.4	92.8	+2.6
HF/6-311++(2d,2p)	95.4	92.8	+2.6
HF/6-311++(2df,2p)	95.4	92.8	+2.6
HF/Aug-CC-pVTZ	95.4	92.5	+2.9
B3LYP/3-21G*	94.3	91.2	+3.1
B3LYP/6-31G(d)	95.1	91.4	+3.7
B3LYP/6-311(d)	95.3	92.1	+3.2
B3LYP/6-311(2d,2p)	95.3	91.4	+3.9
B3LYP/6-311++(2d,2p)	95.3	91.3	+4.0
B3LYP/6-311++(2df,2p)	95.3	91.3	+4.0
B3LYP/Aug-CC-pVTZ	95.2	90.6	+4.6
MP2/6-311++(2df,2p)	95.3	92.8	+2.5
B3PW91/6-311++(2df,2p)	95.3	91.5	+3.8
MPW1PW91/6-311++(2df,2p)	95.4	91.7	+3.7

$$\Delta\sigma^{\mathrm{Li}} = \sigma(\mathrm{Li}^{+}) - \sigma(\mathrm{cluster})$$

B3LYP = Beck's three-parameter hybrid exchange functional and Lee, and Yang and Parr correlation functional.
B3PW91 = Beck's three-parameter hybrid exchange functional and Lee, and Perdew-Wang 1991 correlation functional.
MPW1PW91 = Modified Perdew-Wang exchange functional, and Perdew-Wang 1991 correlation functional.

Empirical Variation of the Li NMR Shielding

Previous arguments had suggested that the NMR shielding could be described by the relationship,

$$\sigma_{\text{iso}}(^{6,7}\text{Li}) = \sigma_0 - C\left[\sum_i \frac{W_i}{r_i^3}\right] \qquad \text{(S1)}$$

This does not appear to describe the Li-O bond variation that we have predicted for the $Li^+(H_2O)_n$ (n = 1-5) clusters. Instead we propose the following modified relationship that allows for a different scaling factor f_i^{N} for a given coordination number N,

$$\sigma_{\text{iso}}(^{6,7}\text{Li}) = \sigma_0 + \left[\sum_i^{\text{N}} \frac{f_i^{\text{N}} W_i}{r_i^3}\right] \approx \sigma_0 + \frac{\text{N} f^{N} W}{r^3} \qquad \text{(S2)}$$

For this relationship it has been assumed that the bond valence W^i is constant (all waters in this case). For these small hydrated clusters, the Li-O bond distances are essentially the same for a given coordination number. The coefficients for this linear fit to the predicted variation shown in Figure S1 are given in Table S2. It is important to note that f^{N} changes with coordination number (N), and is the reason the original relationship in Eq. S1 did not hold. This may suggest that bond valence W varies with coordination, and that changes in the effective charge of the Li may play a role in the observed shielding. This will be pursued in detail in future research efforts.

Table S2: Empirical fit of the ^{7}Li NMR chemical shielding (σ) as a function of Li-O bond length in gas optimized clusters. [a,b]

Complex	N	N$f^{\text{N}}W$ (ppm/Å)	$f^{\text{N}}W$ (ppm/Å)	σ_0 (ppm)	R
$Li^+(H_2O)$	1	-19.77	-19.77	96.135	0.99971
$Li^+(H_2O)_2$	2	-29.99	-14.99	96.286	0.99999
$Li^+(H_2O)_3$	3	-34.37	-11.46	96.208	0.99997
$Li^+(H_2O)_4$	4	-35.55	-8.89	96.078	0.99865
$Li^+(H_2O)_5$	5	-37.53	-7.51	96.295	0.99898

[a] NMR shielding of cluster calculated in the gas phase.
[b] Fits to Eqn. S2.

