

Concentrated aqueous lithium chloride solution dynamics: The role of chemical exchange on anisotropy and vibrational population relaxations

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ABSTRACT

Ultrafast polarization-selective pump-probe experiments, conducted on the OD stretch of dilute HOD, are reported for LiCl/H₂O solutions ranging from 1–24 to 1–128 (ion pairs–water molecules), 2.3–0.4 m. The results are compared to prior and revised experiments on 1–4 to 1–16 concentrations, 13.9–3.5 m. Vibrational population relaxation and anisotropy decays were measured for hydroxyls hydrogen-bonded to chlorides (HBCs). In contrast to higher salt concentrations, at ≤ 1 –32 (1.7 m salt), the HBC population relaxation times and anisotropy decays are concentration independent. 1–32 marks a transition from high concentrations of ion pairs, clusters, and ion networks to concentrations of ion pairs low enough not to affect observable molecular level dynamics. At a concentration of approximately 1–32 and lower salt concentrations, chemical exchange is responsible for HBC anisotropy decay and plays a role in population relaxation. Wavelength-dependent population relaxation was used to obtain lifetime amplitude spectra (LAS), which show distinct species that are not observable with FT-IR. At very high salt concentrations, e.g., 1–6, there are no “pure” water regions, and the LAS has two bands: HBCs and hydroxyls of water oxygens solvating Li⁺. At lower salt concentrations, there is also a “pure” water band in the LAS. The HBC band shape is concentration independent from 1–4 to 1–128.

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I. INTRODUCTION

The solubilities of salts in water vary greatly. Lithium chloride, the subject of the present study, is highly soluble with a maximum solubility at room temperature of 18 molal.¹ At the highest concentrations, insufficient water exists to fully solvate cations and anions. Rather than isolated solvated ions, LiCl and other highly soluble salts form solvent separated ion pairs, contact ion pairs, ion/water clusters, and extended ion/water cluster networks at very high concentrations.^{2,3} At low salt concentrations, Li⁺ and Cl[−] can be fully solvated and separated by intervening water molecules. At these lower concentrations, Li⁺ is solvated by ~4 water oxygens and Cl[−] by ~6–8 hydroxyls.^{4–7}

Pure water at room temperature forms an approximately tetrahedral H-bond network in which a water's oxygen lone pairs are H-bond acceptors, and each water molecule's pair of hydroxyls are H-bond donors. Therefore, water can form up to 4 H-bonds

per molecule.^{8,9} This H-bond network is constantly reorganizing. Anisotropy decay (orientational randomization) occurs in pure water as a single exponential with a time constant of 2.6 ps.^{10–13} Orientational randomization happens through jump reorientation rather than small-step angular diffusion.¹⁴ When ions are introduced, e.g., LiCl, the H-bond network is modified by the solvation of the ions. Studies using x-ray and neutron diffraction experiments in conjunction with molecular dynamics (MD) simulations have demonstrated that water molecules will orient their dipoles toward cations, i.e., oxygen lone pairs will associate with Li⁺; the hydroxyls will form H-bonds with the Cl[−] anions.^{6,7,15} The dynamics of aqueous ionic solutions have been studied with MD simulations,^{16–18} NMR,¹⁹ dielectric relaxation,²⁰ and ultrafast infrared (IR) spectroscopy.^{11,21–24}

Ultrafast IR polarization-selective pump-probe (PSPP) spectroscopy was employed here to investigate the dynamics of hydroxyls in LiCl solutions over a wide range of concentrations. The

experiments were conducted on the OD stretch of dilute HOD in the ion/water solutions to eliminate vibrational excitation transfer among the OH moieties.²⁵ The PSPP experiments measure excited vibrational population and anisotropy decays of the OD mode following ultrafast IR excitation.

Over a very wide LiCl concentration range, i.e., solution concentrations from 1–4 (one ion pair to four water molecules, 13.9 m) to 1–16 studied previously, and revised here,^{23,24} and 1–24 to 1–128 (0.43 m) in the current study, the FT-IR absorption spectra of the OD stretch are featureless and change only slightly with concentration. Therefore, the FT-IR spectra do not provide information on the structure and dynamics of the water species in the ion/water solutions and how water dynamics change with concentration. It is necessary to move beyond linear absorption spectroscopy to investigate the distinct populations of water in these solutions. Nonlinear lifetime amplitude spectroscopy can provide spectra that are inaccessible using linear spectroscopy. As reported previously, at the highest concentrations, the population decays are biexponentials that change as a function of frequency across the inhomogeneously broadened absorption band.^{23,24} The decay time constants are independent of frequency, but the amplitudes of the two decay components change systematically. Plotting the amplitudes vs frequency for the two decays produces two lifetime amplitude spectra (LAS). These spectra are hydroxyls (OD) bound to chloride anions, $\text{Cl}^- \cdots \text{DOH}$ (HBCs), and lithium cation-perturbed hydroxyls bound to water oxygens, $\text{Li}^+ \cdots \text{OHD} \cdots \text{OH}_2$ (LPHs). In the very high concentration range, there is no pure water spectrum (P) in the LAS because there are too few water molecules to have the extended H-bond structure that gives rise to the pure water spectrum.

For salt concentrations $\leq 1\text{--}32$, there is sufficient water for some “pure” water to exist. Pure water, in this context, means a sufficient number of water molecules H-bonded to each other to form regions of extended H-bond networks characteristic of pure water. Here, the high (blue) frequencies of the PSPP population decays, where there is negligible contribution from the LPH, are fit with biexponentials with one component held at the known pure water lifetime. At these relatively low salt concentrations, the LPH band, which is at the lower (redder) frequencies, cannot be measured because of overlap with the large absorption of the first to second excited state (1–2) transition of the pure water and because the vibrational lifetime of the LPH is almost the same as that of pure water. Thus, the LAS for these concentrations have two peaks: a large pure water band and a much smaller HBC band. A remarkable result is that the HBC spectra are independent of the salt concentration from 1–4 (water-in-salt) to 1–128 (salt-in-water). The HBC spectra do not change within experimental error even though the system goes from very crowded networks of ions and water to hydroxyls solvating chloride ions, separated from other ions by intervening water.

While the HBC spectra do not change with concentration, the population relaxation times do. As the salt concentration decreases, the population relaxation times of the hydroxyls H-bonded to chlorides become faster until the salt concentration is $\leq 1\text{--}32$. The HBC population relaxation time is constant for concentrations $\leq 1\text{--}32$ (1.7 m).

As mentioned above, the pure water anisotropy decay is a single exponential with a time constant of 2.6 ± 0.1 ps. There is a difference in the fundamental nature of the hydroxyl anisotropy between the very high salt concentrations (1–4 to $\sim 1\text{--}16$) and the lower salt

concentrations. As reported previously, the orientation anisotropy decays, $r(t)$, are biexponentials for very high salt concentrations.^{23,24} The fast time scale orientational relaxation results from restricted angular sampling, i.e., wobbling-in-a-cone (WIC),^{26–29} in which hydroxyls can only sample limited ranges of angles, the cone of angles. The liquid’s structural relaxation on a longer timescale enables complete orientational randomization.

At salt concentrations $\leq 1\text{--}32$ (1.7 m), the anisotropy process involves a pure water population of hydroxyls undergoing jump reorientation, while the anisotropy decay of hydroxyls bound to chlorides occurs via chemical exchange. The chemical exchange rate is governed by the hydrogen bond strengths of the waters bound to chlorides and by the population of pure water as the exchange partner. Another salt solution, anion BF_4^- , for which the spectrum of the hydroxyl bound to the anion has a peak that is separated from the water band (weaker hydrogen bonds), was studied using 2D IR spectroscopy, and its anion/water chemical exchange time constant was reported.³⁰ From this chemical exchange time and DFT calculations of the energy required for waters H-bonded to Cl^- and BF_4^- to dissociate from these anions, the chemical exchange time of water bound to chlorides in the LiCl solutions was assessed. The population and anisotropy decays of HBCs in the lower concentration solutions are explained using the equations that govern chemical exchange and the calculated HBC chemical exchange time.

II. EXPERIMENTAL METHODS

A. Sample preparation

Samples were prepared from anhydrous LiCl salt (>99%) used as received from Sigma-Aldrich. The salt was stored in a dry box and continuously purged with dry air before use to prevent moisture absorption. Nonlinear experiments were performed on a range of concentrations of aqueous LiCl solutions with molar ratios of 1–10, 1–24, 1–32, 1–48, 1–64, 1–96, and 1–128. The samples were prepared by adding D_2O to give 5% HOD in H_2O . The OD stretch is an excellent probe for water dynamics as it is a local vibrational mode distinct from the OH stretching region of pure water.²⁵ At a molar concentration of 5%, HOD is sufficiently dilute to avoid resonant vibrational energy transfer and has a negligible effect on the structure and dynamical properties of H_2O .^{10,13,31,32}

The solutions were placed in a sample cell with two calcium fluoride windows separated by a 12 μm spacer, which sets the path length. An FT-IR spectrometer purged with dry N_2 and set to a resolution of 0.5 cm^{-1} was used to take linear spectra. The linear spectra of samples prepared with only H_2O were subtracted from the HOD spectra to give background-free linear spectra of the OD stretch. Nonlinear experiments were run three times, with fresh samples prepared for each run.

