

Supporting Information

Concentrated Aqueous Lithium Chloride Solution Dynamics: The Role of Chemical Exchange on Anisotropy and Vibrational Population Relaxations

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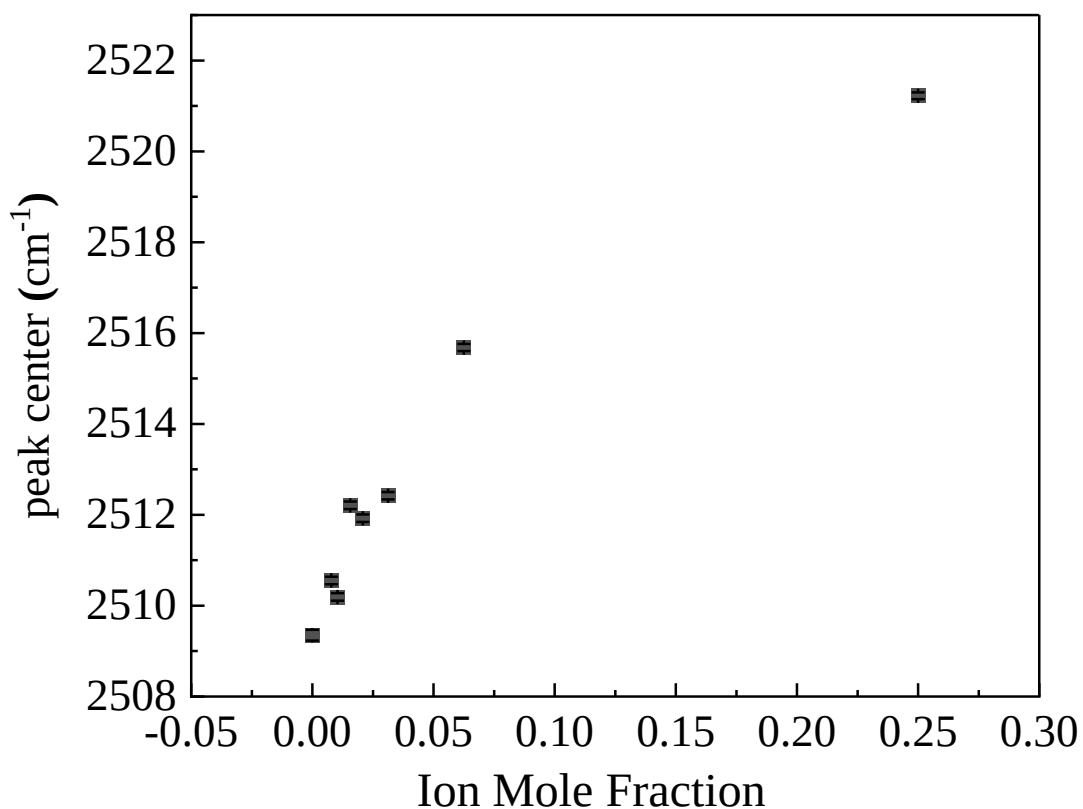


Figure S1. Peak centers from Gaussian fits to the FT-IR spectra of LiCl solutions of concentrations 1-4, 1-16, 1-32, 1-48, 1-64, 1-96, 1-128, and pure water. The data demonstrate a blue shift in the peak center with increasing ion mole fraction.

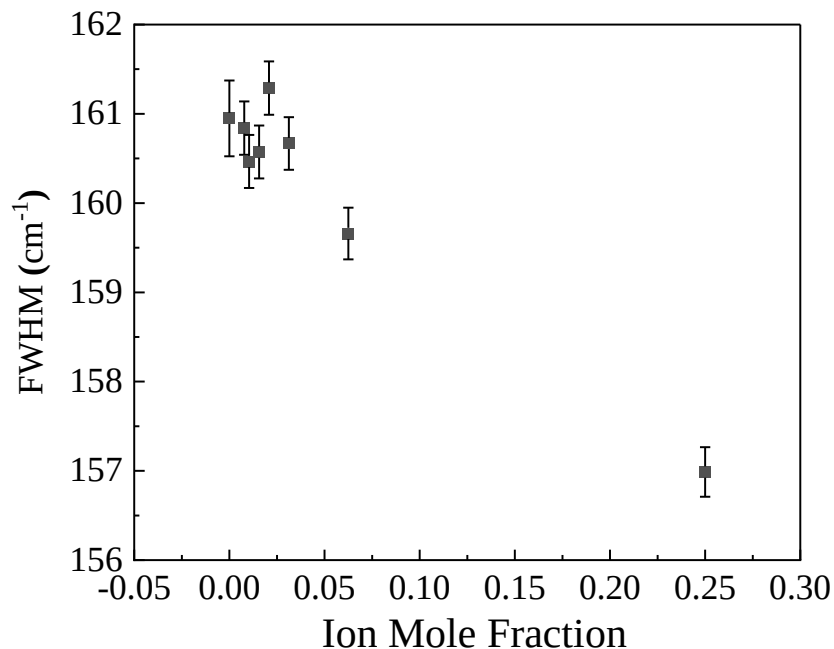


Figure S2. Peak widths from Gaussian fits to the FT-IR spectra of LiCl solutions of concentrations 1-4, 1-16, 1-32, 1-48, 1-64, 1-96, 1-128, and pure water. The data demonstrate a narrowing of the peak compared to pure water at high IMF while the widths of the lower concentrations are constant and the same as pure water with error.

