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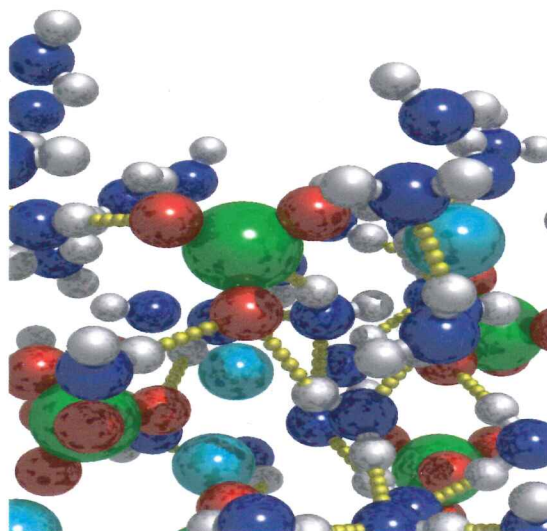
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FRONTIERS ARTICLE

H-bond switching and ligand exchange dynamics in aqueous ionic solution

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ABSTRACT

Aqueous ionic solutions lubricate the chemical machinery of the environment and life. Understanding the impact of ions on the properties of aqueous solutions and how these modified properties influence chemical and conformational dynamics remains an important and elusive objective of physical chemistry research. Here we discuss recent advances in our understanding that have been derived from ultrafast vibrational spectroscopy and molecular dynamics simulations.

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1. Introduction

The unusual properties of liquid water and aqueous solutions result predominantly from the strength and directionality of intermolecular hydrogen bonds (H-bonds). The instantaneous structure of water reflects the constraints imposed by H-bonds on the short-range packing and orientation of water molecules in solution. Dissolution of ionic species in water disrupts this H-bond network and leads to the formation of solute–solvent specific interactions that further modify the structure. Ions also alter the time evolution of the H-bond network. A comprehensive understanding of aqueous ionic solutions requires a detailed understanding of the equilibrium distribution of local structures and the motions and fluctuation rates that allow this distribution to be sampled. Despite extensive experimental and theoretical investigation, a detailed microscopic understanding of the structure and dynamics of aqueous ionic solutions has eluded scientists.

From the structural perspective, the spatial extent of the perturbation induced by an ionic solute and how the perturbation depends upon the nature of the ionic solute remains an area of active investigation and controversy [1,2]. X-ray and neutron scattering, as well as extended X-ray absorption fine structure, represent the standard methods for accessing the short range order in aqueous ionic solution [3,4]. More recently, soft X-ray core hole spectroscopy has provided a new view of the local structure in aqueous ionic solution [5–10]. These spectroscopic measurements have the capacity to measure the local nuclear structure and the magnitude of the charge transfer between the coordinating water and the dissolved ions [11–13], though robustly distinguishing these effects proves difficult and has generated significant contro-

versy. The impact of ions on the macroscopic transport properties of aqueous ionic solutions led to the classification of ions as enhancers or disrupters of H-bond ordering [2]. Assessing the validity of the ion structure making and breaking hypothesis has the potential for broad importance because the influence of ions on biochemical activity correlates with the structure making and breaking hypothesis [14]. An alternative hypothesis attributes the impact of ions on the macroscopic properties of aqueous solutions to the water molecules in direct contact with ion – the water molecules in the first ionic solvation shell [15]. This hypothesis necessitates the presence of two structurally and dynamically distinct classes of water in ionic solutions with comparatively slow exchange between these classes. Time resolved vibrational spectroscopy studies conducted by Bakker and coworkers have been interpreted to support this strongly heterogeneous view of aqueous ionic solutions [15–17]. Most provocatively, Omta et al. concluded that the rotational dynamics of water hydroxyl groups outside of the first solvation shell of the ClO_4^- anions in 6 M NaClO_4 could not be distinguished from the dynamics of pure water [17].