B. Laser system and nonlinear experiments

A detailed description of the laser system used to perform nonlinear IR experiments was given previously.³³ Briefly, a Ti:sapphire oscillator seeds a regenerative amplifier operating at 2 kHz, which pumps an optical parametric amplifier (OPA). The OPA output is difference mixed in an AgGaS_2 crystal, generating mid-infrared (mid-IR) pulses centered at $\sim 4\text{ }\mu\text{m}$ and with a pulse duration of ~ 65 fs.

For PSPP experiments, the mid-IR pulses were split into strong pump and weak probe pulses, which were crossed in the sample. The pump beam was chopped at 1 kHz, and the signal is the difference between the probe intensity with the pump on and the pump off. The probe was horizontally polarized (0°), and the pump was polarized at $+45^\circ$ relative to the probe. After the sample, the probe was resolved using a computer-controlled polarizer cycling between parallel ($+45^\circ$) and perpendicular (-45°) polarizations relative to the pump. A final polarizer before the monochromator sets the polarized signal to approximately horizontal. This polarizer was adjusted until the spectra of the probe beams at $+45^\circ$ and -45° were identical, eliminating polarization bias from the diffraction grating.

The resulting parallel, $S_{\parallel}(t)$, and perpendicular, $S_{\perp}(t)$, signals were analyzed to determine the population relaxation, $P(t)$, and anisotropy decay, $r(t)$, using

$$S_{\parallel}(t) = e^{-t/\tau}(1 + 0.8C_2(t)), \quad (1)$$

$$S_{\perp}(t) = e^{-t/\tau}(1 - 0.4C_2(t)), \quad (2)$$

where τ is the vibrational lifetime for a single component system and $C_2(t)$ is the second-order Legendre polynomial anisotropy correlation function. From Eqs. (1) and (2),

$$P(t) = \frac{1}{3}[S_{\parallel}(t) + 2S_{\perp}(t)], \quad (3)$$

$$r(t) = \frac{S_{\parallel}(t) - S_{\perp}(t)}{S_{\parallel}(t) + 2S_{\perp}(t)} = 0.4C_2(t). \quad (4)$$

$P(t)$ is the excited state vibrational population relaxation for a system with any number of decay components. There is also a long-lived isotropic heating signal that arises from vibrational relaxation. This heating signal is removed from the data using the standard method.^{12,34}

III. RESULTS AND DISCUSSION

A. Linear spectra

The linear FT-IR spectra of aqueous LiCl solutions at concentrations ranging from 1–4 to 1–128, an ion pair per n water molecules and for pure water are shown in Fig. 1.

Pure water produces a wide, inhomogeneously broadened band centered at 2509 cm^{-1} with a full width at half maximum (FWHM) of 160 cm^{-1} (black curve). Increasing H-bond strength shifts the OD hydroxyl stretch to lower frequency (redshifted). When LiCl is added, the OD band is shifted to higher frequencies (blueshifted). This shift results from the water–anion interactions.^{21,35,36} Figure S1 shows the peak centers as a function of ion mole fraction (IMF), demonstrating a larger blueshift with increasing salt concentration. Figure S2 shows the peak widths vs IMF. On average, water–chloride H-bonds are weaker than H-bonds in pure water. The subensemble of hydroxyls (ODs) H-bonded to chlorides produces a blueshifted band, but the shift is insufficient to produce a distinct peak.³⁷ For some anions, the differences between the water–water and water–anion interactions are sufficiently large that distinct peaks appear on the blue side of the water spectrum.^{30,38–40}

The Li^+ also changes the OD spectrum. Water oxygens solvate Li^+ . The high charge density lithium cation withdraws electron

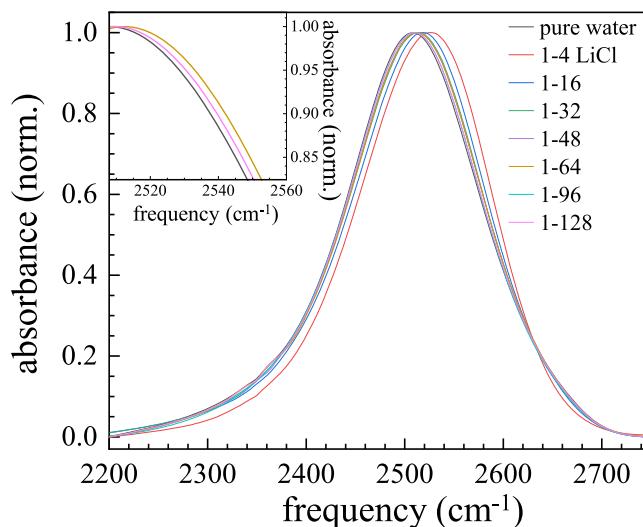


FIG. 1. Normalized and background subtracted linear absorption spectra of the OD stretch of HOD in pure water and aqueous LiCl solutions of molar ratios 1–4,²³ 1–16,²⁴ 1–32, 1–48, 1–64, 1–96, and 1–128 (ion pair per water molecules). The inset shows the small changes at concentrations 1–64 and 1–128 as they approach pure water.

density from the solvating water oxygens, which, in turn, withdraws electron density from the hydroxyl OHs and ODs. The lithium-perturbed hydroxyls form stronger H-bonds to water oxygens. Therefore, the subensemble of LPHs H-bonded to water oxygens has a redshifted band. However, the shift is relatively small and does not offset the blueshift caused by the hydroxyls H-bonded to chlorides. The result of water interacting with Li^+ and Cl^- is a featureless band that is blueshifted at the highest salt concentrations.

B. Lifetime amplitude spectra

The excited vibrational population of the OD stretch of dilute HOD in pure H_2O decays as a single exponential with a decay time constant (lifetime) of $1.8 \pm 0.1\text{ ps}$.¹² In very high concentration LiCl solutions (water-in-salt), there is no “pure” water. At very high salt concentrations 1–4 to 1–16, the decays are biexponential. At these concentrations, the population decays are given by

$$P(t) = A_{LPH}(\lambda)e^{-t/\tau_{LPH}} + A_{HBC}(\lambda)e^{-t/\tau_{HBC}}. \quad (5)$$

$P(t)$ changes with the wavelength, λ , because the amplitudes, A_{LPH} and A_{HBC} , depend on λ . The time constants are independent of wavelength. As the wavelength goes from the blue side of the absorption line to the red side, A_{HBC} decreases and A_{LPH} increases.

Figure 2 shows fits to three population decays at a subset of all the frequencies studied for a concentration of 1–5. The fits (red curves) have the same time constants; only the amplitudes with frequency vary.

The plots of amplitudes as a function of wavelength are the LAS (Lifetime Amplitude Spectra). This paper used an improved method for determining the vibrational lifetimes, which avoids contamination by spectral diffusion. The method did not change the high salt concentration LAS significantly. However, the lithium-perturbed

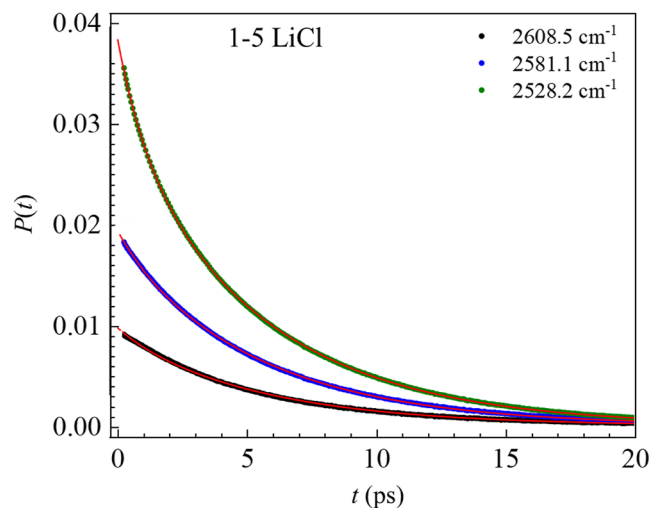


FIG. 2. Vibrational population relaxation of the OD stretch of HOD in a 1–5 LiCl solution at three frequencies. The red curves are biexponential fits to the data.

hydroxyls bound to water oxygens lifetime was determined to be much closer to that of pure water than previously reported.^{23,24} The lifetimes at all concentrations are discussed below and are presented in Table S1.