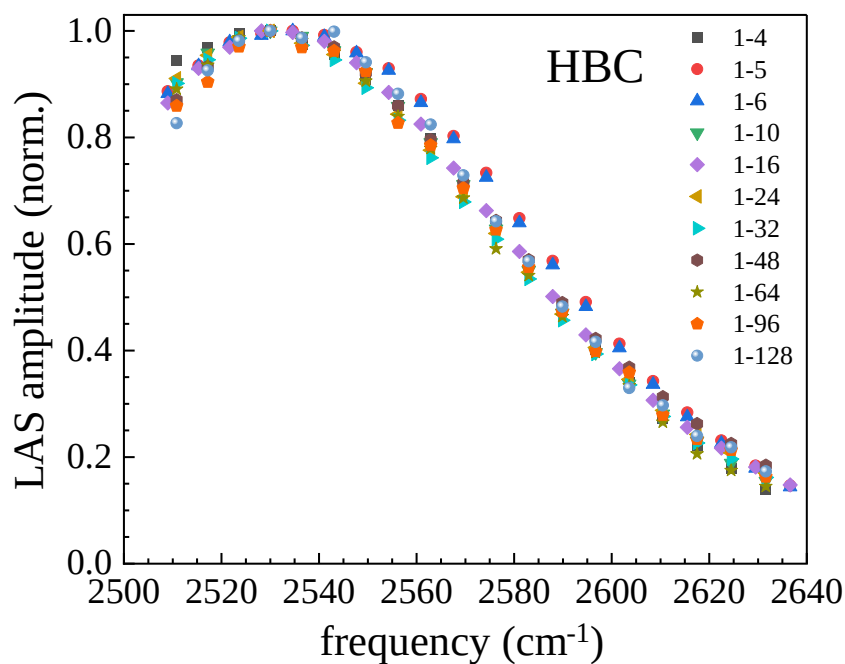


Figure S3. Hydroxyls bound to chlorides (HBCs) normalized Lifetime Amplitude Spectra for eleven salt concentration samples, 1-4 to 1-128, 13.9 m to 0.4 m. The spectra have the same shape independent of the concentration within experimental error.

Table S1. Observed vibrational lifetimes from biexponential fits to the population relaxation of the OD stretch of HOD in aqueous lithium chloride solutions for high, 1-4 to 1-24, and low, 1-32 to 1-128, salt concentrations.

Solution	t_{LPH} (ps) ^a	t_P (ps) ^b	t_{HBC} (ps) ^c
1-4 (13.9 m)	1.9 ± 0.2	-	6.4 ± 0.1
1-5 (11.1 m)	1.7 ± 0.2	-	5.6 ± 0.1
1-6 (9.3 m)	1.5 ± 0.2	-	5.2 ± 0.1
1-10 (5.6 m)	1.4 ± 0.2	-	4.2 ± 0.1
1-16 (3.5 m)	1.9 ± 0.2	-	4.0 ± 0.1
1-24 (2.3 m)	~ 1.7		3.8 ± 0.1
1-32 (1.7 m)	-	1.8 (fixed)	3.6 ± 0.1
1-48 (1.2 m)	-	1.8 (fixed)	3.5 ± 0.1
1-64 (0.9 m)	-	1.8 (fixed)	3.5 ± 0.1
1-96 (0.6 m)	-	1.8 (fixed)	3.5 ± 0.1
1-128 (0.4 m)	-	1.8 (fixed)	3.5 ± 0.1

^a t_{LPH} – lifetime of the lithium-perturbed hydroxyl (OD stretch) population.

^b t_P – lifetime of the pure water (OD stretch) population.

^c t_{HBC} – lifetime of hydroxyls (OD stretch) H-bonded to chloride population.

S1. Density Functional Theory Calculations

Geometry optimizations of a chloride anion bound to 6 water molecules and a BF_4^- anion bound to 4 water molecules were performed using the Gaussian 16 quantum chemistry package¹ at B3LYP/6-31+G(d,p) level of theory with SMD implicit solvent model² of water. To reduce the energy difference caused by possible structural variations and to investigate the difference in the energy barrier for the dissociation of H_2O from the anion solvation shell, relaxed coordinate scans were performed for the distance between the $\text{OH}\cdots\text{Cl}^-/\text{BF}_4^-$ for 2.1 Å with a step size of 0.1 Å using the same level of theory.