These time resolved vibrational studies of aqueous ionic solutions highlight the importance of dynamics in the investigation of liquid media. While the instantaneous structure of water and water solutions will be strongly heterogeneous, for that heterogeneity to be of chemical importance, the heterogeneity must be persistent. The mechanism for and rate of water–water and water–anion H-bond switching, the residence time of water molecules in ionic solvation shells, and the mechanism for and dynamics of ion pairing and ligand exchange represent critical events that significantly determine the dynamical heterogeneity of aqueous ionic solutions. Understanding the variable impact of anions and cations on the properties of water and how this impact depends upon the physical and chemical properties of the ion also represent important research objectives in the study of aqueous ionic solutions.

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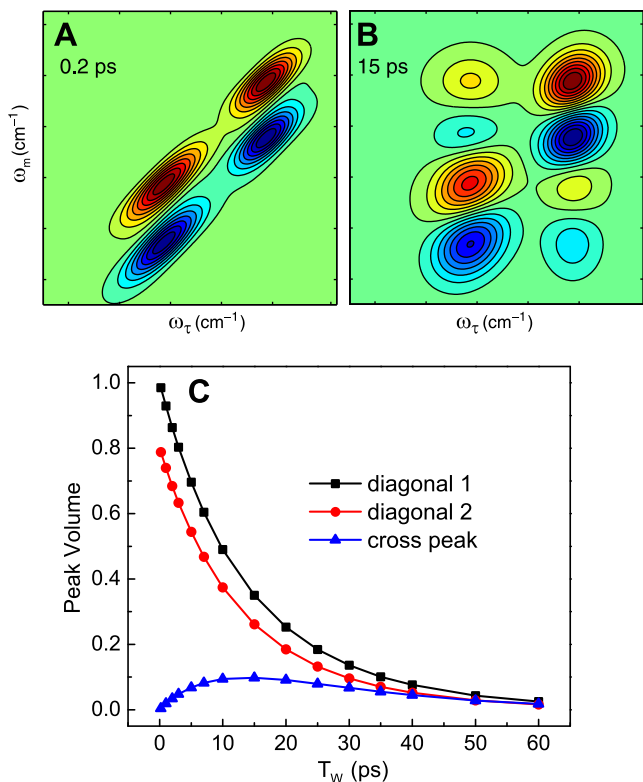


Figure 1. Schematic depiction of 2DIR spectroscopy and the measurement of chemical exchange dynamics. (A) For a small $T_W = 0.2$ ps time delay, analogous to a 0.2 ps pump–probe time delay, the signal is dominated by red peaks along the figure diagonal and blue peaks offset from the diagonal by the vibrational anharmonicity. (B) After a $T_W = 15$ ps waiting time, chemical exchange has occurred, adding two red cross peaks and two blue cross peaks, leading to a total of eight peaks. A cross peak occurs because a vibrationally excited molecule with frequency ω_τ at time zero has undergone a chemical exchange during the T_W waiting time, leading to a change in frequency to ω_m . The experimental spectra presented in Figs. 3 and 4 do not have eight peaks because of spectral overlap. (C) T_W waiting time dependent peak volumes for the diagonal and cross-peak signals.

We present recent advances in our understanding of the dynamics of aqueous ionic solutions derived from ultrafast vibrational spectroscopy and molecular dynamics simulations [18–20]. Vibrational spectroscopy provides a local monitor of structure and dynamics with more transparent interpretation than techniques that monitor the collective response of a solution, such as ultrasonic absorption and dielectric relaxation spectroscopy [21,22]. The short-ranged sensitivity of vibrational spectroscopy means that it cannot provide a complete picture of solution structure and dynamics, but the technique nonetheless provides one of the most powerful approaches for investigating the dynamics of ionic solutions. We utilize multidimensional vibrational correlation spectroscopy, commonly termed 2DIR spectroscopy, a class of ultrafast vibrational spectroscopy measurement ideally suited for the study of conformational dynamics in solution [18–20,23–27]. We have used this technique to study the impact of both anions and cations on the structure and dynamics of aqueous ionic solutions [18–20,27]. These studies have used the deuterated hydroxyl stretch of isotopically mixed water to study the dynamics and mechanism of H-bond switching between water–water and water–anion H-bonds in a NaClO_4 solution [18,20] and they have used the CN stretch of the thiocyanate anion to study ligand exchange around the Mg^{2+} cation in water [19]. The results of each of these studies will be presented, core questions highlighted, and future opportunities discussed.