No water molecules have environments equivalent to pure water at very high salt concentrations. Consider a single water molecule H-bonded to four other water molecules. If those four surrounding molecules interact with ions, even the central water molecule will not behave as it would in pure water. For example, orientational relaxation is a jump reorientation process involving a water molecule, its surrounding H-bonded water molecules, and additional water beyond those.¹⁴ In pure water, these waters undergo concerted H-bond rearrangement, resulting in a particular hydroxyl (an OD in the measurements) jumping to a new orientation with a change in direction of $\sim 60^\circ$.¹⁴ So, a central water molecule surrounded by four waters interacting with ions will not reorient in the same manner as it would in pure water because the surrounding water molecules are H-bonded to ions rather than more water molecules.

In lower salt concentration solutions, a Li^+ is to be solvated by ~ 4 oxygens and a Cl^- is to be solvated by ~ 6 hydroxyls.^{4–7} In a concentration of 1–4, the four water molecules have four oxygens and eight hydroxyls. There are too few water molecules to form pockets of pure water. For 1–16, there are 16 oxygens and 32 hydroxyls. Four oxygens solvating a Li^+ will generate 8 lithium perturbed hydroxyls. The 6 hydroxyls bound to chloride will affect another 6 oxygens. There can be a small number of water molecules not being directly perturbed by ions, but this small number of water molecules is insufficient to form regions with H-bond networks that resemble pure water.

For very high salt concentration samples, the absence of pure water makes it possible to determine the LAS of both the LPH and HBC populations. Figure 3 shows LAS for a high salt concentration. The LAS does not extend to the red because the negative going 1–2 vibrational transition begins to significantly interfere with the

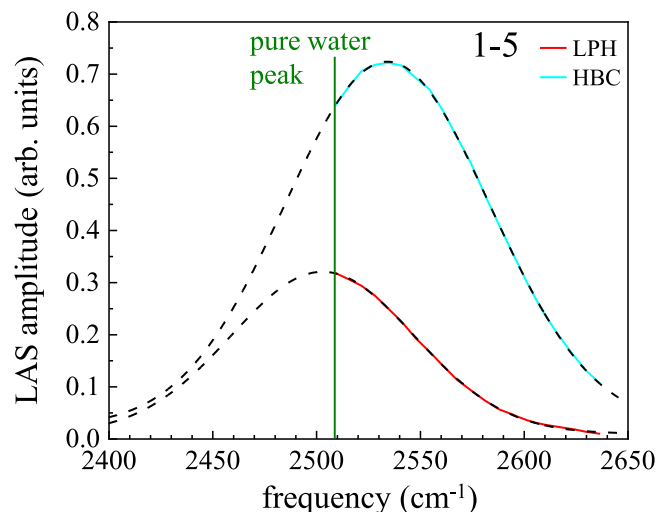


FIG. 3. LAS spectra of high salt concentration (1–5) LiCl solutions. Gaussian fits (black dashed) to the blue side of the HBC (light blue) and LPH (red) spectra for 1–5 concentration, with the fits extended to the red sides of the lines.

0–1 spectra. The peak of the pure water spectrum is centered at 2509 cm^{-1} (green line).^{23,24} The HBC spectra are blueshifted relative to pure water, and the LPH spectra are redshifted. The blueshift of the HBC spectra shows that the H-bonds to chloride are weaker on average than those in pure water.²¹ The LPHs make stronger H-bonds to water oxygens because of the increase in their fractional positive charges. The spectra were fit to Gaussian functions, and the fits were extended to the red so that the shifts of the spectra relative to pure water are apparent. A Gaussian function fits the spectrum of pure water well on the blue side of the line and approximately halfway down the red side. The hydroxyl transition dipoles become larger due to stronger hydrogen bonding as the wavelength becomes longer.⁴¹ The increased transition dipole on the red side of the spectrum produces a non-Gaussian tail to the red. A red tail is likely present in LPH and HBC spectra, but the LAS cannot access this part of the spectra because of overlaps with the 1–2 transitions.

The non-Condon effect results in larger transition dipoles on the red sides of the lines.⁴¹ The subensembles that make up the spectra are not pumped identically. Molecules absorbing on the red side of the line have larger transition dipoles, resulting in more excited states than in the ground state equilibrium population distribution. The higher concentration of excited states on the red side of the line causes short-time spectral diffusion from red to blue that brings the excited state populations to their equilibrium population distributions.²³ The extent and nature of the spectral diffusion affect the line amplitudes. To avoid the influence of the time-dependent spectral diffusion on the PSPP measurements, the fits to the population decays began several picoseconds after $t = 0$. This method was also used for the previously reported 1–4 to 1–16 concentrations, yielding a slightly longer time constant of ~ 1.7 ps for the lithium perturbed hydroxyl component, very close to that of pure water.

The solvation differs at low salt concentrations. For example, a 1–64 concentration has 64 oxygens and 128 hydroxyls per ion pair. Then, with 4 oxygens solvating Li^+ , creating 8 LPHs and 6 HBCs, 14 hydroxyls are directly affected, and 10 oxygens are affected.

That leaves many water molecules essentially unaffected. At ~ 1 –32 (1.7 m), there are still enough water molecules to have first and second water solvation shells. However, there may still be ion pairs at a 1–32 concentration and even the lower salt concentrations. As discussed below, the observables are not affected within experimental error up to a moderate concentration of ion pairs. At higher salt concentrations, the observables change.

There is no pure water region for high salt concentration data, i.e., 1–4 through 1–16 and possibly 1–24. Two species contribute to the LAS. For concentrations of 1–32 through 1–128, there is a high concentration of pure water hydroxyls (P). In addition, hydroxyls are bound to chloride, and lithium-perturbed hydroxyls are bound to other waters. Therefore, in principle, three species contribute to the LAS. The population decay is described by

$$P(t) = A_{LPH}(\lambda)e^{-t/\tau_{LPH}} + A_P(\lambda)e^{-t/\tau_P} + A_{HBC}(\lambda)e^{-t/\tau_{HBC}}. \quad (6)$$

However, even at 1–32, P is much larger than the other two components and dominates the LAS. From experiments on pure water, $\tau_P = 1.8 \pm 0.1$ ps.^{23,24} The LPH population relaxation time is essentially the same, ~ 1.7 ps (see Table S1). The similarity in the lifetimes is not a problem for obtaining the LPH spectrum at high salt concentrations because there is no spectral band from pure water. However, because the LAS is obtained by plotting the amplitude coefficients of the decays with different time constants, it is not possible to obtain the LPH LAS at low salt concentrations. As discussed below, the relaxation time for the HBC population is significantly longer than that of pure water. In addition, the spectrum is blueshifted relative to pure water. By fitting $P(t)$ data on the blue side of the spectrum to a biexponential representing the second and third terms in Eq. (6), we obtained the HBC LAS.

Figure 4 shows the plots of the population decays for concentrations 1–32 (4A) and 1–64 (4B) fit with biexponentials for three wavelengths. In the biexponential fits, the decay time constant for the pure water component is fixed at its known value, $\tau_P = 1.8$ ps. The results of the fits at many wavelengths give the HBC population decay time constant, $\tau_H = 3.5 \pm 0.1$ ps. As discussed in detail below, τ_H has contributions from the vibrational lifetime and the chemical exchange time.

Figure 5(a) shows the HBC spectra for lower salt concentrations. As the salt concentration decreases, the size of the HBC band relative to the pure water band decreases. The plot shows the HBC relative amplitudes obtained in the experiments.

Figure 5(b) displays the HBC LAS for the 1–48 concentration and the pure water, P, LAS spectrum. Because pure water is a single species, we can accurately measure the 0–1 spectrum and know the vibrational anharmonic shift of the 1–2 spectrum. From this information, we can remove a portion of the 1–2 contribution and obtain the 0–1 spectrum to lower frequencies. In Fig. 5(b), the blueshift of the HBC band relative to the P band is evident.

