Computing the ^{7}Li NMR Chemical Shielding of Hydrated Li^{+} Using Cluster Calculations and Time Trajectory Averaging of Molecular Dynamic Simulations

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NMR spectroscopy continues to be an important tool in understanding the coordination and dynamics of alkali metals in a variety of systems and materials. The ability to accurately model NMR chemical shifts, using both empirical and quantum level calculations, is a crucial aspect of understanding the local Li environments. Previous modeling of the ^{7}Li NMR chemical shifts for small aqueous complexes are very limited, with a single report for the $Li^{+}(H_2O)n$ (n = 1 – 4) complexes. (Prado *et al.*, 1980) This is surprising given the importance of Li+ in energy storage and production devices. A major advance in the modeling of NMR chemical shifts in solution has been the introduction of molecular dynamics (MD) or Monte Carlo (MC) simulations with explicit solvent molecules thus incorporating both ensemble and time averaging of coordination environments. Hybrid quantum mechanical/molecular mechanical (QM/MM) or molecular dynamic (QM/MD) methods have been applied to calculating NMR chemical shifts in hydrogen-bond liquids, primarily water.

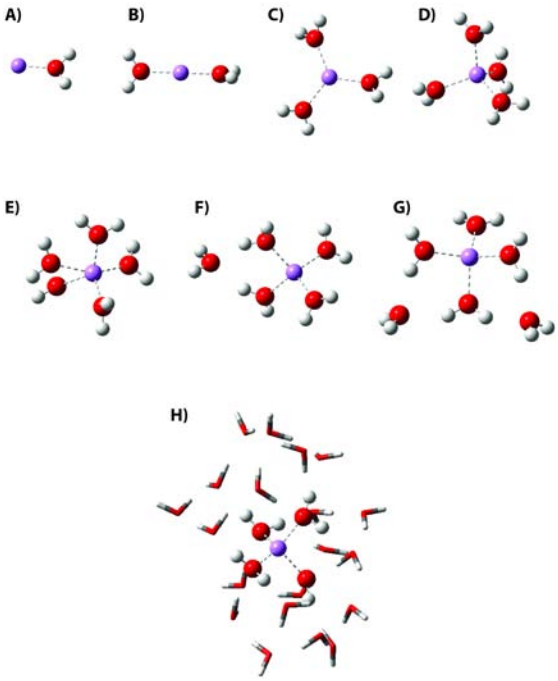

Figure 1: Optimized gas phase hydrated Li^{+} clusters: A) $Li^{+}(H_2O)$, B) $Li^{+}(H_2O)_2$, C) $Li^{+}(H_2O)_3$, D) $Li^{+}(H_2O)_4$, E) $Li^{+}(H_2O)_5$, F) $Li^{+}(H_2O)_4{\bullet}H_2O$, G) $Li^{+}(H_2O)_4{\bullet}2H_2O$ and H) $Li^{+}(H_2O)_4{\bullet}20H_2O$.

In this poster, *Ab initio* molecular dynamic (AIMD) simulations have been used to predict the time-averaged Li NMR chemical shielding for a Li^{+} solution. These results are compared to NMR shielding calculations on smaller $Li^{+}(H_2O)_x$ clusters optimized in either the gas phase or with a PCM solvent (**Figure 1**). An empirical relationship is developed that relates the Li NMR chemical shift with the Li-O bond distance in these hydrated clusters. Li may be unique (with respect to larger cations) in that only a single coordination number (CN) is observed during the MD simulations. This results in the average NMR chemical shift not being a weighted distribution over different CN, but instead a time average over small perturbation to the local N = 4 coordination environment during the MD simulations (**Figure 2**).

The trends introduced by the PCM solvent are described and compared to the time-average chemical shielding observed in the AIMD simulations where large explicit water clusters hydrating the Li^{+} are employed. In addition, these calculations allowed the different structural contributions to the Li NMR shielding to be evaluated.

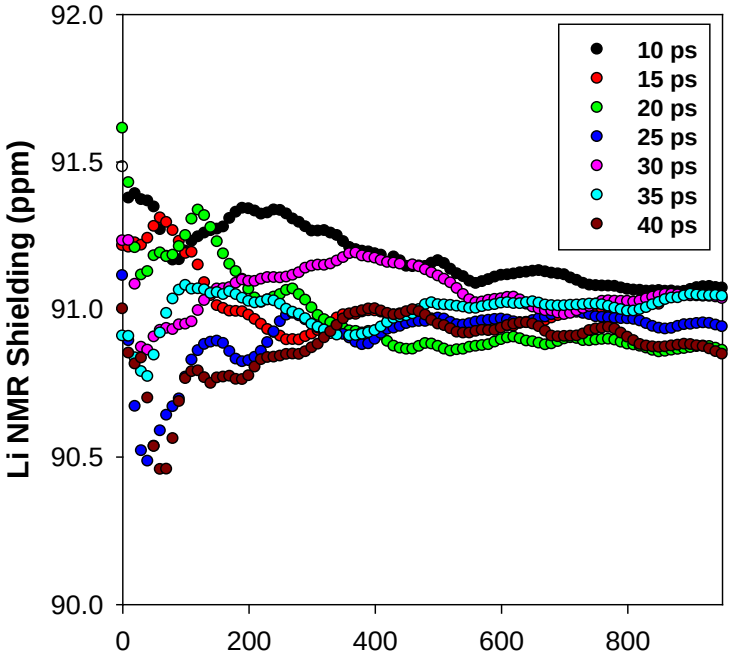

Figure 2: The running time average of the Li NMR chemical shielding (6 Å solvation shell) sampled every 10 fs, for different 1 ps time regions extracted from different regions of the overall AIMD simulation.

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