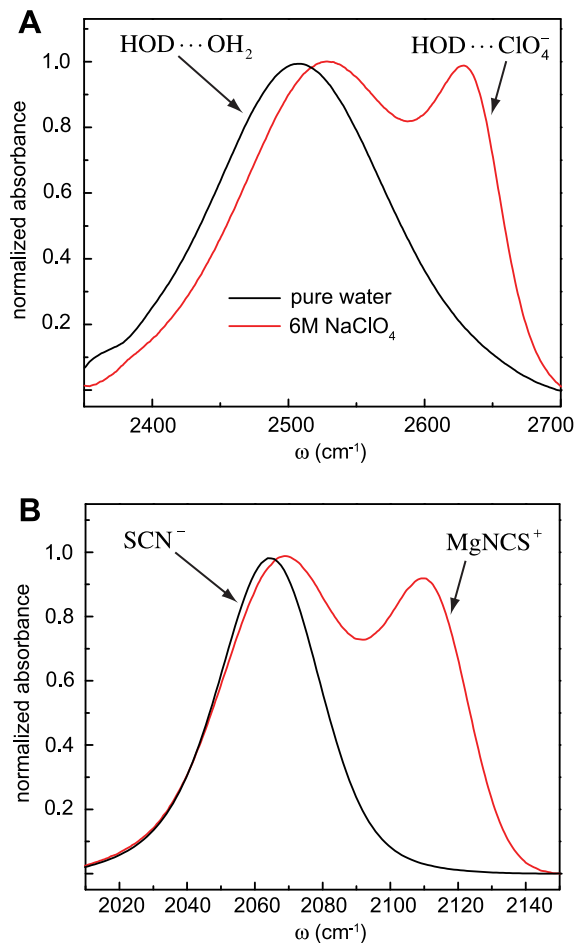


Figure 2. A deuterated hydroxyl stretch absorption spectrum for isotopically mixed water and an aqueous 6 M NaClO_4 solution. (B) Vibrational absorption spectrum for the CN stretch of thiocyanate dissolved in aqueous $\text{Mg}(\text{ClO}_4)_2$. The peak at 2110 cm^{-1} corresponds to the MgNCS^+ contact ion pair, while the peak at roughly 2060 cm^{-1} corresponds to all ionic configurations that do not involve direct contact between the Mg^{2+} and NCS^- . For both spectra distinct chemical configurations lead to distinct vibrational transition frequencies. This provides the opportunity to use 2DIR spectroscopy to study spontaneous fluctuation driven chemical exchange.

2. Observing fluctuation driven chemistry with femtosecond resolution 2DIR spectroscopy

We utilize 2DIR spectroscopy [28] to experimentally investigate aqueous ionic solutions. In specific, we utilize the capacity of 2DIR to study spontaneous chemical exchange to investigate the dynamics of hydrogen bond switching and ligand exchange [18–20,23–27]. Spontaneous fluctuations on the ground electronic state free energy surface drive the vast majority of these critical chemical events, yet our most detailed experimental studies of chemical dynamics have investigated photo-stimulated chemical reactions. Like the truly non-perturbative nuclear spin excitation utilized in NMR spectroscopy, the weakly perturbative vibrational excitations in 2DIR spectroscopy leave the system on the ground electronic state potential energy surface and provide an outstanding complement to molecular dynamics simulations in pursuit of atomistic descriptions of thermal chemical dynamics.