Figure 6(a) shows all the normalized HBC spectra for lower salt concentrations 1–32 to 1–128. They are identical within a small experimental error. The spectrum of hydroxyls bound to chlorides does not change over this concentration range. Figure 6(b) shows some high salt concentration spectra, 1–4, 1–16, and 1–24, and some low salt concentration spectra, 1–64 and 1–128. They are identical within error. In the [supplementary material](#), Fig. S3 shows all

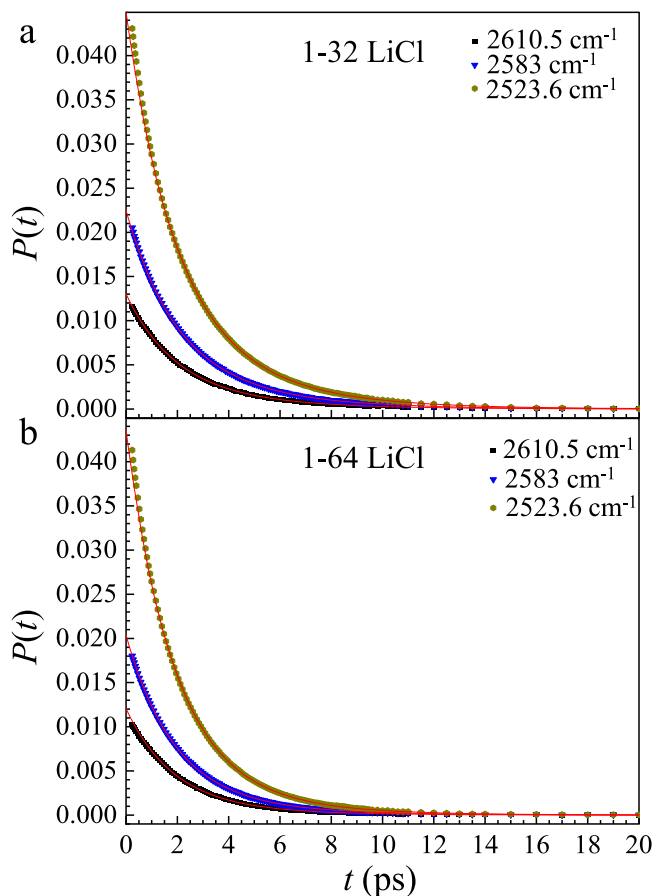


FIG. 4. Vibrational population relaxation of the OD stretch of HOD in (a) 1–32 LiCl solution and (b) 1–64 LiCl solution at three frequencies. The red curves are biexponential fits to the data.

11 concentrations from 1–4 to 1–128. They are identical within experimental error.

The identity of the HBC spectra over such a wide concentration range is remarkable. At 1–4, there are far too few water molecules to fully solvate the ions. At 1–128, there is more than sufficient water to solvate the ions and have them, on average, separated by many additional solvation shells. Nonetheless, the HBC LAS are identical. At 1–4 and other high salt concentrations, the waters solvating chlorides are in environments dense with other ions. The primary determinant of the frequency is the actual H-bond strength of the hydroxyl, which, in this case, is bonded to chlorides. At low salt concentrations, $< \sim 1$ –32, the HBC waters will be H-bonded, on average, to three other water molecules. Increasing the water concentration does not change the spectrum.

An interesting question is why the low and high salt concentration solutions have identical HBC spectra. The answer may lie in how the vibrational frequency of hydroxyls H-bonded to a halogen is affected by charge density. For hydroxyls bound to the series of halogens, F^- , Cl^- , Br^- , and I^- , the hydroxyl vibrational frequency shifts to a higher frequency (blue) as the size of the halogen increases

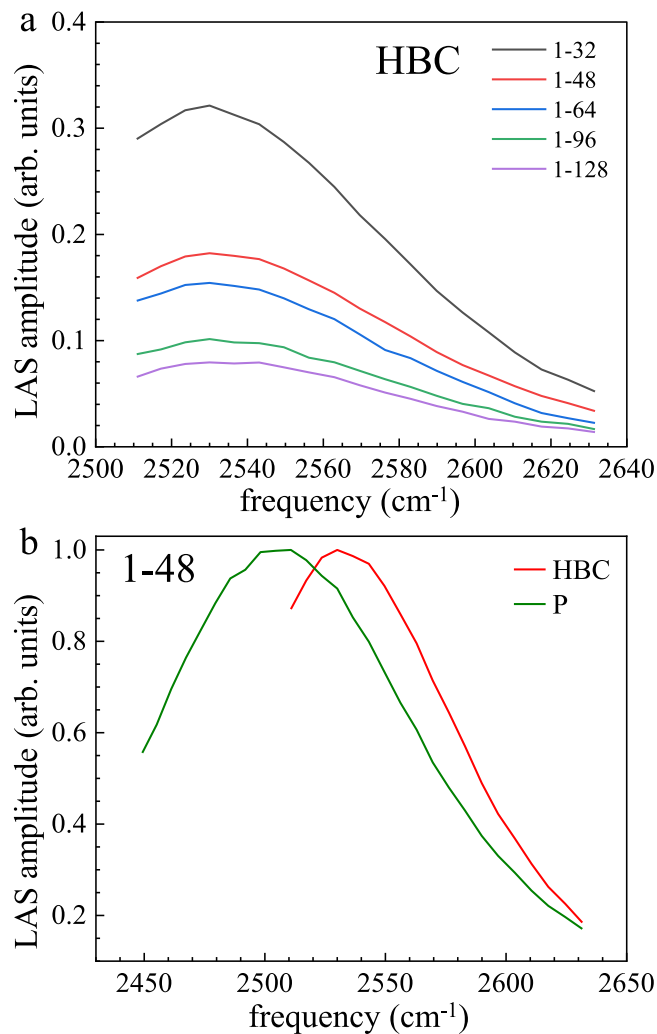


FIG. 5. LAS HBC spectra for low salt concentrations. (a) Various low salt concentration spectra. (b) Comparison of the HBC LAS spectrum for the 1-48 concentration and pure water.

because the charge density decreases.³⁵ A decrease in charge density causes a blueshift, while an increase in charge density causes a redshift.

Many chlorides will be fully solvated at lower salt concentrations, $\leq 1-32$. However, at 1-32, there is likely to be a non-negligible number of ion pairs, both solvent separated ion pairs (SSIP) and contact ion pairs (CIP). In an SSIP, a Li^+ is solvated by an oxygen with one of its hydroxyls bound to a Cl^- and three other water oxygens. The Li^+ will withdraw electron density from the oxygens, which, in turn, will withdraw electron density from its hydrogens, including the hydrogen associated with the Cl^- . The result will be a somewhat stronger H-bond to the Cl^- and a redshift. The HBCs involved in SSIPs will have their hydroxyl stretching mode slightly redshifted. An Li^+ forming a CIP will withdraw electron density from the Cl^- , affecting the remaining HBCs. This reduced electron

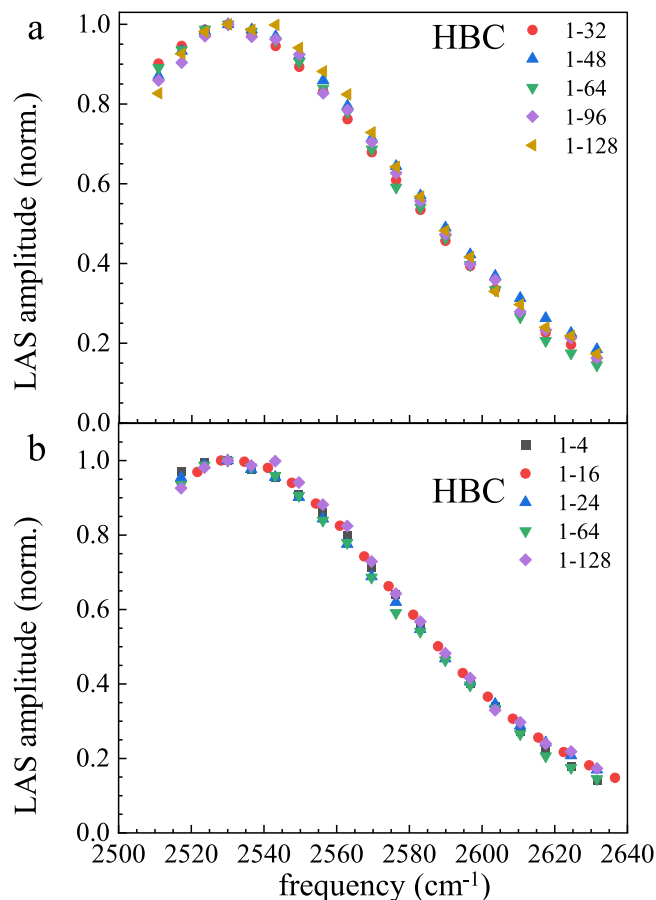


FIG. 6. (a) HBC LAS normalized spectra for low salt concentration samples, 1-32 to 1-128. The spectra have the same shape. (b) Several low and high salt concentration HBC LAS normalized spectra. The concentrations range from 13.9 m (1-4) to 0.4 m (1-128). Nonetheless, they all have the same shapes.

density will weaken the H-bonds, causing a blue vibrational frequency shift. The weakening of the H-bonds may be relatively small as the Li^+ still has three oxygens solvating it, which are richer sources of electron density, and all five of the other hydroxyls solvating the chloride will donate some electron density to the Cl^- . Therefore, the blueshift may not be large.