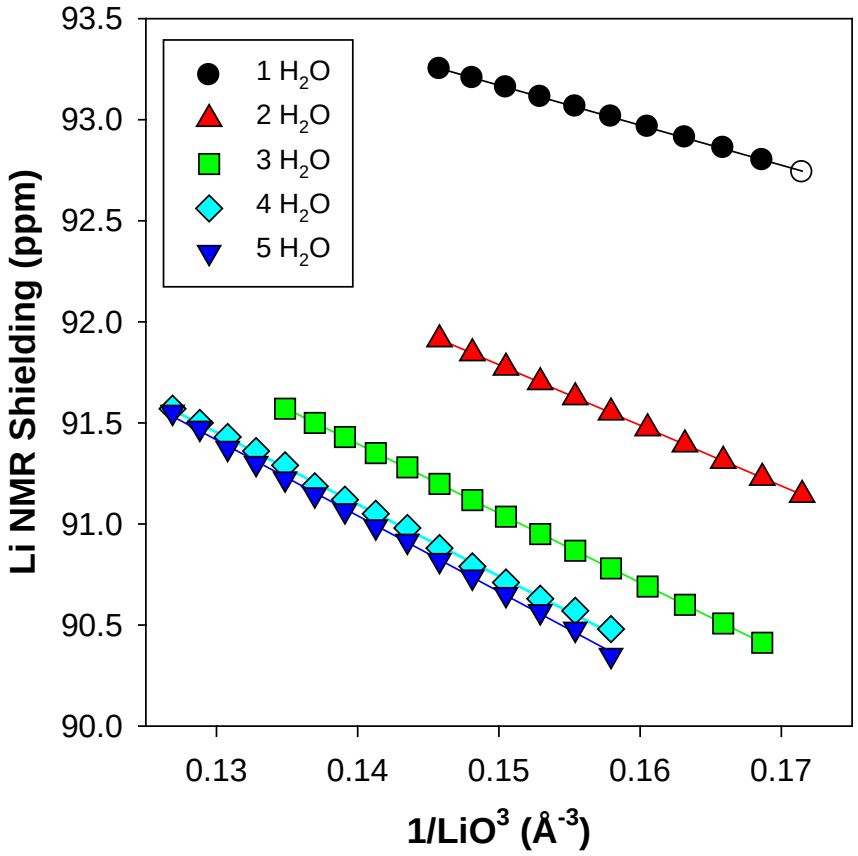

Figure S1: Variation of the predicted Li NMR chemical shielding for the $Li^{+}(H_2O)_n$ clusters as a function of inverse bond distance cubed, $(Li\text{-}O)^{-3}$.

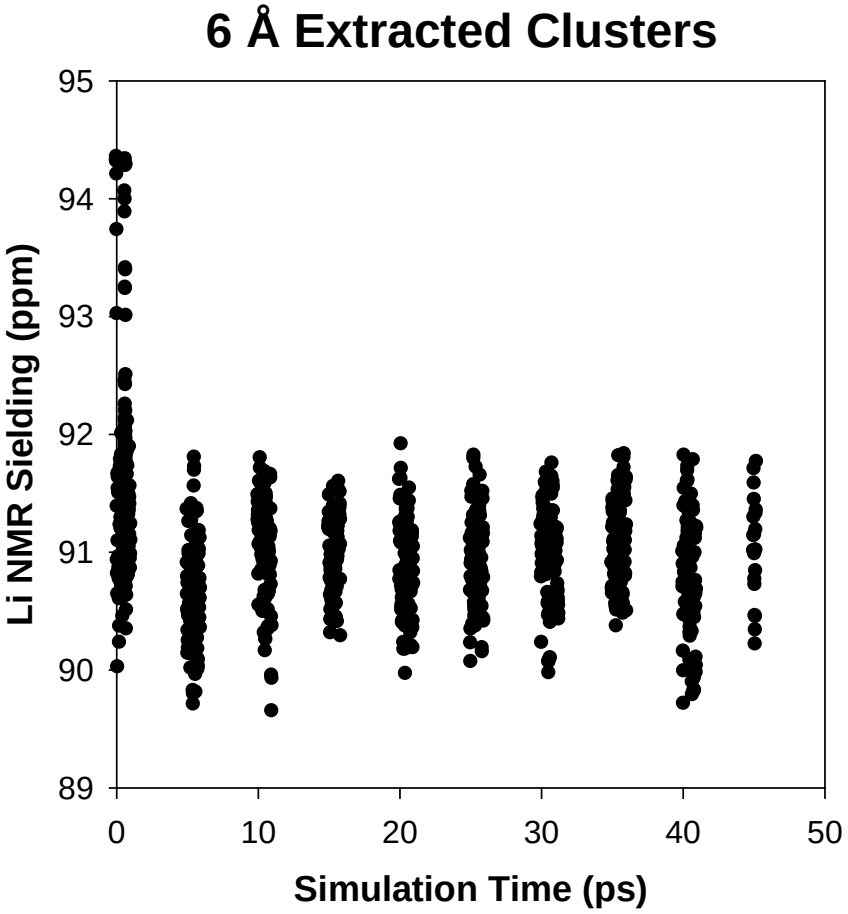

Figure S2: The Li NMR Chemical shielding for all clusters extracted assuming a Li-O cut-off distance of 6 Å. 1 ps regions were analyzed for every 5 ps intervals during the simulation. Note the initial 1 ps results have a high degree of dispersion due to the system not being equilibrated.