The observation of chemical exchange with 2DIR spectroscopy requires the inter-converting species to possess distinct vibrational transition energies. The measurement can observe exchange events with rates, k_{ex} , smaller than the frequency splitting between the vibrational transition frequencies, $\Delta\omega$, associated with the distinct conformations and as small as roughly one-third the rate of

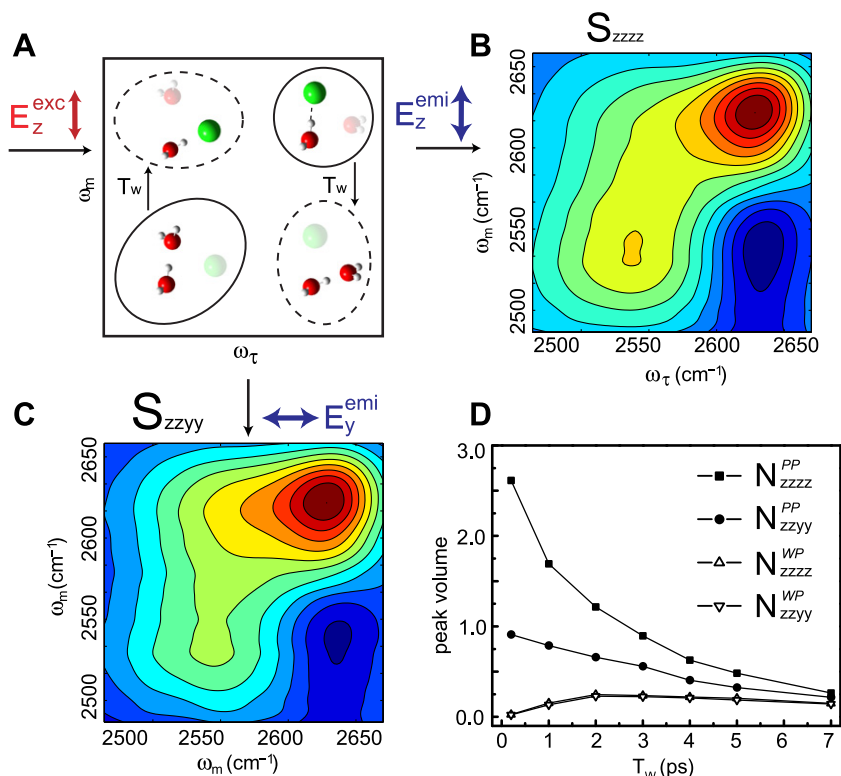


Figure 3. (A) Schematic of the distinct chemical configurations accessed in the experiment roughly aligned to the positions where they contribute to the 2DIR spectra. The positions only reflect the 0–1 transition signal. In the actual measurements, the 0–1 and the 1–2 signals overlap. Experimental 2DIR spectra for a waiting time of $T_w = 3$ ps for the all parallel (B) and crossed polarization geometries (C). Note that the cross peak appears more clearly in the crossed polarization geometry. (D) Peak volumes extracted from the 2DIR spectra for the two polarization geometries as a function of T_w . For the water–perchlorate diagonal peak, corresponding to a signal where the H-bond configuration does not change during the experiment, the parallel polarization signal (N_{zzzz}^{PP}) significantly exceeds the crossed polarization signal (N_{zzyy}^{PP}). This means that orientational memory for this H-bond configuration persists for many picoseconds. For the water–water to water–perchlorate cross peak, corresponding to a signal where the H-bond configuration changes from water–water to water–perchlorate during the T_w waiting time, the parallel polarization signal (N_{zzzz}^{WP}) and the crossed polarization signal (N_{zzyy}^{WP}) have nearly identical intensities. This means that H-bond configuration exchange leads to a loss of orientational memory. A jump angle of 54.7° would lead to zero anisotropy and detailed modeling of the experimental results give a jump angle $\theta = 49 \pm 5^\circ$.

vibrational relaxation, k_L : $k_L/3 \leq k_{ex} \leq \Delta\omega$. Generally speaking, the measurement can access fluctuation driven chemical dynamics occurring on the 1–100 ps time scales. This corresponds to a time range easily accessible to molecular dynamics simulations, including mixed quantum–classical simulations, but not generally accessible to alternative spectroscopic methods more traditionally utilized to investigate fluctuation driven chemistry, such as NMR and EPR.