The effect of having SSIP and CIP at moderate salt concentrations, 1-32, can be that a fraction of the hydroxyls have small redshift and blueshift relative to a hydroxyl bound to a Cl^- fully solvated by water. If the shifts are small, they will not change the LAS within error. As the salt concentration is further reduced from 1 to 32, the fraction of Cl^- forming an ion pair decreases, and the ion pair influence on the spectrum decreases. Figure 6(a) shows no evidence of a concentration dependence in the spectra within experimental error, which is consistent with the above discussion.

The additional question is why the moderately low and high salt concentration spectra are the same [Fig. 6(b)]. At 1-4, chlorides cannot have complete water solvent shells or be solvated by five water

molecules and a single Li^+ . Each chloride's solvation shell can contain multiple ion pairs, both SSIPs and CIPs.^{2,3} An SSIP shifts the hydroxyl vibration somewhat to the red, and the CIP shifts it somewhat to the blue. With a Cl^- having several ion pair types, the shifts will tend to balance out. In Fig. 6(b), the 1–4 and 1–128 spectra look virtually identical. For the 1–128 concentration, there will be very few ion pairs, while 1–4 will have multiple ion pairs for each chloride. At lower salt concentrations, most Cl^- will be fully solvated by water, but some will form SSIPs and CIPs. The two types of pairs shift the spectra in opposite directions. If the shifts are small, they are not observable within the experimental error. At higher salt concentrations, the chlorides will form many ion pairs. These may balance each other out and, again, not produce observable shifts. The above is a reasonable hypothesis, which explains our observations. The AIMD simulations of moderate to high concentration LiCl solutions, which can determine the HBC vibrational frequencies, would be capable of testing this hypothesis.

C. Population relaxation

Equation (5) is used to describe $P(t)$ for high salt concentrations at which there are only two species, lithium-perturbed hydroxyls and hydroxyls bound to chloride. These have distinct population relaxation times; both $P(t)$ s were obtained (Table S1). Examples of the data and fits are shown in Fig. 2. Equation (6) describes the population decay for low salt concentrations with three species: LPH, P, and HBC. At low salt concentrations, P is the main species. As discussed above, the relaxation time of the LPH is almost the same as that of P and cannot be resolved at concentrations with significant P concentration. Therefore, only the HBC and P relaxation times can be obtained at low salt concentrations. For both high and low salt concentrations, the population decay is biexponential with the following form:

$$P(t) = aP_1(t) + bP_2(t). \quad (7)$$

Specifically for low salt concentrations, the decay is

$$P(t) = A_P(\lambda)e^{-t/\tau_P} + A_{HBC}(\lambda)e^{-t/\tau_{HBC}}. \quad (8)$$

By making measurements on the blue side of the line, there is little or no influence from the redshifted LPH spectrum. Its amplitude is low, and the decay constant is not distinguishable from the P decay constant.

The P lifetime is known accurately from measurements on pure water. It is 1.8 ps. Biexponential decays at many wavelengths were measured on the blue side of the absorption line. One decay time constant is fixed at 1.8 ps, and the other parameters are allowed to float. Examples of the data and fits can be seen in Fig. 4. The HBC decay time as a function of concentration was determined from 1–4 to 1–128.

Figure 7 shows a plot of the data. Table S1 gives the HBC population relaxation times for 11 concentrations from 1–4 to 1–128. As seen in the plot and the table, the HBC population relaxation times, τ_{HBC} , become faster as the salt concentration decreases. At low salt concentrations, the relaxation time is independent of concentration. The decay constants are the same beginning at a concentration of 1–32 (1.7 m) within experimental error. At lower concentrations, the chemical exchange of hydroxyls dissociating from Cl^- , as

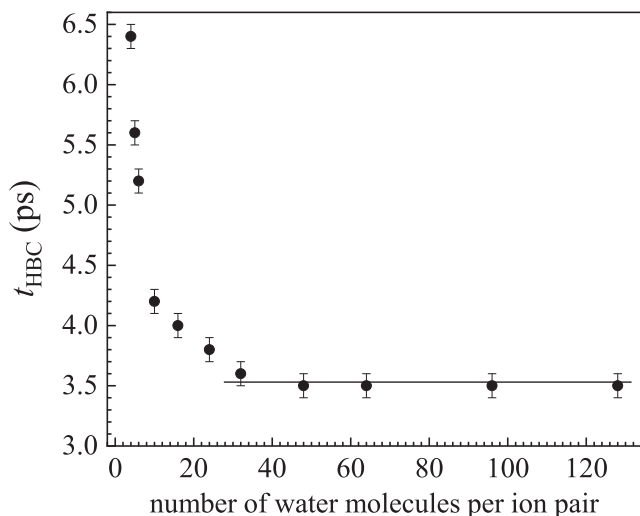


FIG. 7. HBC hydroxyl (OD) stretch population decay as a function of concentration. As the salt concentration decreases, the population decay is faster until a concentration of 1–32 (1.7 m). The lifetimes are independent of concentration within experimental error for salt concentrations <1 –32 (1.7 m).

detailed below, becomes relevant and combines with the vibrational lifetime to give the observed HBC population decay time. Nonetheless, the presence of chemical exchange does not change the fact that the observed relaxation times are concentration independent within experimental error for salt concentrations ≤ 1 –32. A method for determining the vibrational lifetime from the observed population relaxation time and the chemical exchange time is presented below.

The lifetime is sensitive to the local environment. The hydroxyl stretch, in this case, the OD stretch of HOD, relaxes by transferring its vibrational energy into a combination of intramolecular and intermolecular modes.⁴² In H_2O , the OD stretch of HOD has a frequency of 2509 cm^{-1} . The HOD bend frequency is 1480 cm^{-1} .⁴³ The bend plus a rocking libration has a frequency of 1850 cm^{-1} .⁴³ Then, for example, the stretch can relax by creating two quanta of the bending mode and annihilating one or more solution continuum modes (phonons) to conserve energy. Or it could relax into the bend + rocking mode and create one or more phonons to conserve energy.

The HBC OD stretch lifetime relaxation pathways will differ significantly when an OD is H-bonded to a chloride because the chloride has no accepting modes that can participate in the intermolecular component of energy conservation in the relaxation process. Therefore, even in the low salt concentration limit, the HBC OD lifetime will differ from the pure water value of 1.8 ps. In addition, the observed population decay is the lifetime decay with an additional contribution from chemical exchange.

The first solvation shell of a chloride consists of ~ 6 water molecules H-bonded to the Cl^- . Water molecules H-bonded to chloride will dissociate, and water molecules in the second solvation shell will form H-bonds with the chloride, becoming part of the first solvation shell. Because the system is in equilibrium, the rates of water molecules dissociating from the chloride and associating with the

chloride are the same. This switching of water molecules H-bonded to chlorides is chemical exchange.

D. Chemical exchange

The chemical exchange is illustrated in Fig. 8. Water hydroxyls bound to other water molecules exchange to become bound to chlorides and vice versa. At the same time, the excited populations are decreasing due to their vibrational lifetimes. In previous publications,^{23,24} the LiCl high salt concentration range, 1–4 to 1–16 (13.9–3.5 m), was studied. At these concentrations, there is no region of pure water. Without a population of pure water and a relatively small number of water molecules overall, chemical exchange becomes so slow compared to the vibrational lifetimes that it does not affect the population decay [Eq. (3)] or the anisotropy decay [Eq. (4)]. At lower salt concentrations, ≤ 1 –32, chemical exchange plays a role in both dynamical processes.

The orientational relaxation in pure water is a single exponential with a 2.6 ± 0.1 ps time constant.^{11,12} As discussed briefly above and described in detail previously, in contrast to pure water, the decays in the high concentration LiCl solutions are biexponentials, indicative of two processes contributing to water reorientation.²⁴ Water molecules are components of extended ion/water networks.^{23,24} In high salt concentrations solutions, very crowded ion environments, $r(t)$ [Eq. (4)] is determined by all the interactions of HOD with its surroundings.^{16,17,44,45} In concentrations 1–4 through 1–16 and possibly 1–24, the two processes contributing to orientational dynamics are described using the wobbling-in-a-cone model.^{21,22} In this model, water molecules undergo restricted angular diffusion at short times, wobbling in a cone of angles, which gives rise to the fast component of the biexponential decays. The wobbling is followed by the structural evolution of the surrounding medium, which enables complete orientational randomization on a longer timescale, the slow component of the biexponential.^{26,27,29} The concentration dependence of the cone angles, wobbling time constants, and complete orientational relaxation time constants were presented previously.^{23,24}

A substantial amount of pure water exists at ≤ 1 –32 salt concentrations. Pure water undergoes orientational randomization as a

single exponential process via the jump reorientation mechanism.¹⁴ The jump angle is $\sim 60^\circ$. Here, we assume that the water not associated with ions undergoes orientational relaxation in the same manner as pure water with the same orientational relaxation time of 2.6 ps. We further assume that when a water molecule dissociates from being H-bonded to a Cl^- , it does so with the same mechanism. 2D IR angularly resolved chemical exchange experiments in aqueous ClO_4^- solutions observing the OD stretch of HOD showed that the exchange from water H-bonded to ClO_4^- s to H-bonded to water molecules occurs with jumps of $\sim 49 \pm 4^\circ$, very similar to pure water.⁴⁰ In those experiments and chemical exchange experiments with BF_4^- as the anion,³⁰ the anions were chosen because the vibrational spectra of water H-bonded to the anions were shifted far enough to the blue to have distinct peaks in the absorption spectrum. The shift is caused by very weak H-bonding to these anions. The separated water and water bound to anion spectra made it possible to perform 2D-IR chemical exchange experiments.^{30,40} These experiments observe the growth of off-diagonal peaks in the 2D IR spectrum. The growth was analyzed to yield the exchange rates. In those experiments, the role that exchange played in the anisotropy decays of the water H-bonded to the anions was not addressed.