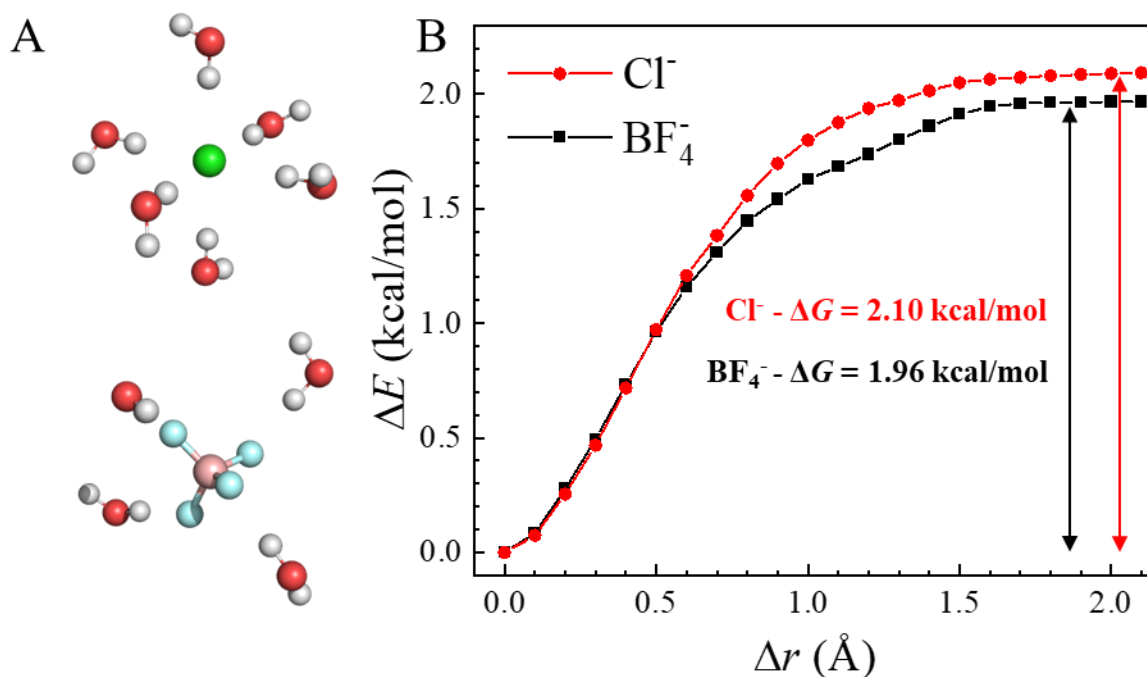


Figure S4. (A) DFT-optimized structure of a Cl^- bound to 6 H_2O (top), and a BF_4^- bound to 4 H_2O (bottom). (B) Relaxed potential energy surface scan for the bond length between $\text{Cl}^-/\text{BF}_4^-$ and OH. The results show a dissociation energy of approximately 2.10 kcal/mol for H_2O bound to Cl^- and 1.96 kcal/mol for H_2O bound to BF_4^- .

S2. Chemical Exchange Equations

Equations reproduced from Ref 46.³

$$N_P = \frac{N_P(t=0)}{2\Delta} [(\Delta + m) \exp(-\frac{1}{2}(s + \Delta)t) + (\Delta - m) \exp(-\frac{1}{2}(s - \Delta)t)] \quad (S1)$$

$$N_{PH} = \frac{N_P(t=0)}{\Delta} [k_{PH} (-\exp(-\frac{1}{2}(s + \Delta)t) + \exp(-\frac{1}{2}(s - \Delta)t))] \quad (S2)$$

$$N_H = \frac{N_H(t=0)}{2\Delta} [(\Delta + m) \exp(-\frac{1}{2}(s - \Delta)t) + (\Delta - m) \exp(-\frac{1}{2}(s + \Delta)t)] \quad (S3)$$

$$N_{HP} = \frac{N_H(t=0)}{\Delta} [k_{HP} (-\exp(-\frac{1}{2}(s + \Delta)t) + \exp(-\frac{1}{2}(s - \Delta)t))] \quad (S4)$$

$$s = k_P + k_H + k_{PH} + k_{HP} \quad (S5)$$

$$\Delta = \sqrt{s^2 - 4(k_P k_H + k_P k_{HP} + k_H k_{PH})} \quad (S6)$$

$$m = k_P + k_{PH} - k_{HP} - k_H \quad (S7)$$

Here, N_i denotes a population, which may be pure water (P), HBC (H), water bound to chloride that was pure water (PH), and water bound to pure water that was bound to chloride (HP). The rate constants, k_i , are the inverse of the time constants for chemical exchange ($k_{HP} = 1/t_{HP}$).

Because the system is in equilibrium, $N_P(t=0)k_{PH} = N_H(t=0)k_{HP}$.

1. M. T. Frisch, G.; Schlegel, H. B.; Scuseria, G.; Robb, M.; Cheeseman, J.; Scalmani, G.; Barone, V.; Petersson, G.; Nakatsuji, H., (Gaussian, Inc., Wallingford, CT, 2016).
2. A. V. Marenich, C. J. Cramer and D. G. Truhlar, J. Phys. Chem. B **113** (18), 6378-6396 (2009).
3. R. Yuan, C. Yan and M. Fayer, J. Phys. Chem. B **122** (46), 10582-10592 (2018).