A schematic depiction of how 2DIR spectroscopy monitors equilibrium conformational dynamics can be seen in Figure 1. 2DIR spectroscopy uses resonant vibrational excitation with femtosecond duration mid-IR pulses to label molecules with their initial frequencies (ω_τ) and then correlate these initial frequencies with the final frequencies (ω_m) associated with these same molecules after an experimentally controlled waiting time (T_w). Figure 1A and B shows characteristic 2DIR spectra demonstrating how chemical exchange manifests in the 2DIR spectra, while Figure 1C shows the resultant populations.

3. The correlated dynamics of water rotation and hydrogen bond exchange

Hydrogen bonds provide the intermolecular adhesion that dictates the unique properties of liquid water and aqueous solutions. A structural definition of a H-bond requires at least two degrees of freedom. For a H-bond donated by a water molecule, the water oxygen on the donator must closely approach the atom functioning

as the hydrogen acceptor and the angle between these three atoms, with the hydrogen atom functioning as the vertex, must be reasonably close to 180° . The directionality of H-bonds leads to local ordering and orientation in water and aqueous solutions, but these local H-bond networks exist briefly, disbanding and reforming on the picosecond time scale. Given the structural requirements of a H-bond, the switching of H-bonds should be strongly correlated with the rotation of the hydroxyl group donating the H-bond.

The rotational dynamics of water have been presumed to adhere to the Debye model for rotational motion in dense molecular liquids [15,29–32]. The Debye model attributes the orientational motion of water molecules to rotational diffusion, implying that the reorientation occurs via infinitesimally small angular steps with uncorrelated angular momenta. Given the strong angular dependence of the H-bond interaction energy in water, orientational diffusion appears a peculiar physical mechanism for reorientation in water. Physical uncertainties aside, the Debye model persisted because experiments observed the predicted exponential orientational dynamics in the time domain or Lorentzian line-widths in the frequency domain [33,34].

Recent molecular dynamics simulations performed by Laage and Hynes, however, brought the hegemony of the Debye model into question [29,30,35,36]. Based on the detailed analysis of the angular trajectories associated with H-bond exchange events, they proposed that water molecules primarily reorient via prompt large angular jumps associated with H-bond exchange, rather than orientational diffusion. Simulations indicate that the mechanism applies generally in aqueous solutions [30,35–37], including

aqueous ionic solutions [20,36], but the substantial complexities inherent in simulating the structural and dynamical properties of water highlight the importance of validating this proposal experimentally. Wanting to understand the mechanism of H-bond exchange in aqueous solution and stimulated by the findings of Laage and Hynes, we investigated the dynamics of H-bond switching with polarization resolved 2DIR spectroscopy studies of 6 M NaClO₄ dissolved in water [20]. These studies provided strong experimental support for the angular jump exchange mechanism.

In aqueous ionic solutions, both water molecules and the anions function as H-bond acceptors. In concentrated perchlorate solutions, the deuterated hydroxyl groups donating H-bonds to perchlorate anions (OD_P) have a distinct excitation frequency from the deuterated hydroxyl groups donating H-bonds to other water molecules (OD_W), Figure 2A. We investigated the deuterated hydroxyl stretch of isotopically mixed water for two reasons: (1) to ensure the vibrational mode being excited provides a local probe of predominantly one H-bond [38,39] and (2) because the lifetime of the OD stretch exceeds that of the OH stretch. The distinct excitation frequencies of the OD_W and OD_P H-bond configurations provide the spectroscopic handles necessary for 2DIR spectroscopy to resolve H-bond switching events between the OD_W and OD_P configurations. The addition of polarization dependence [20,40,41] to the measurement provides the opportunity to determine if the orientational memory of the molecules that have exchanged H-bond configurations differ from those that remain in the same H-bond configuration.