In this study, the water H-bonded to Cl^- has a blueshift, but it is insufficient to give a distinct spectrum (see Fig. 1). Nonetheless, we can address issues associated with chemical exchange and examine the effects of exchange on the population and anisotropy decays.

Previous papers have given the equations that describe chemical exchange and the exchange's effects on the populations involved in 2D IR chemical exchange experiments.^{30,40,46} The kinetics are illustrated in Fig. 8. 2D IR experiments have been performed on salt solutions when the two species that are exchanging can be resolved in an FT-IR spectrum.^{30,40,46} Using 2D IR experiments that observe the growth of off-diagonal peaks in the spectra to measure the exchange kinetics, water/anion chemical exchange times for salt solutions were reported.^{30,40,46} In one study, a solution of NaBF_4 was found to have an ion-to-water exchange (dissociation) time of 7 ps.

The known hydroxyl dissociation time from BF_4^- and density function theoretical calculations (Gaussian 16 quantum chemistry package at the B3LYP/6-31+G(d,p) level of theory with the SMD implicit solvent model of water) were used to obtain the dissociation time of a hydroxyl from Cl^- . The same procedure was used to determine the change in free energy for a hydroxyl leaving the first solvation shell of each anion. The details and figures are given in the [supplementary material](#). The optimized structure and energy were determined for six hydroxyls bound to Cl^- and four hydroxyls bound to BF_4^- with implicit water solvation.⁴⁷ One hydroxyl was moved a small step (0.1 Å) away from the anion, and then, the entire structure was re-optimized. This procedure, i.e., a small step and then structure optimization, which increased the energy, was continued until the energy plateaued (see Fig. S4). The dissociation energy is the difference between the plateau energy and the energy of the initial optimized structure.

The following equation was used to obtain the dissociation time of a hydroxyl from Cl^- :

$$\tau_{\text{Cl}^-}^d = \frac{e^{\Delta G_{\text{Cl}^-}/kT}}{e^{\Delta G_{\text{BF}_4^-}/kT}} \tau_{\text{BF}_4^-}^d \quad (9)$$

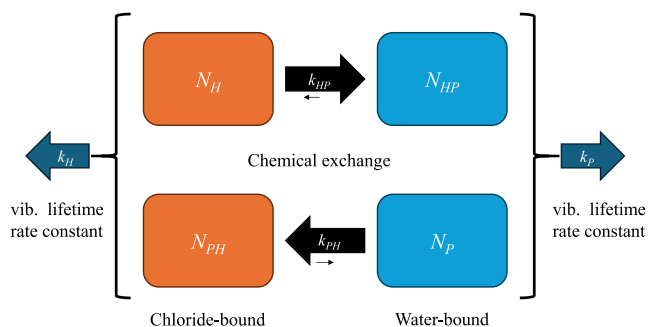


FIG. 8. Diagram of the chemical exchange dynamics present in the samples. N_H and N_P are the populations of ODs initially bound to chloride and water, respectively. N_{PH} is the population of hydroxyls initially bound to water after they become bound to chlorides, and vice versa for N_{HP} . Exchange occurs with the rate constants k_{HP} and k_{PH} ; vibrational lifetime decays occur with the lifetime rate constants k_P and k_H .

The superscript d indicates dissociation time. The BF_4^- hydroxyl dissociation time is 7 ps.³⁰ The Cl^- and BF_4^- hydroxyl dissociation energies are 2.10 kcal/mol and 1.96 kcal/mol, respectively. Equation (9) gives a Cl^- dissociation time of 9 ps. The electronic structure calculations give ΔG s, but the entropy changes are only for the species involved in the calculations. Because an implicit water solvent was used, there is no molecular second solvation shell. The water molecules H-bonded to the anion comprise the first solvation shell. The second solvation shell is composed of water molecules that do not interact directly with the anion. We are making an approximation that a water molecule moving from the anion's first solvation shell into the pure water second solvation shell of Cl^- or BF_4^- produces essentially the same change in entropy. Then, this component of the entropy change in ΔG for the two anions is the same and divides out. As discussed below, an error in the dissociation time of a hydroxyl from Cl^- affects the numerical value of the lifetime, but it is a mild effect. The primary purpose here is to show the chemical exchange's role in the measured dynamical observables and to illustrate the mechanism for the orientation relaxation of hydroxyls bound to chlorides.

To investigate the influence of chemical exchange on the HBC population relaxation, $P(t)$, and the anisotropy decay, $r(t)$, we employ a set of coupled kinetic equations [Eqs. (S1)–(S7) of the [supplementary material](#)], which implement the schematic shown in Fig. 8.⁴⁶ The solutions were used to calculate the observables of interest here.⁴⁷

1. The role of chemical exchange in population relaxation

In Sec. III B, the population relaxation decays composed of pure water hydroxyls and hydroxyls bound to chloride were fit as biexponentials (see Fig. 4). The HBC population decayed with a time constant of 3.5 ps. This decay time is a combination of the vibrational lifetime and a contribution from chemical exchange. Adding a chemical exchange component makes the observed population decay, $P(t)$, faster than the vibrational lifetime. Using the chemical exchange time constant for HBCs to become pure waters, $t_{HP} = 9$ ps, and Eqs. (S1)–(S7), it was determined that the HBC vibrational lifetime for all concentrations $\leq 1\text{--}32$ is 4.3 ps.

Figure 9 shows a comparison of an analytical 3.5 ps exponential decay (black squares) with the results of the chemical exchange model calculation of the decays for concentrations of 1–32 (red solid curve) and 1–64 (blue dashed curve).

The exchange model curves are the results of fits to the experimental biexponential $P(t)$ curves. In the fits, there is only one adjustable parameter, the HBC vibrational lifetime. All the other parameters are known. Consider the concentration of 1–32. The number of water molecules H-bonded to a chloride is taken to be 6, which is N_H . N_H does not change as the salt concentration decreases. These six water molecules are the first solvation shell of the chlorides. There are also four water molecules solvating the Li^+ . Therefore, on average, there are 22 water molecules not in either of the ion's first solvation shells. So, N_P , the “pure” water population, is 22. Twenty-two water molecules are more than sufficient to form the second solvation shell. For lower salt concentrations, e.g., 1–64, there are substantially more water molecules not in the first solvation shell of either ion. N_P increases as the salt concentration decreases. For a concentration of 1– n , N_P is $n - 10$. The rate constant, k_P , is the

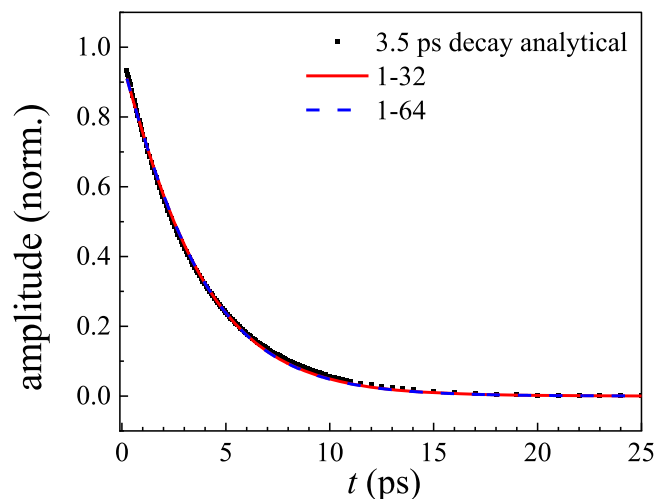


FIG. 9. An analytical 3.5 ps analytical exponential decay curve (black squares) representing the HBC component of the biexponential population decay (Fig. 4) and the results of the exchange model calculation of the HBC portion of the decay for concentrations 1–32 (red solid curve) and 1–64 (blue dashed curve). The exchange model decay curves have two contributions: the vibrational lifetime and the exchange of water hydroxyls H-bonded to chlorides to hydroxyls H-bonded to water molecules.

inverse of the pure water hydroxyl (OD) lifetime, $k_P = 1/1.8$ ps = 0.56 ps^{−1}; $k_{HP} = 1/9$ ps = 0.11 ps^{−1}. The system is in equilibrium. Thus, the rate from H to HP equals the rate from P to PH , $N_H k_{HP} = N_P k_{PH}$. We know N_H (6) and k_{HP} (0.11 ps^{−1}), which are constant at all concentrations $\leq 1\text{--}32$, as shown by the identity of the 1–32 and 1–64 curves in Fig. 9. We also know N_P for all concentrations. Therefore, we know k_{PH} at all concentrations.

We used the exchange model to fit the experimental $P(t)$ curves (see Fig. 4) at many wavelengths and concentrations. There is only one adjustable parameter, $k_H = 1/\tau_H$, where τ_H is the hydroxyl (OD) bound to chloride vibrational lifetime. The fits to many wavelengths and all concentrations give $\tau_H = 4.3 \pm 0.2$ ps. As shown in Fig. 9, the exchange model with the constants enumerated above does an excellent job reproducing the observed 3.5 ps decay found when fitting a biexponential to the $P(t)$ data. The 9 ps HBC dissociation time is approximate. However, while the exact value makes a difference in the HBC vibrational lifetime extracted from the calculations, the result is not highly sensitive. For example, if $\tau_{HP} = 14$ ps rather than 9 ps, the resulting lifetime of hydroxyls bound to chlorides is 4.0 ps rather than 4.3 ps. The exchange time cannot be shorter than the observed 3.5 ps population relaxation time, nor can it be so long that it becomes too slow (>20 ps) to account for the orientational relaxation.

2. The role of chemical exchange in anisotropy relaxation

Anisotropy decay, $r(t)$, is usually caused by molecular reorientation. For hydroxyls (OD) bound to chlorides, reorientation, which causes the molecular transition dipole under observation to randomize its direction, will not occur. A chloride's first solvation shell consists of six H-bonded water molecules. These six water molecules are H-bonded to the surrounding water molecules that comprise the

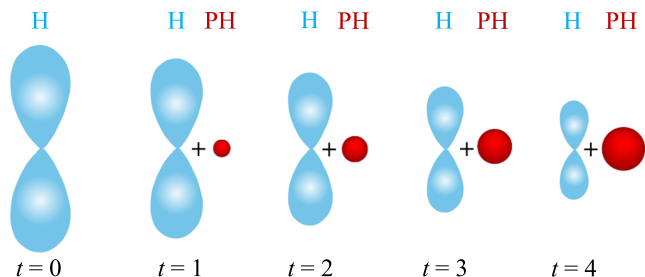


FIG. 10. Illustration of the time dependence of the anisotropy evolution of HBCs. The pump pulse initially excites a Cos^2 distribution (blue) of HBCs. It maintains its shape but decays in amplitude because of the vibrational lifetime and chemical exchange, $H \rightarrow HP$. A spherical distribution of orientations grows due to chemical exchange, $P \rightarrow PH$, i.e., water not associated with an ion (the N_{PH} population) becomes H-bonded to a chloride.

second solvation shell. A chloride with its first solvation shell will not rotate as an intact unit as a molecule in solution would.

Figure 10 schematically illustrates the chemical exchange mechanism for the HBCs' anisotropy decay. At $t = 0$, the pump pulse produces a Cos^2 distribution of vibrationally excited HBCs (blue distributions). These HBCs will not undergo anisotropy decay through orientation randomization. The amplitude of the Cos^2 distribution will decay because of the vibrational lifetime and the chemical exchange $H \rightarrow HP$. After the time intervals 1, 2, 3, and 4, the Cos^2 distribution shrinks, but the reduction in amplitude does not cause anisotropy decay.

After $t = 0$, initially excited pure water molecules will exchange and become HBCs, $P \rightarrow PH$. We assume that the PHs have random distributions (red) for several reasons. First, the pure water (HOD in H_2O) orientational relaxation rate, 2.6 ps, is fast compared to the exchange time. Therefore, on average, the pure water, P , will have undergone substantial anisotropy decay before it exchanges to become a PH . In addition, the exchange process will cause orientational changes of the incoming hydroxyls. The incoming hydroxyl is unlikely to associate with the chloride with its O–D bond vector directly along the same axis as it previously had as pure water. It will then change the orientation to maximize the H-bond strength and accommodate the other HBCs already attached to the surface. The fast water reorientation and the angular changes accompanying the H-bond formation support the use of the model of the random PH distribution (red spheres in Fig. 10).

The result is that at any time t , the HBC component of the anisotropy is determined by the sum of a perfectly orientated subensemble, the H s, and a perfectly random subensemble, the PH s. The aligned subensemble shrinks as time progresses, and the random subensemble grows initially before shrinking due to the lifetime. The time-dependent sum of these two distributions causes the anisotropy decay.

There are three components in calculating the parallel and perpendicular anisotropy decays. First, there is the pure water. The parameters are known from previous studies on bulk water. The vibrational lifetime is 1.8 ps, and the orientational relaxation time constant is 2.6 ps.^{10–13} The other two components were discussed in connection with the schematic in Fig. 10. The initially excited

HBCs produce the polarized contribution that decays in amplitude from the lifetime decay and $H \rightarrow HP$ chemical exchange, but it does not undergo relaxation of its initial anisotropy. The third component is the exchange of $P \rightarrow PH$. As discussed above, the PH s are an isotropic subensemble, which adds to the polarized H subensemble (see Fig. 10).

Equations (S1)–(S7), with the exchange and lifetime decays for the salt concentrations ≤ 1 –32, were employed to fit the population decays and give the HBC lifetime of 4.3 ps. To model $S_{\parallel}(t)$ and $S_{\perp}(t)$, Eqs. (1) and (2) were used. The N_H component is perfectly polarized. Then, $C_2^H(t) = 1$ for all t . The N_{PH} component has no polarization, so $C_2^{PH}(t) = 0$ for all t . Using these relations gives

$$S_{\parallel}^{ex}(t) = 1.8 \frac{N_H(t)}{N_H(t) + N_{PH}(t)} + \frac{N_{PH}(t)}{N_H(t) + N_{PH}(t)}, \quad (10)$$

$$S_{\perp}^{ex}(t) = 0.6 \frac{N_H(t)}{N_H(t) + N_{PH}(t)} + \frac{N_{PH}(t)}{N_H(t) + N_{PH}(t)}, \quad (11)$$

$$(S_{\parallel}^{ex}(t) - S_{\perp}^{ex}(t))/1.2 = C_2^{ex}(t). \quad (12)$$

The time dependence of $C_2(t)$ enters through the amplitudes of N_H and N_{PH} , which are determined by the chemical exchange equations. The data are calculated by adding the exchange terms (denoted with the superscript ex) to the pure water orientational relaxation terms (denoted with the superscript p) for which the lifetime (1.8 ps) and the orientational relaxation time (2.6 ps) are known,

$$S_{\parallel}^p(t) = e^{-t/1.8} (1 + 0.8e^{-t/2.6}), \quad (13)$$

$$S_{\perp}^p(t) = e^{-t/1.8} (1 - 0.4e^{-t/2.6}). \quad (14)$$

Then, the functions used to analyze the data are

$$S_{\parallel}(t) = P_0 S_{\parallel}^p(t) + H_0 S_{\parallel}^{ex}(t), \quad (15)$$

$$S_{\perp}(t) = P_0 S_{\perp}^p(t) + H_0 S_{\perp}^{ex}(t). \quad (16)$$

P_0 and H_0 are the relative numbers of pure water molecules to HBCs at a given frequency, which were determined from the LAS described above. In calculating $S_{\parallel}(t)$ and $S_{\perp}(t)$ with Eqs. (15) and (16), there are no adjustable parameters other than scaling the experimental data for comparison with the calculations.