A schematic of the measurement and a selection of experimental spectra can be found in Figure 3. In the polarization selective 2DIR measurement, the first two pulses that control the frequency labeling of OD stretches have parallel polarizations that preferentially excite transition dipole moments parallel to the excitation polarization. During the T_W waiting time, the excited molecules randomize their orientation in addition to undergoing H-bond exchange between the OD_W and OD_P configurations (Figure 3A). If the H-bond exchange minimally perturbs the vibrationally excited hydroxyl group orientation, both the diagonal and the cross-peak intensities will exhibit similar polarization dependence. However, if the molecules exchange via large angular jumps, the cross-peak signal that results solely from OD_W–OD_P exchanged populations will show distinctly different polarization dependence from the diagonal peaks (Figure 3B and C).

The experimental 2DIR spectra for a time delay of $T_W = 3$ ps can be found in Figure 3B and C. The positive peaks shown in red along the diagonal ($\omega_\tau = \omega_m$) result from the fundamental vibrational transition ($v = 0 \rightarrow 1$) within each H-bond configuration. Figure 3D also shows the laser polarization and T_W -dependent peak volumes for distinct H-bond configurations. We label the peak volumes, $I_{llmm}^{(ij)}$, for the diagonal ($i = j$) and the off diagonal ($i \neq j$) peaks with i and j referring to the H-bond configurations associated with ω_τ and ω_m and l and m referring to the laser polarization. The cross-peak at $(\omega_\tau, \omega_m) = (2534, 2633)$ cm⁻¹ results from OD_W switching to OD_P, $I_{llmm}^{(WP)}$. The vibrationally excited molecules that have switched between the OD_P and OD_W configurations project nearly equivalent signal intensities for perpendicular and parallel polarizations, in stark contrast to the $I_{llmm}^{(PP)}$ signal which shows a strong polarization dependence, Figure 3D. The anisotropic cross-peak signal, $I_{zzzz}^{(WP)} - I_{zzyy}^{(WP)}$, provides the clearest access to the magnitude of the jump angle θ . This signal will be proportional to the second order Legendre polynomial of $\cos \theta$, $I_{zzzz}^{(WP)} - I_{zzyy}^{(WP)} \propto \langle P_2(\cos \theta) \rangle$, where $P_2(\cos \theta) = (3 \cos^2 \theta - 1)/2$ and $\langle \dots \rangle$ corresponds to an ensemble average. A jump angle of 54.7° would lead to an anisotropy of zero and detailed modeling of the experimental results give a jump angle $\theta = 49 \pm 5^\circ$.

Polarization selective 2DIR spectroscopy also provided us with the opportunity to revisit the findings of Bakker and co-workers

regarding the orientational motion of hydroxyl groups H-bonded to other water molecules in aqueous perchlorate solutions [15,17]. Our measurements and molecular dynamics simulations have failed to reproduce the findings of Omta et al. [18,42]. We observe significantly slower orientational motion for the OD_W hydroxyl groups ($\tau_r = 6 \pm 1$ ps) that remain within the OD_W configuration than we do for pure water ($\tau_r = 3.3 \pm 0.5$ ps for the 1–2 excited state absorption) [42]. Interestingly, we only observe moderately faster orientational dynamics for the OD_W hydroxyl groups that remain within the OD_W configuration than we do for the OD_P ($\tau_r = 8.3 \pm 1$ ps) hydroxyl groups that remain within the OD_P configuration, as predicted by molecular dynamics simulations. The origin of the discrepancy between the two measurements has yet to be determined [42].