Figure 11 shows the $S_{\perp}(t)$ and $S_{\parallel}(t)$ data for two concentrations (black squares) and the no adjustable parameter calculations (red curves). Given that there are no adjustable parameters, the agreement between the data and the corresponding calculated curve is very good for the datasets shown in Fig. 11, and the agreement is the same for all wavelengths and salt concentrations ≤ 1 –32. These results demonstrate that the chemical exchange model (Fig. 10) for the anisotropy decay of the hydroxyls H-bonded to chlorides is consistent with the experimental data. Previous 2D IR experiments that studied water exchange to and from anions did not address the anisotropy decays of the hydroxyls bound to the anions.^{30,40} It is noteworthy that chemical exchange information can be extracted from experiments in which the hydroxyls bound to anions do not give rise to a distinct peak in the absorption spectra. A distinct peak remains a prerequisite for 2D IR chemical exchange experiments. However, a reasonable value of the $H \rightarrow HP$ exchange time

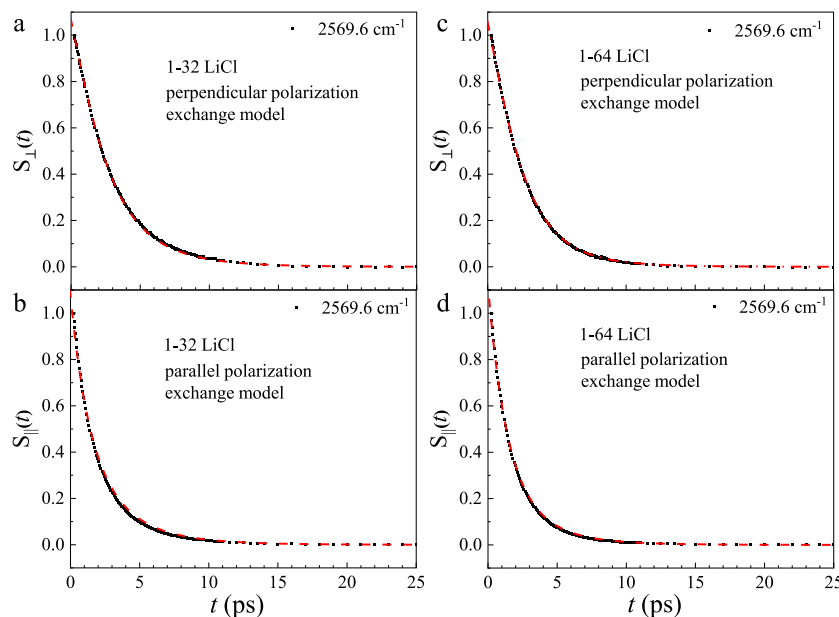


FIG. 11. (a) and (b) are the perpendicular and parallel polarization data (black squares) for concentration 1–32, and (c) and (d) are the perpendicular and parallel polarization data (black squares) for concentration 1–64. The red dashed curves are the no adjustable parameter calculations using the model illustrated in Fig. 10 and the exchange equations (S1)–(S7). The agreement between the no adjustable parameter calculations and the data is very good.

is necessary for the analysis presented here. We determined the $H \rightarrow HP$ exchange time from the previously measured exchange time for BF_4^- using DFT calculations.

Returning to the possible presence of ion pairs at lower concentrations ($\leq 1-32$) at which the population and the anisotropy decays are independent of concentration, the observables used here cannot determine if there are ion pairs. By varying the population numbers, for example, reducing $N_H(t=0)$ from 6 (which assumes full solvation) to 5.4, which assumes 60% of chlorides are involved in an ion pair, the fits to the decays are not noticeably changed. As the salt concentration is reduced from 1–32 to 1–128, the chloride fraction involved in ion pairs will decrease. Even without using the exchange model, Fig. 7 shows that the HBC components of the biexponential decays are independent of concentration. These results do not demonstrate the absence of ion pairing for concentrations $\leq 1-32$. They only indicate that the dynamics of the HBCs observed in the experiments are not sensitive to a moderate or small extent of ion pairing. The situation is different for high salt concentrations at which there is little water. Both the population and anisotropy decays are affected by extensive ion pairing.

IV. CONCLUDING REMARKS

We examined the dynamic of water molecules solvating chloride anion in LiCl solutions with ultrafast IR experiments on the hydroxyl stretch (OD stretch of dilute HOD in H_2O). The primary focus was on the low end of high concentration salt solutions (0.4–1.7 m). The results were compared to prior and new experiments on very high salt concentration (2.3–13.9 m) solutions. The total range of concentrations studied spans water-in-salt solutions to much lower salt concentration, salt-in-water solutions. Population and anisotropy decays were measured. For LiCl solutions with salt concentrations $\leq 1-32$ (one LiCl per 32 water molecules, 1.7 m), the population and anisotropy decays of hydroxyls H-bonded to

chlorides (HBCs) are concentration independent. An important question is what concentration marks the beginning of low salt concentration solutions. The answer is that the transition in terms of the water population lifetime dynamics occurs at a relatively high LiCl concentration, ~ 1.7 m. 1.7 m is the concentration at which a substantial fraction of solvated chlorides are surrounded by environments that are not distinguishable from those of pure water. There can still be some ion pairing for salt concentrations of $\leq 1-32$, but the extent is too small to influence the dynamic observables within experimental error. The dynamic observable change for salt concentrations $> 1-32$ is significant (see Fig. 7). At these high concentrations, the amount of water is small, and the extent of ion pair is large, so the typical environment of a chloride ion is substantially different from that of pure water.

Measurements of the population decays as a function of wavelength were used to obtain Lifetime Amplitude Spectra (LAS). At the highest concentrations, the LAS show two distinct spectra. One spectrum is for HBCs. This spectrum is blueshifted relative to hydroxyls of pure water. The other is from hydroxyls of oxygens solvating Li^+ . This spectrum is redshifted compared to that of pure water. There are so few water molecules at very high concentrations that no pure water LAS exists. At lower concentrations, the pure water band is prominent. This band arises from collections of water molecules that are sufficiently large to have the extended H-bond network characteristic of pure water. It subsumes the peak from water molecules solvating Li^+ because the OD stretch lifetime of these water molecules is almost identical to the pure water OD lifetime. However, the significantly blueshifted HBC band is still readily observable (see Fig. 5). Therefore, the HBC LAS spectrum can be measured over the entire concentration range, 13.9–0.4 m (1–4 to 1–128), and dynamical experiments can be conducted on the HBCs at lower concentrations where the hydroxyls of water molecules solvating Li^+ cannot be accessed. A remarkable result is that the hydroxyls solvating Cl^- spectra are the same within a small

experimental error for the entire concentration range (see Figs. 6 and S3). This result is unsurprising for lower salt concentrations, ≤ 1 –32. The dynamic observables are also independent of concentration. However, the chlorides are involved in multiple ion pair interactions at high concentrations that contain little water. It was argued that some of these interactions blueshift the hydroxyl spectrum, and some cause a redshift. It was hypothesized that these multiple interactions essentially cancel, leaving the spectrum unchanged within experimental error.

The dynamic observables were analyzed using chemical exchange theory in the lower concentration range, ≤ 1 –32. The population decay results from the vibrational lifetime relaxation of the initially excited HBCs to the ground vibrational state and chemical exchange, $H \rightarrow HP$, in which hydroxyls H-bonded to chlorides dissociate and join the pure water subensemble. Data analysis showed that the observed population decay of 3.5 ps results from a 4.3 ps lifetime and a 9 ps chemical exchange component. The fits to the population relaxation had only one adjustable parameter, the vibrational lifetime.

Analysis of the influence of chemical exchange on the anisotropy decay is more complex. The model is embodied in Fig. 10. At $t = 0$, vibrationally excited HBCs have maximum anisotropy, with the orientational correlation function, $C_2 = 1$ (a Cos^2 distribution). This subensemble does not undergo anisotropy decay, but its magnitude decreases due to the vibrational lifetime and the $H \rightarrow HP$ chemical exchange. The $P \rightarrow PH$ chemical exchange adds a completely depolarized subensemble, $C_2 = 0$, to the total ensemble, increasing in relative magnitude as time increases. The time-dependent sum of these two subensembles determines the anisotropy as time increases, resulting in a decay of the anisotropy. The anisotropy data could be reproduced with this model with no adjustable parameters.

The results presented here show that LiCl aqueous solutions' molecular level dynamical properties stop changing as the LiCl concentration was lowered below ~ 1.7 m (≤ 1 –32). An important distinction needs to be made between molecular-level properties and bulk properties. Bulk properties, such as the viscosity, the density, and the dielectric constant, continue to change as the salt concentration is reduced below 1.7 m.^{48–52} These properties depend on the presence of ions. At lower concentrations, the bulk properties change because there are fewer non-interacting ions, not because the solvated ion molecular level surroundings are changing.

SUPPLEMENTARY MATERIAL

See the [supplementary material](#) for FTIR peak centers and widths as a function of ion mole fraction, the LAS spectra of HBCs for 11 concentrations from 13.9 to 0.4 m, a table of observed vibrational lifetimes from fits to the population relaxation, density functional theory calculations, and chemical exchange equations.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Tristan R. Heck: Conceptualization (equal); Formal analysis (equal); Investigation (equal); Methodology (equal); Writing – original draft (equal). **Junkun Pan:** Conceptualization (equal); Formal analysis (equal); Investigation (equal). **Michael D. Fayer:** Conceptualization (equal); Formal analysis (equal); Funding acquisition (equal); Investigation (equal); Methodology (equal); Project administration (equal); Supervision (equal); Writing – original draft (equal); Writing – review & editing (equal).

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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