4. Ligand exchange dynamics in aqueous solution

Water not only solvates ionic species in aqueous ionic solutions, but also mediates a wide range of chemical reactions including ligand exchange. Ligand exchange represents the central reaction in inorganic synthesis and a critical reaction in transition metal catalysis. The solvent has been proposed to play a central role in ligand exchange reactions in general, and ion pairing reactions in specific [43–46]. While the ion–ion separation provides the intuitive reaction coordinate [47,48], fluctuations in the solvent structure surrounding the ion pair explicitly influence the solution phase reaction mechanism [44]. In addition to simulation studies of ion pairing, a multitude of studies using a variety of techniques have been used to investigate the residence time of water molecules in the first solvation shell of cations [49–52]. Changes in the simulation methodology and data analysis procedures lead to significant variations in the equilibrium between the free ions and the contact ion pair [52], water residence times [49–51], and potentially the reaction mechanisms extracted from simulation.

NMR has proven to be a powerful approach to studying the interaction between water and transition metal ions in solution, generally being the tool of choice for measuring key properties such as the residence time of water in the first solvation shell. The more chemically inert alkali metal and alkaline earth cations, however, do not generally have sufficiently large chemical shifts and sufficiently long residence times to be measured with NMR. For these cations, ultrasonic absorption spectroscopy has been the dominant tool for measuring water residence time. The ultrasonic absorption measurement of Eigen and Tamm represent a benchmark study. They generally extracted water residence times in the range of a nanosecond [45] and these rates still remain prominently cited in the literature [53,54]. A thorough investigation of the literature, however, shows a wide range of proposed residence times. For instance, Eigen assigned a residence time of 10 ns for water in the first solvation shell of Ca²⁺ [45], quasi-elastic neutron scattering measurements indicate a water residence time of <150 ps for Ca²⁺ [55], and molecular dynamics simulations give water residence times ranging from 16 ps to 150 ps depending upon the simulation methodology [51]. Three orders of magnitude uncertainty in the water residence time clearly demonstrates the need for a time domain measure of the dynamics of ion pairing and ligand exchange in the first solvation shell of simple cations in aqueous solution.

The frequency and orientation of the hydroxyl stretch of water proves to be insensitive to the cation–water interaction, so cation solvation and ion pairing cannot be investigated with the hydroxyl stretch of water. We have chosen to use a molecular anion to investigate the anion–cation interaction directly and the water–cation interaction indirectly. Figure 2B shows the spectrum for the CN stretch of thiocyanate (NCS⁻) in a solution of 3.4 M Mg(ClO₄)₂

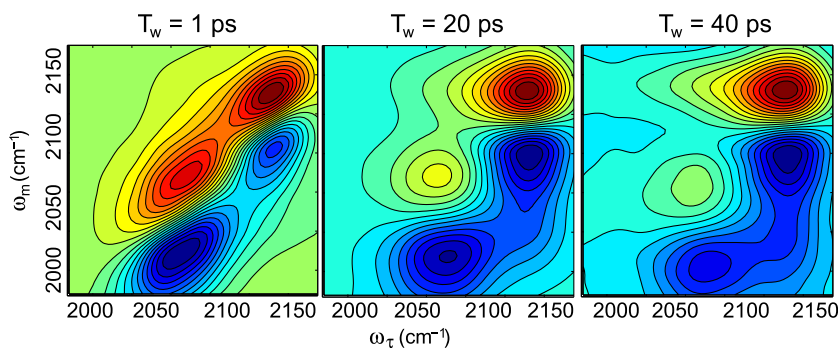


Figure 4. 2DIR spectra of the CN stretch of thiocyanate obtained from an aqueous solution of $\text{Mg}(\text{ClO}_4)_2$ and NaSCN dissolved in D_2O at a series of T_w waiting times. Two cross peaks (ω_m, ω_τ) can be clearly seen in the T_w equal to 20 ps and 40 ps at ($2060 \text{ cm}^{-1}, 2110 \text{ cm}^{-1}$) for the 0–1 transitions and ($2110 \text{ cm}^{-1}, 2010 \text{ cm}^{-1}$) for the 1–2 transitions.

and 1.2 M NaNCS dissolved in water. The higher frequency peak corresponds to the MgNCS^+ contact ion pair, while all other SCN^- configurations lead to absorption at 2068 cm^{-1} . ‘Free’ anions refer to anions with cation independent translational and rotational motion. For concentrated ionic solutions, these free anionic species will dominate over solvent separated species, which require the cation and anion not only to be in close proximity, but also require the solvent separated ions to move as an intact unit [56]. While the close proximity requirement will clearly be met in a concentrated ionic solution, the absence of solvent separated ion pair rotational resonances in the dielectric relaxation spectra indicate that solvent separated ion pairs do not represent a kinetically stable configuration. The use of a mixed ionic solution allows us to independently control the thiocyanate absorption and the relative concentration of the contact ion pair and free NCS^- configurations.

The distinct vibrational transition energies for the contact ion pair and the free anion configurations provide the opportunity to use 2DIR spectroscopy to investigate the equilibrium dynamics of ion association and dissociation in aqueous ionic solutions. As exhibited in Figure 4, the measurements have proven successful. We observe the cross-peak to grow in with an exchange time constant of $52 \pm 10 \text{ ps}$, clearly demonstrating the chemical inter-conversion between the free and contact ion pair configurations, but they present interpretive challenges [19]. In principle, three distinct ligand exchange reactions could be occurring: (1) a free NCS^- could be replacing a water molecule in the first solvation shell of the Mg^{2+} , (2) a free NCS^- could be replacing a perchlorate anion in the first solvation shell of the Mg^{2+} , or (3) a free NCS^- could be replacing a different NCS^- anion in the first solvation shell of the Mg^{2+} .

NMR and ultrasonic absorption spectroscopy have determined the residence time of water in the first solvation shell of Mg^{2+} to be microseconds, so we can rule out the exchange of water and NCS^- [21,45,46,57–60]. For the roughly 7 M perchlorate solution in our initial study, Mg^{2+} ions will have an appreciable concentration of perchlorate anions in the first solvation shell of Mg^{2+} [61], so we assigned the exchange process observed in the 2DIR measurement to perchlorate–thiocyanate anion exchange. To investigate the validity of this initial interpretation, we have investigated the thiocyanate concentration dependence and the counter anion dependence of the exchange dynamics. Preliminary analysis of these measurements supports our initial interpretation.

5. Future prospects

The dynamics of the water hydroxyl stretch has proven to be a powerful tool for investigating hydrogen bond dynamics in water and aqueous solutions. Our investigation of the orientation jump mechanism for H-bond exchange provides another clear demon-

stration of this power. These successes should not, however, obscure the limitations of this approach to studying the dynamics of aqueous solutions. The hydroxyl group provides a sensitive probe of H-bond donation, and consequently the impact of anions on the dynamics of water, but provides little to no information about the impact of the cation on the structure and dynamics of water or how water mediates ion pairing in aqueous solution. We have chosen to use the molecular anion thiocyanate as a probe of ligand exchange around the solvated cation to further our studies of aqueous ionic solutions. While our understanding of these measurements presently lags behind our understanding of measurements of hydroxyl stretch dynamics, they have the potential to greatly enhance our understanding of alkali metal and alkaline earth cation solvation and ion pairing in water.

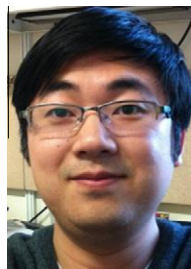
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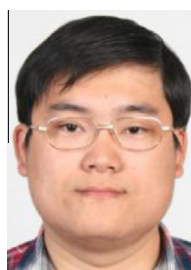
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